

Package ‘seacarb’

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Description Calculates parameters of the seawater carbonate system and assists the design of ocean acidification perturbation experiments.

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 alkalinity

Example data file for function at

Description

The variables are:

- volume: Volume of acid added to the sample in ml
- E: Potential measured during the titration in mV
- temperature: Temperature in degrees Celsius
- weight: Weight of the sample in g
- S: Salinity
- normality : Normality of the acid
- ETris: Potential used for the calibration of the electrode in mV
- pHTris: pH used for the calibration of the electrode with the TRIS buffer

Usage

alkalinity

Format

A data frame with 29 rows and 8 variables

Source

Data come from a potentiometric titration performed by Steeve Comeau.

 amp

pH value of the AMP buffer

Description

pH value of the AMP buffer (on the total scale in mol/kg)

Usage

amp(S=35, T=25)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC

Details

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

AMP pH value of the AMP buffer (on the total scale in mol/kg)

Author(s)

Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

See Also

[tris](#), [pHslope](#), [pH](#).

Examples

```
##Example from Dickson et al. (2007)
amp(S=35, T=25)
```

at *Calculates total alkalinity from potentiometric titration data*

Description

Calculates total alkalinity from potentiometric titration data

Usage

```
at(S=35, T=25, C=0.1, d=1, pHTris=NULL, ETris=NULL, weight, E, volume)
```

Arguments

S	Salinity, default is 35. S must be a single value, not a vector.
T	Temperature in degrees Celsius, default is 25oC, can be given as a vector or as a single value.
C	Normality of the acid, default is 0.1. C must be a single value, not a vector.
d	Density of the acid, default is 1. d must be a single value, not a vector.
pHTris	pH used for the calibration of the electrode with the TRIS buffer. pHTris must be a single value, not a vector.

ETris	Potential used for the calibration of the electrode in mV. ETris must be a single value, not a vector.
weight	Weight of the sample in g. weight must be a single value, not a vector.
E	Potential measured during the titration in mV. E must be a vector.
volume	Volume of acid added to the sample in ml. volume must be a vector.

Details

Total alkalinity is estimated using the non-linear least-square procedure described by Dickson et al. (2007).

Value

AT Total alkalinity in mol/kg)

Author(s)

Steeve Comeau, Heloise Lavigne and Jean-Pierre Gattuso

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication 3*, 1-191.

See Also

alkalinity

Examples

```
data(alkalinity)
data <- alkalinity
AT <- at(S=data$S[1], T=data$temperature, C=data$normality[1], pHTris=data$pHTris[1],
        ETris=data$ETris[1], E=data$E, weight=data$weight[1], volume=data$volume)
```

bjerrum

Bjerrum plot

Description

Plot the concentration of the various ionic forms of a molecule as a function of pH

Usage

```
bjerrum(K1=K1(), K2=NULL, K3=NULL, phmin=2, phmax=12, by=0.1, conc=1,
        type="l", col="black", ylab="Concentration (mol/kg)", add=FALSE, ...)
```

Arguments

K1	First dissociation constant
K2	Second dissociation constant, default is NULL
K3	Third dissociation constant, default is NULL
phmin	Minimum pH value, default is 2
phmax	Maximum pH value, default is 12
by	Increment on the pH axis, default is 0.1
conc	concentration of molecule, default is 1
type	Type of plot, default is line
col	Color of plot, default is black
ylab	Label of Y axis, default is (mol/kg)
add	false:start new, true: add to current, default is false
...	Graphical parameters (see par) and any further arguments of plot, typically plot.default , may also be supplied as arguments to this function. Hence, the high-level graphics control arguments described under par and the arguments to title may be supplied to this function.

Details

Note that the concentration is plotted in mol/kg only if conc is given is mol/kg

Author(s)

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References

Zeebe, R. E. and Wolf-Gladrow D. A., 2001 *CO₂ in seawater: equilibrium, kinetics, isotopes*. Amsterdam: Elsevier, 346 pp.

See Also

[matplot](#), [par](#), [speciation](#).

Examples

```
## Plot the bjerrum plot for the carbonate system using the default values
bjerrum(K1(),K2(),main="DIC speciation",lwd=2)
abline(v=-log10(K1()),col="grey")
mtext(side=3,at=-log10(K1()),"pK1")
abline(v=-log10(K2()),col="grey")
mtext(side=3,at=-log10(K2()),"pK2")
legend("left",lty=1:3,lwd=2,legend=c(expression(CO[2]),expression(HCO[3]^"-"),
expression(CO[3]^"2-")))

## Plot the bjerrum plot for phosphate using the default values
bjerrum(K1p(),K2p(),K3p(),main="phosphate speciation",lwd=2)
```

```

legend("left",lty=1:4,lwd=2,legend=c(expression(H[3]~P0[4]),
expression(H[2]~P0[4]^"-"),
expression(HPO[4]^"2-"),expression(P0[4]^"3-")))

## Plot the bjerrum plot for the carbonate system using the values other
## than the default ones, showing the effect of temperature
bjerrum(K1(T=25,S=35),K2(T=25,S=35),conc=1.3,main="effect of temperature" )
bjerrum(K1(T=0,S=35),K2(T=0,S=35),conc=1.3,add=TRUE,col="red")
legend("left",lty=1,col=c("black","red"),legend=c("T=25 oC","T=0 oC"))
legend("right",lty=1:3,legend=c(expression(CO[2]),expression(HCO[3]^"-"),
expression(CO[3]^"2-")))

## Plot the bjerrum plot for the carbonate system using the values other
## than the default ones, showing the effect of salinity
bjerrum(K1(T=25,S=35),K2(T=25,S=35),conc=1.3,main="effect of salinity" )
bjerrum(K1(T=25,S=5),K2(T=25,S=5),conc=1.3,add=TRUE,col="blue")
legend("left",lty=1,col=c("black","blue"),legend=c("S=35","S=5"))
legend("right",lty=1:3,legend=c(expression(CO[2]),expression(HCO[3]^"-"),
expression(CO[3]^"2-")))

## Plot the bjerrum plot for the carbonate system using the values other
## than the default ones, showing the effect of pressure
bjerrum(K1(P=0),K2(P=0),conc=1.3,main="effect of pressure" )
bjerrum(K1(P=300),K2(P=300),conc=1.3,add=TRUE,col="green")
legend("left",lty=1,col=c("black","green"),legend=c("P=0","P=300"),title="atm")
legend("right",lty=1:3,legend=c(expression(CO[2]),expression(HCO[3]^"-"),
expression(CO[3]^"2-")))

```

bor *Total boron concentration (mol/kg)*

Description

total boron concentration (*mol kg⁻¹*)

Usage

bor(S, b)

Arguments

S Salinity, default is 35
b "I10" for using the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "I10"

Value

bor total boron concentration (*mol kg⁻¹*)

Author(s)

Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

DOE 1994 *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. ORNL/CDIAC-74. Oak Ridge, Tenn.: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.

Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

```
bor(35, "110")
```

buffer

Buffer parameters of the seawater carbonate system

Description

Returns buffer parameters of the seawater carbonate system.

Usage

```
buffer(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0, k1k2="x",
kf="x", ks="d", pHscale="T", b="110")
```

Arguments

flag select the couple of variables available. The flags which can be used are:

flag = 1 pH and CO₂ given

flag = 2 CO₂ and HCO₃ given

flag = 3 CO₂ and CO₃ given

flag = 4 CO₂ and ALK given

flag = 5 CO₂ and DIC given

flag = 6 pH and HCO₃ given

flag = 7 pH and CO₃ given

flag = 8 pH and ALK given

flag = 9 pH and DIC given

flag = 10 HCO₃ and CO₃ given

flag = 11 HCO₃ and ALK given

flag = 12 HCO₃ and DIC given

	flag = 13 CO ₃ and ALK given
	flag = 14 CO ₃ and DIC given
	flag = 15 ALK and DIC given
	flag = 21 pCO ₂ and pH given
	flag = 22 pCO ₂ and HCO ₃ given
	flag = 23 pCO ₂ and CO ₃ given
	flag = 24 pCO ₂ and ALK given
	flag = 25 pCO ₂ and DIC given
var1	enter value of the first variable in mol/kg, except for pH and for pCO ₂ in μatm
var2	enter value of the second variable in mol/kg, except for pH
S	Salinity
T	Temperature in degrees Celsius
Patm	Surface atmospheric pressure in atm
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg; set to 0 if NA
Sit	Concentration of total silicate in mol/kg; set to 0 if NA
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickson (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	choice of pH scale: "T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"l10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "l10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.

- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag“pHscale”.

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

PhiD	PhiD, chemical buffer factor (dpH/d[DIC]); input/output of dissolved CO_2 (unit pH per mol/kg)
BetaD	BetaD, homogeneous or Revelle buffer factor (dln(p CO_2)/dln[DIC]); input/output of dissolved CO_2
PiD	PiD, chemical buffer factor (dp CO_2 /d[DIC]); input/output of dissolved CO_2 (μatm per mol/kg)

PhiB	PhiB, chemical buffer factor (dpH/d[DIC]); from input/output of bicarbonate (unit pH per mol/kg)
BetaB	BetaB, homogeneous buffer factor (dln(pCO ₂)/dln[DIC]); input/output of bicarbonate
PiB	PiB, chemical buffer factor (dpCO ₂ /d[DIC]); input/output of dissolved CO ₂ (μatm per mol/kg)
PhiC	PhiC, chemical buffer factor (dpH/d[DIC]); input/output of carbonate (unit pH per mol/kg)
BetaC	BetaC, homogeneous buffer factor (dln(pCO ₂)/dln[DIC]); input/output of carbonate
PiC	PiC, chemical buffer factor (dpCO ₂ /d[DIC]); input/output of carbonate (μatm per mol/kg)
PhiH	PhiH, chemical buffer factor (dpH/d[ALK]); input/output of strong acid (unit pH per mol/kg)
PiH	PiH, chemical buffer factor (dpCO ₂ /d[ALK]); input/output of strong acid (μatm per mol/kg)

Author(s)

Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.
- Khoo H. K., Ramette R. W., Culberson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.
- Frankignoulle M., 1994 A complete set of buffer factors for acid/base CO₂ system in seawater. *Journal of Marine Systems* **5**, 111-118.
- Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.
- Lueker T. J., Dickson A. G. and Keeling C. D., 2000 Ocean pCO₂ calculated from dissolved inorganic carbon, alkalinity, and equations for K₁ and K₂: validation based on laboratory measurements of CO₂ in gas and seawater at equilibrium. *Marine Chemistry* **70** 105-119.
- Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.
- Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Perez F. F. and Fraga F., 1987 Association constant of fluoride and hydrogen ions in seawater. *Marine Chemistry* **21**, 161-168.

Roy R. N., Roy L. N., Vogel K. M., Porter-Moore C., Pearson T., Good C. E., Millero F. J. and Campbell D. M., 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45oC. *Marine Chemistry* **44**, 249-267.

Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

```
## Computation with a couple of variables
buffer(flag=8, var1=8.2, var2=0.00234, S=35, T=25, Patm=1, P=0, Pt=0,
Sit=0, pHscale="T", kf="pf", k1k2="1", b="110")

## Using vectors as arguments
flag <- c(8, 2, 8)
var1 <- c(8.2, 7.477544e-06, 8.2)
var2 <- c(0.002343955, 0.001649802, 2400e-6)
S <- c(35, 35, 30)
T <- c(25, 25, 30)
P <- c(0, 0, 0)
Pt <- c(0, 0, 0)
Sit <- c(0, 0, 0)
kf <- c("pf", "pf", "pf")
k1k2 <- c("1", "1", "1")
pHscale <- c("T", "T", "T")
b <- c("110", "110", "110")
buffer(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt,
Sit=Sit, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)

## Test for all flags

flag <- c(1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 21, 22, 23, 24, 25)

var1 <- c(8.200000, 7.477544e-06, 7.477544e-06, 7.477544e-06, 7.477544e-06, 8.2,
8.2, 8.2, 8.2, 0.001685024, 0.001685024, 0.001685024, 0.0002888382,
0.0002888382, 0.002391252, 264.2008, 264.2008, 264.2008, 264.2008, 264.2008)

var2 <- c(7.477544e-06, 0.001685024, 0.0002888382, 0.002391252, 0.001981340,
0.001685024, 0.0002888382, 0.002391252, 0.001981340, 0.0002888382, 0.002391252,
0.001981340, 0.002391252, 0.001981340, 0.001981340, 8.2, 0.001685024,
0.0002888382, 0.002391252, 0.001981340)

##buffer(flag=flag, var1=var1, var2=var2)
```

buffesm	<i>Buffer capacities of the seawater carbonate system as defined by Egleston et al. (2010)</i>
---------	--

Description

Returns the six buffer factors of the seawater carbonate system as defined by Egleston, Sabine and Morel (2010), denoted here as ESM. Also returns the classic Revelle factor (relative change in pCO₂ over that for DIC). In ESM, there are errors in the equations in Table 1 for S , Ω_{DIC} , and Ω_{Alk} . These errors have been corrected here. The results of this routine have been validated: they produce results that are identical to those shown in ESM's Fig. 2. This routine was inspired and adapted from seacarb's "buffer" function. Its input arguments are identical to those in the "buffer" and "carb" functions of seacarb.

Usage

```
buffesm(flag, var1, var2, S=35, T=25, Patm=1.0, P=0, Pt=0, Sit=0, k1k2="x",
kf="x", ks="d", pHscale="T", b="110")
```

Arguments

flag	select the couple of variables available. The flags which can be used are: flag = 1 pH and CO ₂ given flag = 2 CO ₂ and HCO ₃ given flag = 3 CO ₂ and CO ₃ given flag = 4 CO ₂ and ALK given flag = 5 CO ₂ and DIC given flag = 6 pH and HCO ₃ given flag = 7 pH and CO ₃ given flag = 8 pH and ALK given flag = 9 pH and DIC given flag = 10 HCO ₃ and CO ₃ given flag = 11 HCO ₃ and ALK given flag = 12 HCO ₃ and DIC given flag = 13 CO ₃ and ALK given flag = 14 CO ₃ and DIC given flag = 15 ALK and DIC given flag = 21 pCO ₂ and pH given flag = 22 pCO ₂ and HCO ₃ given flag = 23 pCO ₂ and CO ₃ given flag = 24 pCO ₂ and ALK given flag = 25 pCO ₂ and DIC given
var1	enter value of the first variable in mol/kg, except for pH and for pCO ₂ in μatm

var2	enter value of the second variable in mol/kg, except for pH
S	Salinity
T	Temperature in degrees Celsius
Patm	Surface atmospheric pressure in atm, default 1 atm
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg; set to 0 if NA
Sit	Concentration of total silicate in mol/kg; set to 0 if NA
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickon (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	choice of pH scale: "T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"l10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "l10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag? "pHscale".

For K0:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

gammaDIC	γ_{DIC} , ocean's capacity to buffer changes in $[CO_2]$ due to accumulation of CO_2 from the atmosphere $(\partial \ln[CO_2]/\partial DIC)^{-1}$ (units = mol/kg; multiply by 1000 to get mmol/kg, i.e., the units presented in Egleston et al., 2010)
betaDIC	β_{DIC} , ocean's capacity to buffer changes in $[H^+]$ due to accumulation of CO_2 from the atmosphere $(\partial \ln[H^+]/\partial DIC)^{-1}$ (units = mol/kg)
omegaDIC	Ω_{DIC} , ocean's capacity to buffer changes in $[CO_3^{2-}]$ due to accumulation of CO_2 from the atmosphere $(\partial \ln[CO_3^{2-}]/\partial DIC)^{-1}$; same as $(\partial \ln \Omega_A/\partial DIC)^{-1}$ and $(\partial \ln \Omega_C/\partial DIC)^{-1}$ (units= mol/kg)
gammaALK	γ_{ALK} , ocean's capacity to buffer changes in $[CO_2]$ due to changes in alkalinity $(\partial \ln[CO_2]/\partial ALK)^{-1}$ (units = mol/kg)
betaALK	β_{ALK} , ocean's capacity to buffer changes in $[H^+]$ due to changes in alkalinity $(\partial \ln[H^+]/\partial ALK)^{-1}$ (units = mol/kg)
omegaALK	Ω_{ALK} , ocean's capacity to buffer changes in $[CO_3^{2-}]$ due to changes in alkalinity $(\partial \ln[CO_3^{2-}]/\partial ALK)^{-1}$; same as $(\partial \ln \Omega_A/\partial ALK)^{-1}$ and $(\partial \ln \Omega_C/\partial ALK)^{-1}$ (units = mol/kg)
R	Revelle factor, relative change in $[CO_2]$ or pCO_2 over the relative change in DIC $(\partial \ln[CO_2]/\partial \ln DIC)^{-1}$ (unitless)

Author(s)

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References

- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO_2 measurements. *PICES Special Publication* **3**, 1-191.
- Eggleston, E. S., Sabine, C. L. and Morel, F. M. M., 2010 Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity, *Global Biogeochem. Cycles* **24**, GB1002, doi:10.1029/2008GB003407.
- Khoo H. K., Ramette R. W., Culbertson C. H. and Bates R. G., 1977 Determination of hydrogen ion concentration in seawater from 5 to 40°C: standard potentials at salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.
- Frankignoulle M., 1994 A complete set of buffer factors for acid/base CO_2 system in seawater. *Journal of Marine Systems* **5**, 111-118.
- Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.
- Lueker T. J., Dickson A. G. and Keeling C. D., 2000 Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2 : validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry* **70** 105-119.
- Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.
- Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.
- Perez F. F. and Fraga F., 1987 Association constant of fluoride and hydrogen ions in seawater. *Marine Chemistry* **21**, 161-168.
- Roy R. N., Roy L. N., Vogel K. M., Porter-Moore C., Pearson T., Good C. E., Millero F. J. and Campbell D. M., 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Marine Chemistry* **44**, 249-267.
- Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

```
## Computation with a couple of variables
buffesm(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Pt=0,
Sit=0, pHscale="T", kf="pf", k1k2="1", b="110")

## Using vectors as arguments
```



```

flag <- c(8, 2, 8)
var1 <- c(8.2, 7.477544e-06, 8.2)
var2 <- c(0.002343955, 0.001649802, 2400e-6)
S <- c(35, 35, 30)
T <- c(25, 25, 30)
P <- c(0, 0, 0)
Pt <- c(0, 0, 0)
Sit <- c(0, 0, 0)
kf <- c("pf", "pf", "pf")
k1k2 <- c("1", "1", "1")
pHscale <- c("T", "T", "T")
b <- c("110", "110", "110")
buffesm(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt,
Sit=Sit, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)

## Test for all flags
flag <- c(1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 21, 22, 23, 24, 25)

var1 <- c(8.200000, 7.477544e-06, 7.477544e-06, 7.477544e-06, 7.477544e-06, 8.2,
8.2, 8.2, 8.2, 0.001685024, 0.001685024, 0.001685024, 0.0002888382,
0.0002888382, 0.002391252, 264.2008, 264.2008, 264.2008, 264.2008, 264.2008)
var2 <- c(7.477544e-06, 0.001685024, 0.0002888382, 0.002391252, 0.001981340,
0.001685024, 0.0002888382, 0.002391252, 0.001981340, 0.0002888382, 0.002391252,
0.001981340, 0.002391252, 0.001981340, 0.001981340, 8.2, 0.001685024,
0.0002888382, 0.002391252, 0.001981340)
buffesm(flag=flag, var1=var1, var2=var2)

## Compute 2 additional factors of interest (ratios of relative changes)
be <- buffesm(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt,
Sit=Sit, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)
# Ratio of gammaDIC/betaDIC = d ln [H+] / d ln pCO2
Hfac <- (be$gammaDIC/be$betaDIC) #H+ factor
# Ratio of gammaDIC/omegaDIC = d ln [CO32-] / d ln pCO2
Satfac <- (be$gammaDIC/be$omegaDIC) #Saturation factor

```

carb

Parameters of the seawater carbonate system

Description

Returns parameters of the seawater carbonate system.

Usage

```
carb(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0,
k1k2="x", kf="x", ks="d", pHscale="T", b="110")
```

Arguments

flag	select the couple of variables available. The flags which can be used are: flag = 1 pH and CO ₂ given flag = 2 CO ₂ and HCO ₃ given flag = 3 CO ₂ and CO ₃ given flag = 4 CO ₂ and ALK given flag = 5 CO ₂ and DIC given flag = 6 pH and HCO ₃ given flag = 7 pH and CO ₃ given flag = 8 pH and ALK given flag = 9 pH and DIC given flag = 10 HCO ₃ and CO ₃ given flag = 11 HCO ₃ and ALK given flag = 12 HCO ₃ and DIC given flag = 13 CO ₃ and ALK given flag = 14 CO ₃ and DIC given flag = 15 ALK and DIC given flag = 21 pCO ₂ and pH given flag = 22 pCO ₂ and HCO ₃ given flag = 23 pCO ₂ and CO ₃ given flag = 24 pCO ₂ and ALK given flag = 25 pCO ₂ and DIC given
var1	Value of the first variable in mol/kg, except for pH and for pCO ₂ in μ atm
var2	Value of the second variable in mol/kg, except for pH
S	Salinity
T	Temperature in degrees Celsius
Patm	Surface atmospheric pressure in atm, default 1 atm
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg; set to 0 if NA
Sit	Concentration of total silicate in mol/kg; set to 0 if NA
k1k2	"l" for using K ₁ and K ₂ from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35°C and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using K _f from Perez and Fraga (1987) and "dg" for using K _f from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33°C and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using K _s from Dickson (1990) and "k" for using K _s from Khoo et al. (1977), default is "d"

pHscale	"T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"I10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "I10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

S	Salinity
T	Temperature in degrees Celsius
Patm	Surface atmospheric pressure in atm
P	Hydrostatic pressure in bar
pH	pH
CO2	CO2 concentration (mol/kg)
pCO2	pCO2, CO2 partial pressure (μatm)
fCO2	fCO2, CO2 fugacity (μatm)
HCO3	HCO3 concentration (mol/kg)
CO3	CO3 concentration (mol/kg)
DIC	DIC concentration (mol/kg)
ALK	ALK, total alkalinity (mol/kg)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state

Author(s)

Heloise Lavigne and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

- Dickson A. G. and Riley J. P., 1979 The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water. *Marine Chemistry* **7**, 89-99.
- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.
- Khoo H. K., Ramette R. W., Culberson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **22**, vol49 29-34.

- Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.
- Lueker T. J., Dickson A. G. and Keeling C. D., 2000 Ocean pCO₂ calculated from dissolved inorganic carbon, alkalinity, and equations for K₁ and K₂: validation based on laboratory measurements of CO₂ in gas and seawater at equilibrium. *Marine Chemistry* **70** 105-119.
- Millero F. J., 1995. Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.
- Millero F. J., 2010. Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.
- Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.
- Perez F. F. and Fraga F., 1987 Association constant of fluoride and hydrogen ions in seawater. *Marine Chemistry* **21**, 161-168.
- Roy R. N., Roy L. N., Vogel K. M., Porter-Moore C., Pearson T., Good C. E., Millero F. J. and Campbell D. M., 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Marine Chemistry* **44**, 249-267.
- Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.
- Weiss, R. F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, **2**, 203-215.
- Weiss, R. F. and Price, B. A., 1980. Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347-359.
- Zeebe R. E. and Wolf-Gladrow D. A., 2001 *CO₂ in seawater: equilibrium, kinetics, isotopes*. Amsterdam: Elsevier, 346 pp.

Examples

```
## With a couple of variables
carb(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Pt=0, Sit=0,
pHscale="T", kf="pf", k1k2="1", ks="d", b="110")

## Using vectors as arguments
flag <- c(8, 2, 8)
var1 <- c(8.2, 7.477544e-06, 8.2)
var2 <- c(0.002343955, 0.001649802, 2400e-6)
S <- c(35, 35, 30)
T <- c(25, 25, 30)
P <- c(0, 0, 0)
Pt <- c(0, 0, 0)
Sit <- c(0, 0, 0)
kf <- c("pf", "pf", "pf")
k1k2 <- c("1", "1", "1")
pHscale <- c("T", "T", "T")
b <- c("110", "110", "110")
```

```

carb(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P,
      Pt=Pt, Sit=Sit, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)

## Test with all flags
flag <- c((1:15), (21:25))
var1 <- c(8.200000, 7.308171e-06, 7.308171e-06, 7.308171e-06, 7.308171e-06,
8.2, 8.2, 8.2, 8.2, 0.001646857, 0.001646857, 0.001646857, 0.0002822957,
0.0002822957, 0.00234, 258.2164, 258.2164, 258.2164, 258.2164, 258.2164 )
var2 <- c(7.308171e-06, 0.001646857, 0.0002822957, 0.00234, 0.001936461,
0.001646857, 0.0002822957, 0.00234, 0.001936461, 0.0002822957,
0.00234, 0.001936461, 0.00234, 0.001936461, 0.001936461, 8.2,
0.001646857, 0.0002822957, 0.00234, 0.001936461)
carb(flag=flag, var1=var1, var2=var2)

## Test using a data frame
data(seacarb_test_P0) #test data set for P=0 (surface)
tab <- seacarb_test_P0

## method 1 using the column numbers
##carb(flag=tab[[1]], var1=tab[[2]], var2=tab[[3]], S=tab[[4]], T=tab[[5]],
## P=tab[[6]], Sit=tab[[8]], Pt=tab[[7]])

## method 2 using the column names
##carb(flag=tab$flag, var1=tab$var1, var2=tab$var2, S=tab$S, T=tab$T, P=tab$P,
## Sit=tab$Sit, Pt=tab$Pt)

```

d2p

Converts depth in meters to pressure in dbar

Description

Converts depth in meters to pressure in dbar

Usage

```
d2p(depth, lat=40)
```

Arguments

depth	Depth in meters
lat	Latitude in degrees, N and S is irrelevant, default is 40o

Value

pressure	Pressure corresponding to the depth given, in dbar
----------	--

Author(s)

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References

Saunders P. M., 1981. Practical conversion of pressure to depth. *J. Phys. Oceanogr.* **11**: 573-574.

See Also

[p2d](#)

Examples

```
d2p(depth=7500, lat=30)
```

f2pCO2

Converts the CO2 fugacity to CO2 partial pressure

Description

Converts fCO2 (fugacity of CO2) into pCO2 (partial pressure in CO2)

Usage

```
f2pCO2(T = 25, Patm=1.0, P=0, fCO2)
```

Arguments

T	Temperature in degrees Celsius, default is 25oC
Patm	Surface atmospheric pressure in atm, default 1 atm
P	Hydrostatic pressure in bar, default is 0 bar (surface)
fCO2	Fugacity of CO2 in μatm , the same units as that for the pCO2 output

Value

pCO2	Partial pressure of CO2 in μatm , the same units as that for the fCO2 input
------	--

Author(s)

Heloise Lavigne, Jean-Pierre Gattuso, and James Orr <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007. Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.

Weiss, R. F. and Price, B. A., 1980. Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347-359, 1980.

Weiss, R. F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, **2**, 203-215.

Weiss, R. F. and Price, B. A., 1980. Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347-359.

See Also

[p2fC02](#).

Examples

`f2pC02(T=25, Patm=1.0, P=0, fC02=380)`

K0	<i>Henry's constant mol/(kg/atm)</i>
----	--------------------------------------

Description

Henry's constant mol/(kg/atm)

Usage

`K0(S = 35, T = 25, P = 0, Patm = 1.0)`

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
Patm	Surface atmospheric pressure in atm, default 1 atm

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between -1 and 45oC.

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

K0	Henry's constant mol/(kg/atm)
----	-------------------------------

Author(s)

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References

Weiss R. F., 1974 Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry* **2**, 203-215.

Examples

$K_0(S=35, T=25, P=0)$

K1

First dissociation constant of carbonic acid (mol/kg)

Description

First dissociation constant of carbonic acid (mol/kg)

Usage

$K_1(S = 35, T = 25, P = 0, k_{1k2}="x", pHscale="T", k_{SWS2scale}=0, k_{total2SWS_P0}=0)$

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. It is not required when k1k2 is "m10" and the hydrostatic pressure is 0. If it is required and not given, it is computed, which slows down computations.
ktotal2SWS_P0	Conversion factor from the total scale to the SWS at an hydrostatic pressure of 0. It is only required when k1k2 is "l" or "r". If it is required and not given, it is computed, which slows down computations.

Details

The Lueker et al. (2000) constant is recommended by Guide to Best Practices for Ocean CO₂ Measurements (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.

- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

The pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

K1 First dissociation constant of carbonic acid (mol/kg)

Author(s)

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References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.

DOE 1994 *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. ORNL/CDIAC-74. Oak Ridge,Tenn.: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Lueker T. J., Dickson A. G., and Keeling C. D., 2000 Ocean pCO2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO2 in gas and seawater at equilibrium. *Marine Chemistry* **70** 105-119.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H., and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.

Roy R. N., Roy L. N., Vogel K. M., Porter-Moore C., Pearson T., Good C. E., Millero F. J. and Campbell D. M., 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45oC. *Marine Chemistry* **44**, 249-267.

See Also

[K2](#).

Examples

K1(S=35,T=25,P=0,k1k2="1",pHscale="T")

K1p *First dissociation constant of phosphoric acid (mol/kg)*

Description

First dissociation constant of phosphoric acid (mol/kg)

Usage

K1p(S = 35, T = 25, P = 0, pHscale = "T", kSWS2scale = 0)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	Choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. If it is required and not given, it is computed, which slows down computations.

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between 0 and 45oC.

The pressure correction was applied on the seawater scale. Hence, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

K1p First dissociation constant of phosphoric acid (mol/kg)

Author(s)

Jean-Marie Epitalon and Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

See Also

[K2p](#), [K3p](#).

Examples

K1p(35, 25, 0)

K2	<i>Second dissociation constant of carbonic acid (mol/kg)</i>
----	---

Description

Second dissociation constant of carbonic acid (mol/kg)

Usage

K2(S = 35, T = 25, P = 0, k1k2 = "x", pHscale = "T", kSWS2scale=0, ktotalsWS_P0=0)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. It is not required when k1k2 is "m10" and the hydrostatic pressure is 0. If it is required and not given, it is computed, which slows down computations.
ktotalsWS_P0	Conversion factor from the total scale to the SWS at an hydrostatic pressure of 0. It is only required when k1k2 is "l" or "r". If it is required and not given, it is computed, which slows down computations.

Details

The Lueker et al. (2000) constant is recommended by Guide to Best Practices for Ocean CO₂ Measurements (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45°C.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35°C.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50°C.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50°C. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

The pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

K2 Second dissociation constant of carbonic acid (mol/kg)

Author(s)

Jean-Marie Epitalon and Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

The Lueker et al. (2000) constant is recommended by Guide to Best Practices for Ocean CO₂ Measurements (2007). The Roy et al. (1993) constants is recommended by DOE (1994).

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

DOE 1994 *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. ORNL/CDIAC-74. Oak Ridge, Tenn.: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Lueker T. J., Dickson A. G. and Keeling C. D., 2000 Ocean pCO₂ calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO₂ in gas and seawater at equilibrium. *Marine Chemistry* **70** 105-119.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.

Roy R. N., Roy L. N., Vogel K. M., Porter-Moore C., Pearson T., Good C. E., Millero F. J. and Campbell D. M., 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45oC. *Marine Chemistry* **44**, 249-267.

See Also

[K1](#).

Examples

K2(35, 25, 0)

K2p

Second dissociation constant of phosphoric acid (mol/kg)

Description

Second dissociation constant of phosphoric acid (mol/kg)

Usage

K2p(S = 35, T = 25, P = 0, pHscale = "T", kSWS2scale = 0)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. If it is required and not given, it is computed, which slows down computations.

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between 0 and 45oC.

The pressure correction was applied on the seawater scale. Hence, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

K2p Second dissociation constant of phosphoric acid (mol/kg)

Author(s)

Jean-Marie Epitalon and Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication 3*, 1-191.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

See Also

[K1p](#), [K3p](#).

Examples

K2p(35, 25, 0)

K3p *Third dissociation constant of phosphoric acid (mol/kg)*

Description

Third dissociation constant of phosphoric acid (mol/kg)

Usage

K3p(S = 35, T = 25, P = 0, pHscale = "T", kSWS2scale = 0)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. If it is required and not given, it is computed, which slows down computations.

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between 0 and 45oC.

The pressure correction was applied on the seawater scale. Hence, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

K3p Third dissociation constant of phosphoric acid (mol/kg)

Author(s)

Jean-Marie Epitalon and Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication 3*, 1-191.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

See Also

[K1p](#), [K2p](#).

Examples

K3p(35, 25, 0)

Kb *Dissociation constant of boric acid (mol/kg)*

Description

Dissociation constant of boric acid (mol/kg)

Usage

Kb(S = 35, T = 25, P = 0, pHscale="T", kSWS2scale=0, ktotalsWS_P0=0)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from SWS pH scale to chosen scale at chosen pressure; if needed and not given, it is computed; if given, computation speed is increased
ktotal2SWS_P0	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. It is not required when the selected pH scale is SWS and the hydrostatic pressure is 0. If it is required and not given, it is computed, which slows down computations.

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 5 and 45 and T ranging between 0 and 45oC.

The pressure correction is applied on the seawater scale. Hence, values are first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value transformed back to the required scale (T, F or SWS).

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

Kb Dissociation constant of boric acid (mol/kg)

Author(s)

Jean-Marie Epitalon and Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

- Dickson A. G., 1990 Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep-Sea Research* **37**, 755-766.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.
- DOE 1994 *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. ORNL/CDIAC-74. Oak Ridge, Tenn.: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.
- Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Examples

```
Kb(S=35,T=25,P=0,pHscale="T")
```

kconv

*Conversion factors to change the pH scale of dissociation constants***Description**

Conversion factors from the total scale to the free and seawater scales

Usage

```
kconv(S=35,T=25, P=0, kf, Ks, Kff)
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994); if the fonction Kf was used previously, the default value is the value given for the argument kf in the fonction Kf. If the Kf function was not used previously, the default value is "pf", except if T is outside the range 9 to 33oC or of S is outside the range 10 to 40. In these cases, the default is "dg".
Ks	Stability constant of hydrogen sulfate (mol/kg) at given S, T and P, optional; if not given, it will be computed, if given, it allows for speed optimisation
Kff	Stability constant of hydrogen fluoride (mol/kg) on free pH scale at given S, T and P, optional; if not given, it will be computed, if given, it allows for speed optimisation and kf parameter is then ignored

Details

It is critical to consider that each formulation is valid in specific ranges of temperature and salinity:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

Note that kconv may be called in many functions (i.e. K1, K2, K1P, K2P, K3P, Kw, Ksi, etc...) without user controls it. To force a particular formulation for Kf, it is recommended to call kconv() first then pass the resulting conversion factors to these functions.

Value

The function returns a list with 3 conversion factors :

```

ktotal2SWS      to convert from the total scale to seawater scale
ktotal2free     to convert from the total scale to the free scale
kfree2SWS       to convert from the free scale to the seawater scale

```

Author(s)

Karline Soetaert <K.Soetaert@nioo.knaw.nl>

References

Dickson A.G. and F.J. Millero, 1987 A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research* **34**:1733-1743.

See Also

[pHconv](#).

Examples

```

##To convert dissociation constants from the total scale to the free scale
## (at salinity=35, temperature=25oC and atmospheric pressure):
kconv(35,25,0)
conv <- kconv()
c(K1_total=K1(),K1_SWS=K1()*conv$ktotal2SWS,K1_free=K1()*conv$ktotal2free)

```

Kf

Equilibrium constant of hydrogen fluoride (mol/kg)

Description

Stability constant of hydrogen fluoride (mol/kg)

Usage

```
Kf(S = 35, T = 25, P = 0, kf = "x", pHscale="T", Ks_p0=0, Ks_p=0)
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
kf	"pf" for using Kf from Perez and Fraga (1987) "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994), default is "pf". Attention do not use a vector for this argument.

pHscale	choice of pH scale: "T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
Ks_p0	Stability constant of hydrogen sulfate (mol/kg) at pressure zero; needed if kf = "pf" ; if needed and not given, it is computed; if given, computation speed is increased
Ks_p	Stability constant of hydrogen sulfate (mol/kg) at chosen pressure if not given, it is computed; if given, computation speed is increased

Details

The Perez and Fraga (1987) constant is recommended by Guide to Best Practices for Ocean CO₂ Measurements (2007). The Dickson and Riley (1979 in Dickson and Goyet, 1994) constant is recommended by DOE (1994).

It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

The pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

Kf Stability constant of hydrogen fluoride (mol/kg)

Author(s)

Jean-Marie Epitalon and Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G. and Riley J. P., 1979 The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water. *Marine Chemistry* **7**, 89-99.

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

DOE 1994 *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. ORNL/CDIAC-74. Oak Ridge, Tenn.: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Perez F. F. and Fraga F., 1987 Association constant of fluoride and hydrogen ions in seawater. *Marine Chemistry* **21**, 161-168.

Examples

```
Kf(S=35, T=25, P=0, kf="pf", pHscale="T")
```

kfg	<i>variable for internal use</i>
-----	----------------------------------

Description

nothing

Khs	<i>Dissociation constant of hydrogen sulfide (mol/kg)</i>
-----	---

Description

Dissociation constant of hydrogen sulfide (mol/kg)

Usage

```
Khs(S=35, T=25, P=0, pHscale="T")
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between 0 and 45oC.

The pressure correction is applied on the seawater scale. Hence, the values are first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value is transformed back to the required scale (T, F or SWS).

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

Khs Dissociation constant of hydrogen sulfide

Author(s)

Karline Soetaert <K.Soetaert@nioo.knaw.nl> and Heloise Lavigne

References

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* 59: 661-677.

Examples

Khs(S=35,T=25,P=0, pHscale="T")

Kn *Dissociation constant of ammonium (mol/kg)*

Description

Dissociation constant of ammonium on the total scale (mol/kg)

Usage

Kn(S=35, T=25, P=0, pHscale="T")

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between 0 and 45oC.

The pressure correction is applied on the seawater scale. Hence, values are first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value is transformed back to the required scale (T, F or SWS).

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

Kn Dissociation constant of ammonium (mol/kg)

Author(s)

Karline Soetaert <K.Soetaert@nioo.knaw.nl> and Heloise Lavigne

References

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Examples

Kn(S=35,T=25,P=0, pHscale="T")

Kn *Stability constant of hydrogen sulfate (mol/kg)*

Description

Stability constant of hydrogen sulfate (mol/kg)

Usage

Ks(S = 35, T = 25, P = 0, ks="d")

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
ks	"d" for using Ks from Dickson (1990), "k" for using Ks from Khoo et al. (1977), default is "d"

Details

The Dickson (1990) constant is recommended by Guide to Best Practices for Ocean CO₂ Measurements (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

The pressure correction is applied on the free scale.

Value

Ks Stability constant of hydrogen sulfate (mol/kg), pHscale = free scale

Author(s)

Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO_2 measurements. *PICES Special Publication* **3**, 1-191.

Khoo H. K., Ramette R. W., Culberson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **22**, vol49 29-34.

Examples

$\text{Ks}(\text{S}=35, \text{T}=25, \text{P}=0, \text{ks}=\text{"d"})$

Ksi *Dissociation constant of Si(OH)_4*

Description

Dissociation constant of Si(OH)_4 on total scale (mol/kg)

Usage

$\text{Ksi}(\text{S}=35, \text{T}=25, \text{P}=0, \text{pHscale}=\text{"T"}, \text{kSWS2scale}=0)$

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25°C
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. If it is required and not given, it is computed, which slows down computations.

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between 0 and 45°C.

The pressure correction is applied on the seawater scale. Hence, values are first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value is transformed back to the required scale (T, F or SWS).

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

Ksi Dissociation constant of Si(OH)₄ (mol/kg)

Author(s)

Karline Soetaert <K.Soetaert@nioo.knaw.nl> and Heloise Lavigne

References

DOE 1994 *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. ORNL/CDIAC-74. Oak Ridge, Tenn.: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Examples

Ksi(S=35, T=25, P=0, pHscale="T")

Kspa *Solubility product of aragonite (mol/kg)*

Description

Solubility product of aragonite (mol/kg)

Usage

Kspa(S = 35, T = 25, P = 0)

Arguments

S Salinity, default is 35
 T Temperature in degrees Celsius, default is 25°C
 P Hydrostatic pressure in bar (surface = 0), default is 0

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 5 and 44 and T ranging between 5 and 40oC.

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

Kspa Solubility product of aragonite (mol²/kg)

Author(s)

Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Mucci A., 1983 The solubility of calcite and aragonite in seawater at various salinities, temperature, and one atmosphere total pressure. *American Journal of Science* **283**: 780-799.

See Also

[Kspc](#).

Examples

Kspa(S=35, T=25, P=0)

Kspc	<i>Solubility product of calcite (mol/kg)</i>
------	---

Description

Solubility product of calcite (mol/kg)

Usage

Kspc(S = 35, T = 25, P = 0)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 5 and 44 and T ranging between 5 and 40oC.

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

Kspc Solubility product of calcite (mol²/kg)

Author(s)

Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Mucci A., 1983 The solubility of calcite and aragonite in seawater at various salinities, temperature, and one atmosphere total pressure. *American Journal of Science* **283**: 780-799.

See Also

[Kspa](#).

Examples

Kspc(S=35, T=25, P=0)

Kw *Ion product of water (mol²/kg²)*

Description

Ion product of water (mol²/kg²)

Usage

Kw(S = 35, T = 25, P = 0, pHscale = "T", kSWS2scale=0)

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
kSWS2scale	Conversion factor from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated. If it is required and not given, it is computed, which slows down computations.

Details

This formulation is only valid for specific ranges of temperature and salinity:

- S ranging between 0 and 45 and T ranging between 0 and 45oC.

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

Kw	Ion product of water (mol ² /kg ²)
----	---

Author(s)

Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta* **59** 661-677.

Examples

Kw(S=35, T=25, P=0, pHscale="T")

Description

Describes the various approaches that can be used to alter the seawater carbonate system. Its main purpose is to assist the design of ocean acidification perturbation experiments.

Usage

```
oa(flag, var1, var2, pCO2f, pCO2s=1e6, S=35, T=25, P=0,
Pt=0, Sit=0, k1k2='x', kf='x', ks="d", pHscale="T", plot=FALSE, b="110")
```

Arguments

flag	select the couple of variables available to describe the initial seawater. The flags which can be used are: flag = 1 pH and CO ₂ given flag = 2 CO ₂ and HCO ₃ given flag = 3 CO ₂ and CO ₃ given flag = 4 CO ₂ and ALK given flag = 5 CO ₂ and DIC given flag = 6 pH and HCO ₃ given flag = 7 pH and CO ₃ given flag = 8 pH and ALK given flag = 9 pH and DIC given flag = 10 HCO ₃ and CO ₃ given flag = 11 HCO ₃ and ALK given flag = 12 HCO ₃ and DIC given flag = 13 CO ₃ and ALK given flag = 14 CO ₃ and DIC given flag = 15 ALK and DIC given flag = 21 pCO ₂ and pH given flag = 22 pCO ₂ and HCO ₃ given flag = 23 pCO ₂ and CO ₃ given flag = 24 pCO ₂ and ALK given flag = 25 pCO ₂ and DIC given
var1	Value of the first variable available to describe the initial seawater, in mol/kg except for pH and for pCO ₂ in uatm
var2	Value of the second variable available to describe the initial seawater, in mol/kg except for pH
pCO2f	pCO ₂ target value, in uatm

pCO2s	pCO2s is the pCO ₂ , in uatm, of the “high-CO ₂ ” seawater that will be mixed with “normal seawater”. The default value is 10 ⁶ uatm, that is seawater bubbled with pure CO ₂ gas and saturated with CO ₂ .
S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25
P	Hydrostatic pressure in bar (surface = 0), default is 0
Pt	Concentration of total phosphate in mol/kg, default is 0
Sit	Concentration of total silicate in mol/kg, default is 0
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickon (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	"T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
plot	A plot of the different perturbation methods can be plotted in a DIC vs ALK field with pCO ₂ isoclines are drawn in the back. Default is false.
b	"l10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "l10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.

- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a list built as follows:

description	A table describing in plain English the various ways to reach the target pCO ₂ . Note that if a vector is given in argument only the first value is used.
perturbation	Table providing key parameters for the following methods: <i>CO₂ bubbling</i> : high-CO ₂ air is bubbled in seawater. The first parameter is the value of the pCO ₂ in the air required to bubble the seawater (in uatm). <i>SW mixing</i> : mixing of “normal” and “high-CO ₂ ” seawater. The first parameter, “Weight fraction high-CO ₂ SW” or wf, is the weight fraction of the high-CO ₂ seawater per kg seawater. <i>Addition of acid</i> : strong acid is added to seawater. Note that this method is not recommended because it does not closely mimic natural ocean acidification (Gattuso and Lavigne, 2009). The first parameter, H ⁺ (mol/kg), is the amount of H ⁺ that must be added (mol/kg). The acid must be fortified with NaCl in order to have the same salinity than seawater.

Addition of HCO₃ and acid: bicarbonate (HCO₃) and a strong acid are added. The first parameter, HCO₃, is the amount of HCO₃ that must be added (mol/kg). The second parameter, H⁺, is the quantity of H⁺ that must be added (mol/kg). The acid must be fortified with NaCl in order to have the same salinity than seawater.

Addition of CO₃ and acid: carbonate, CO₃, and a strong acid are added. The first parameter, HCO₃, is the quantity of CO₃ that must be added (mol/kg). The second parameter, H⁺, is the quantity of H⁺ that must be added (mol/kg).

summary Table summarizing the carbonate chemistry before and after applying each perturbation: pCO₂ bubbling, mixing with high-CO₂ seawater, addition of strong acid, and addition of bicarbonate/carbonate and strong acid.

Warnings

- It is recommended to use concentrated solutions of acid or base in order to add small volumes.
- The addition of strong acid does not simulate well natural ocean acidification (higher concentration of dissolved inorganic carbon at constant total alkalinity) since it generates a decrease in total alkalinity while dissolved inorganic carbon is kept constant.
- Other important advice is provided in Gattuso and Lavigne (2009), Schulz et al. (2009) and in the “Guide for Best Practices on Ocean Acidification Research and Data Reporting” (<http://www.epoca-project.eu/index.php/Home/Guide-to-OA-Research/>)

Author(s)

Heloise Lavigne and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO₄ in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.
- Khoo H. K., Ramette R. W., Culberson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.
- Gattuso J.-P. and Lavigne H., 2009 Technical note: approaches and software tools to investigate the impact of ocean acidification. *Biogeosciences* **21**, 6:2121-2133.
- Lueker T. J., Dickson A. G. and Keeling C. D., 2000 Ocean pCO₂ calculated from dissolved inorganic carbon, alkalinity, and equations for K₁ and K₂: validation based on laboratory measurements of CO₂ in gas and seawater at equilibrium. *Marine Chemistry* **70** 105-119.
- Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.
- Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Perez F. F. and Fraga F., 1987 Association constant of fluoride and hydrogen ions in seawater. *Marine Chemistry* **21**, 161-168.

Roy R. N., Roy L. N., Vogel K. M., Porter-Moore C., Pearson T., Good C. E., Millero F. J. and Campbell D. M., 1993 The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45oC. *Marine Chemistry* **44**, 249-267.

Schulz K. G., Barcelos e Ramos J., Zeebe R. E. and Riebesell U., 2009 CO2 perturbation experiments: similarities and differences between dissolved inorganic carbon and total alkalinity manipulations. *Biogeosciences* **6**, 2145-2153.

Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Zeebe R. E. and Wolf-Gladrow D. A., 2001 *CO2 in seawater: equilibrium, kinetics, isotopes*. Amsterdam: Elsevier, 346 pp.

See Also

[carb](#), [pgas](#), [pmix](#), [ppH](#), [pTA](#).

Examples

```
oa(flag=24, var1=384, var2=2325e-6, pCO2s=1e6, pCO2f=793, S=34.3, T=16,
P=0, pHscale="T", kf="pf", k1k2="1", ks="d", plot=TRUE, b="110")
```

Om

Carbonate saturation state for magnesian calcites

Description

Calculates the calcium carbonate saturation state for magnesian calcite

Usage

```
Om(x, flag, var1, var2, k1k2='x', kf='x', ks="d", pHscale="T", b="110")
```

Arguments

x	mole fraction of magnesium ions, note that the function is only valid for x ranging between 0 and 0.25
flag	select the couple of variables available. The flags which can be used are: flag = 1 pH and CO2 given flag = 2 CO2 and HCO3 given flag = 3 CO2 and CO3 given flag = 4 CO2 and ALK given

	flag = 5 CO ₂ and DIC given
	flag = 6 pH and HCO ₃ given
	flag = 7 pH and CO ₃ given
	flag = 8 pH and ALK given
	flag = 9 pH and DIC given
	flag = 10 HCO ₃ and CO ₃ given
	flag = 11 HCO ₃ and ALK given
	flag = 12 HCO ₃ and DIC given
	flag = 13 CO ₃ and ALK given
	flag = 14 CO ₃ and DIC given
	flag = 15 ALK and DIC given
	flag = 21 pCO ₂ and pH given
	flag = 22 pCO ₂ and HCO ₃ given
	flag = 23 pCO ₂ and CO ₃ given
	flag = 24 pCO ₂ and ALK given
	flag = 25 pCO ₂ and DIC given
var1	Value of the first variable in mol/kg, except for pH and for pCO ₂ in μatm
var2	Value of the second variable in mol/kg, except for pH
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35°C and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33°C and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickson (1990) and "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	"T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"l10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "l10"

Details

It is important to note that this function is **only valid** for:

- Salinity = 35
- Temperature = 25 degrees Celsius
- Hydrostatic pressure = 0 bar (surface)
- Concentration of total phosphate = 0 mol/kg
- Concentration of total silicate = 0 mol/kg

Note that the stoichiometric solubility products with respect to Mg-calcite minerals have not been determined experimentally. The saturation state with respect to Mg-calcite minerals is therefore calculated based on ion activities, i.e.,

$$\Omega_x = \frac{\{Ca^{2+}\}^{1-x}\{Mg^{2+}\}^x\{CO_3\}^{2-}}{K_x}$$

The ion activity {a} is calculated based on the observed ion concentrations [C] multiplied by the total ion activity coefficient, γ_T , which has been determined experimentally or from theory (e.g. Millero & Pierrot 1998): {a}= γ_T [C]. Because a true equilibrium cannot be achieved with respect to Mg-calcite minerals, K_x represents a metastable equilibrium state obtained from what has been referred to as stoichiometric saturation (Thorstenson & Plummer 1977; a term not equivalent to the definition of the stoichiometric solubility product, see for example Morse et al. (2006) and references therein). In the present calculation calcium and magnesium concentrations were calculated based on salinity. Total ion activity coefficients with respect to Ca^{2+} , Mg^{2+} , and CO_3^{2-} were adopted from Millero & Pierrot (1998).

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a list with

OmegaMgCa_biogenic

Mg-calcite saturation state for minimally prepared biogenic Mg-calcite.

OmegaMgCa_biogenic_cleaned

Mg-calcite saturation state for cleaned and annealed biogenic Mg-calcite.

Author(s)

Heloise Lavigne, Andreas J. Andersson and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Only the references related to the saturation state of magnesian calcite are listed below; the other references are listed under the carb function.

Andersson A. J., Mackenzie F. T., Nicholas R. B., 2008, Life on the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers. *Marine Ecology Progress Series* **373**, 265-273.

Bischoff W. D., Bertram M. A., Mackenzie F. T. and Bishop F.C., 1993 Diagenetic stabilization pathways of magnesian calcites. *Carbonates and Evaporites* **8**, 82-89.

Millero F. J. and Pierrot D., 1998. A chemical equilibrium model for natural waters. *Aquatic Geochemistry* **4**, 153-199.

Morse J. W., Andersson A. J. and Mackenzie F. T., 2006. Initial responses of carbonate-rich shelf sediments to rising atmospheric pCO₂ and ocean acidification: Role of high Mg-calcites. *Geochimica et Cosmochimica Acta* **70**, 5814-5830.

Thorstenson D.C. and Plummer L.N., 1977. Equilibrium criteria for two component solids reacting with fixed composition in an aqueous phase-example: the magnesian calcites. *American Journal of Science* **277**, 1203-1233.

Examples

```
Om(x=seq(0.01, 0.252, 0.01), flag=8, var1=8.2, var2=0.00234,
    k1k2='x', kf='x', ks="d", pHscale="T", b="110")
```

p2d *Converts pressure in dbar to depth in meters*

Description

Converts pressure in dbar to depth in meters

Usage

```
p2d(pressure, lat=40)
```

Arguments

pressure	Pressure in dbar
lat	Latitude in degrees, N and S is irrelevant, default is 40o

Value

depth	Depth corresponding to the pressure given, in meters
-------	--

Author(s)

Heloise Lavigne and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Saunders P. M., 1981. Practical conversion of pressure to depth. *J. Phys. Oceanogr.* **11**: 573-574.

See Also

[d2p](#)

Examples

```
p2d(pressure=7686, lat=30)
```

p2fCO2 *Converts pCO2 (partial pressure in CO2) into fCO2 (fugacity of CO2)*

Description

Converts pCO2 (partial pressure in CO2) into fCO2 (fugacity of CO2)

Usage

p2fCO2(T = 25, Patm=1.0, P=0, pCO2)

Arguments

T	Temperature in degrees Celsius, default is 25oC
Patm	Surface atmospheric pressure in atm, default 1 atm
P	Hydrostatic pressure in bar, default is 0 bar (surface)
pCO2	Partial pressure in CO2 in μ atm, the same units as that for the fugacity output

Value

fCO2 Fugacity of CO2 in μ atm, the same units as that for the pCO2 input.

Author(s)

Heloise Lavigne, Jean-Pierre Gattuso, and James Orr <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.

Weiss, R. F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, **2**, 203-215.

Weiss, R. F. and Price, B. A., 1980. Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347-359.

See Also

[f2pCO2](#).

Examples

p2fCO2(T=25, Patm=0.97, P=0, pCO2=380)

p2xCO2

*Converts partial pressure of CO2 to mole fraction of CO2***Description**

Converts pCO2 (partial pressure of CO2) into xCO2 (mole fraction of CO2)

Usage

p2xCO2(S=35, T=25, Patm=1.0, pCO2)

Arguments

S	Salinity on the practical salinity scale, default is 35
T	Temperature in degrees Celsius, default is 25oC
Patm	Atmospheric pressure in atmospheres, default is 1.0 (this is not the hydrostatic pressure)
pCO2	Partial pressure of CO2 in μatm

Details

The xCO2 (ppm) is computed from pCO2 (μatm) using the following equation: $xCO2 = pCO2 / (Patm - pH2O)$, where pH2O is the vapor pressure of seawater computed following best practices (Dickson et al., 2007). That computed pH2O is identical, when rounded to the 4th decimal place, with that computed by the equation from Weiss and Price (1980).

Value

xCO2 Mole fraction of CO2 in ppm.

Author(s)

James Orr <james.orr@lsce.ipsl.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R. (2007) Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.

Weiss, R. F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, **2**, 203-215.

Weiss, R. F. and Price, B. A. (1980) Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347-359.

See Also

[x2pCO2](#) and [vapress](#)

Examples

```
## Convert atmospheric pressure from mbar to atm
Patm_mbar = 1052          # in millibar
Patm      = Patm_mbar / 1013.25 # in atm
## Compute xCO2 from pCO2
pCO2 = 380
xCO2 = p2xC02(T=25, S=35, Patm=Patm, pCO2=pCO2)
print(xCO2)
## The result is 377.1546 ppm
```

pCa

*pCa***Description**

Calculates the changes in the saturation states of aragonite and calcite resulting from the manipulation of the calcium concentration

Usage

```
pCa(flag, var1, var2, Ca, S=35, T=20, P=0, Pt=0, Sit=0, k1k2="x",
kf="x", ks="d", pHscale="T", b="110")
```

Arguments

flag select the couple of variables available. The flags which can be used are:

- flag = 1 pH and CO2 given
- flag = 2 CO2 and HCO3 given
- flag = 3 CO2 and CO3 given
- flag = 4 CO2 and ALK given
- flag = 5 CO2 and DIC given
- flag = 6 pH and HCO3 given
- flag = 7 pH and CO3 given
- flag = 8 pH and ALK given
- flag = 9 pH and DIC given
- flag = 10 HCO3 and CO3 given
- flag = 11 HCO3 and ALK given
- flag = 12 HCO3 and DIC given
- flag = 13 CO3 and ALK given
- flag = 14 CO3 and DIC given
- flag = 15 ALK and DIC given
- flag = 21 pCO2 and pH given
- flag = 22 pCO2 and HCO3 given
- flag = 23 pCO2 and CO3 given
- flag = 24 pCO2 and ALK given
- flag = 25 pCO2 and DIC given

var1	Value of the first variable in mol/kg, except for pH and for pCO ₂ in μatm
var2	Value of the second variable in mol/kg, except for pH
Ca	Calcium concentration in mol/kg
S	Salinity
T	Temperature in degrees Celsius
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg
Sit	Concentration of total silicate in mol/kg
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickson (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	choice of pH scale: "T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"l10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "l10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

comment	The initial or final state water
S	Salinity
T	Temperature in degrees Celsius
P	Pressure in bar
pH	pH
CO2	CO2 concentration (mol/kg)
pCO2	pCO2, CO2 partial pressure (μ atm)
fCO2	fCO2, CO2 fugacity (μ atm)
HCO3	HCO3 concentration (mol/kg)
CO3	CO3 concentration (mol/kg)
DIC	DIC concentration (mol/kg)
ALK	ALK, total alkalinity (mol/kg)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state

Author(s)

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References

Ben-Yaakov S. and Goldhaber M. B., 1973 The influence of sea water composition on the apparent constants of the carbonate system. *Deep-Sea Research* **20**, 87-99.

Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO_2 measurements. *PICES Special Publication* **3**, 1-191.

Gattuso J.-P. and Lavigne H., 2009 Perturbation experiments to investigate the impact of ocean acidification: approaches and software tools. *Biogeosciences* **6**, 4413-4439.

Khoo H. K., Ramette R. W., Culbertson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.

Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

```
pCa(flag=15, var1=2302e-6, var2=2050e-6, Ca=0.01028, S=35, T=20, P=0,
Pt=0, Sit=0, pHscale="T", kf="pf", k1k2="1", ks="d", b="110") # with normal Ca concentration
pCa(flag=15, var1=2302e-6, var2=2050e-6, Ca=0.01028/2, S=35, T=20, P=0,
Pt=0, Sit=0, pHscale="T", kf="pf", k1k2="1", ks="d", b="110") # with 0.5 * Ca concentration
```

Description

Pressure corrections are based on the following equations:

$$\ln \frac{K_i^P}{K_i^0} = -\frac{\Delta V_i}{RT} \cdot P + 0.5 \frac{\Delta K_i}{RT} \cdot P^2$$

with

$$\Delta V_i = a_0 + a_1 T + a_2 T^2$$

and

$$\Delta K_i = b_0 + b_1 T + b_2 T^2$$

The variables are:

- K indicating the type of equilibrium constant
- coefficient a_0
- coefficient a_1
- coefficient a_2
- coefficient b_0
- coefficient b_1
- coefficient b_2

Usage

Pcoeffs

Format

A data frame with 14 rows and 7 variables

Details

For Kb, to be consistent with Millero (1979) a2 was changed to -2.608e-3 instead of 2.608e-3 (value given in Millero, 1995) For Kw, coefficients are from Millero (1983).

Source

Millero F. J., 1979 The thermodynamics of the carbonate system in seawater. *Geochemica et Cosmochemica Acta* **43**: 1651-1661.

Millero F. J., 1983 Influence of pressure on chemical processes in the sea. pp. 1-88. In J. P. Riley and R. Chester (eds.), *Chemical Oceanography*. Academic Press, New York.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

See Also

Pcorrect

Pcorrect

Pressure correction of equilibrium constants

Description

Computes the pressure correction of the equilibrium constants

Usage

```
Pcorrect(Kvalue, Ktype, T=25, S=35, P=0, pHscale="T",
         kconv2ScaleP0=0, kconv2Scale=0)
```

Arguments

Kvalue	Value of the constant at P=0 (hydrostatic pressure in bar, surface = 0)
Ktype	Name of the constant, <ul style="list-style-type: none"> • K1 First dissociation constant of carbonic acid (mol/kg) • K2 Second dissociation constant of carbonic acid (mol/kg) • Kb Dissociation constant of boric acid (mol/kg) • Kw Ion product of water (mol²/kg²) • Ks Stability constant of hydrogen sulfate (mol/kg) • Kf Stability constant of hydrogen fluoride (mol/kg) • Kspc Solubility product of calcite (mol/kg) • Kspa Solubility product of aragonite (mol/kg) • K1p First dissociation constant of phosphoric acid (mol/kg) • K2p Second dissociation constant of phosphoric acid (mol/kg) • K3p Third dissociation constant of phosphoric acid (mol/kg) • Khs Dissociation constant of hydrogen sulfide (mol/kg) • Kn Dissociation constant of ammonium (mol/kg) • Ksi Dissociation constant of Si(OH)₄ (mol/kg)
T	Temperature in degrees Celsius, default is 25°C
S	Salinity, default is 35
P	Hydrostatic pressure in bar (surface = 0), default is 0
pHscale	pHscale of the constant given in Kvalue
kconv2ScaleP0	Conversion factor from the pH scale selected to the SWS (or free for Kf) scale at pressure zero. It is computed if it is not given, which significantly slows down the computation
kconv2Scale	Conversion factor from the pH scale selected to the SWS (or free for Kf) scale at the hydrostatic pressure value indicated. It is computed if it is not given, which significantly slows down the computation

Details

- The pressure correction is applied on the seawater scale for K1, K2, K1p, K2p, K3p, Kb, Khs, Kn, Ksi and Kw. Hence the K value is first converted on the seawater scale if needed. After pressure correction, the constant is converted back to the initial pH scale.
- The pressure correction is applied on the free scale for Kf.
- There is no issue of pH scale for Ks, Kspa and Kspc.

Value

The equilibrium constant given in argument but after pressure correction

Author(s)

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References

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta* **59** 661-677.

See Also

Pcoeffs

Examples

```
k10 <- K1(T=25, P=0, S=35)
Pcorrect(Kvalue=k10, Ktype="K1", P=300, T=25, S=35, pHscale="T")
```

pgas

pgas

Description

Calculates the carbonate chemistry after changes in pCO₂ generated by gas bubbling

Usage

```
pgas(flag, var1, var2, pCO2g, S=35, T=20, P=0, Pt=0, Sit=0, k1k2="x",
kf="x", ks="d", pHscale="T", b="110")
```

Arguments

flag	select the couple of variables available. The flags which can be used are: flag = 1 pH and CO ₂ given flag = 2 CO ₂ and HCO ₃ given flag = 3 CO ₂ and CO ₃ given flag = 4 CO ₂ and ALK given flag = 5 CO ₂ and DIC given flag = 6 pH and HCO ₃ given flag = 7 pH and CO ₃ given flag = 8 pH and ALK given flag = 9 pH and DIC given flag = 10 HCO ₃ and CO ₃ given flag = 11 HCO ₃ and ALK given flag = 12 HCO ₃ and DIC given flag = 13 CO ₃ and ALK given flag = 14 CO ₃ and DIC given flag = 15 ALK and DIC given flag = 21 pCO ₂ and pH given flag = 22 pCO ₂ and HCO ₃ given flag = 23 pCO ₂ and CO ₃ given flag = 24 pCO ₂ and ALK given flag = 25 pCO ₂ and DIC given
var1	Value of the first variable in mol/kg, except for pH and for pCO ₂ in μ atm
var2	Value of the second variable in mol/kg, except for pH
pCO _{2g}	CO ₂ partial pressure of the gas used for bubbling in μ atm
S	Salinity
T	Temperature in degrees Celsius
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg
Sit	Concentration of total silicate in mol/kg
k1k2	"l" for using K ₁ and K ₂ from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35°C and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using K _f from Perez and Fraga (1987) and "dg" for using K _f from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33°C and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using K _s from Dickson (1990), "k" for using K _s from Khoo et al. (1977), default is "d"

pHscale	"T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"I10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "I10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

- For K_s, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For K_n, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

comment	The initial or final state water
S	Salinity
T	Temperature in degrees Celsius
P	Pressure in bar
pH	pH
CO ₂	CO ₂ concentration (mol/kg)
pCO ₂	pCO ₂ , CO ₂ partial pressure (μ atm)
fCO ₂	fCO ₂ , CO ₂ fugacity (μ atm)
HCO ₃	HCO ₃ concentration (mol/kg)
CO ₃	CO ₃ concentration (mol/kg)
DIC	DIC concentration (mol/kg)
ALK	ALK, total alkalinity (mol/kg)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state

Author(s)

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References

- Dickson A. G. and Riley J. P., 1979 The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water. *Marine Chemistry* **7**, 89-99.
- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO₄ in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.
- Gattuso J.-P. and Lavigne H., 2009 Perturbation experiments to investigate the impact of ocean acidification: approaches and software tools. *Biogeosciences* **6**, 4413-4439.

Khoo H. K., Ramette R. W., Culberson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.

Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.

Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

```
pgas(flag=15, var1=2302e-6, var2=2050e-6, pCO2g=750, S=35, T=20, P=0,
Pt=0, Sit=0, pHscale="T", kf="pf", k1k2="1", ks="d", b="110")
```

pH *Potentiometric pH*

Description

Calculation of potentiometric pH

Usage

```
pH(Ex=-67,Etris=-72.4,S=35,T=25)
```

Arguments

Ex	e.m.f. of the seawater sample in mV, default is 67
Etris	e.m.f. of the TRIS buffer in mV, default is -72.4
S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25°C

Details

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

pH Potentiometric pH (in mol/kg on the total scale)

Author(s)

Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

See Also

[tris](#), [amp](#), [pHslope](#).

Examples

```
##Example from Dickson et al. (2007)
pH(Ex=-67,Etris=-72.4,S=35,T=25)
```

pHconv

Conversion of pH

Description

Converts pH from one scale to another one chosen between the total scale, the free scale and the seawater scale

Usage

```
pHconv(flag=1,pH=8.10,S=35,T=25, P=0, ks="d")
```

Arguments

flag	choice of the type of conversion : flag=1: seawater scale to total scale flag=2: free scale to total scale flag=3: total scale to seawater scale flag=4: total scale to free scale flag=5: seawater scale to free scale flag=6: free scale to seawater scale default is flag=1
pH	Enter the value of pH which need to be converted, default is 8.100
S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
ks	"d" for using Ks from Dickon (1990), "k" for using Ks from Khoo et al. (1977), default is "d"

Details

The Dickson (1990) constant is recommended by the Guide to Best Practices for Ocean CO₂ Measurements (2007). It is critical to consider that each formulation is valid in specific ranges of temperature and salinity:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Value

The function returns the values of pH converted

Author(s)

Heloise Lavigne and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A.G. and F.J. Millero, 1987 A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research* **34**:1733-1743.

Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

Khoo H. K., Ramette R. W., Culberson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40oC: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.

See Also

[kconv](#).

Examples

```
##To convert pH=8.10 from the seawater scale to the total scale
##at salinity=35, temperature=25oC and atmospheric pressure:
```

```
pHc <- pHconv(flag=1, pH=8.10, S=35, T=25, P=0, ks="d")
```

```
##note that pHc is the value of the pH converted in total scale
```

```
## By using vectors
```

```
## to convert the pH values : 8, 8.05, 8.10, 8.15, 8.20
```

```
## from the free to the total scale

pH <- c(8, 8.05, 8.10, 8.15, 8.20)
pHc <- pHconv(flag=2, pH=pH, S=35, T=25, P=0, ks="d")

## note that pHc is a vector containing the value of the pH converted
## to the total scale
```

pHinsi

pH at in situ temperature

Description

pH at in situ temperature

Usage

```
pHinsi(pH=8.2, ALK=2.4e-3, Tinsi=20, Tlab=25, S=35, Pt=0, Sit=0, k1k2 = "x",
kf = "x", ks="d", pHscale = "T", b="110")
```

Arguments

pH	pH measured in the laboratory
ALK	ALK, total alkalinity (mol/kg)
Tinsi	In situ temperature in degrees Celsius
Tlab	Measurement temperature in degrees Celsius
S	Salinity
Pt	value of the concentration of total phosphate in mol/kg
Sit	the value of the total silicate in mol/kg
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickon (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	choice of pH scale: "T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"110" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "110"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

pH pH at in situ temperature

Author(s)

Jean-Pierre Gattuso, <gattuso@obs-vlfr.fr>

References

Hunter K. A., 1998. The temperature dependence of pH in surface seawater. *Deep-Sea Research (Part I, Oceanographic Research Papers)* **45**(11):1919-1930.

Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantoc oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.

Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

pHinsi (pH=8.2, ALK=2.4e-3, Tinsi=25, Tlab=25, S=35, Pt=0, Sit=0)

pHslope *Slope of the calibration curve of a pH electrode*

Description

Slope of the calibration curve of a pH electrode (percent of theoretical slope)

Usage

pHslope(Etris=-72.4, Eamp=4.9, S=35, T=25)

Arguments

Etris	e.m.f. of the TRIS buffer in mV, default is -72.4
Eamp	e.m.f. of the AMP buffer in mV, default is 4.9
S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC

Details

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

pHslope Slope of the calibration curve (in percent of theoretical slope)

Author(s)

Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

See Also

[tris](#), [amp](#), [pH](#).

Examples

```
##Example from Dickson et al. (2007)
pHslope(Etris=-72.4,Eamp=4.9,S=35,T=25)
```

pmix

pmix

Description

Calculates the carbonate chemistry after mixing of two water samples with different pCO₂

Usage

```
pmix(flag, var1, var2, pCO2s, wf, S=35, T=20, P=0, Pt=0, Sit=0, k1k2="x",
kf="x", ks="d", pHscale="T", b="110")
```

Arguments

flag select the couple of variables available. The flags which can be used are:
flag = 1 pH and CO₂ given
flag = 2 CO₂ and HCO₃ given
flag = 3 CO₂ and CO₃ given
flag = 4 CO₂ and ALK given
flag = 5 CO₂ and DIC given

	flag = 6 pH and HCO ₃ given
	flag = 7 pH and CO ₃ given
	flag = 8 pH and ALK given
	flag = 9 pH and DIC given
	flag = 10 HCO ₃ and CO ₃ given
	flag = 11 HCO ₃ and ALK given
	flag = 12 HCO ₃ and DIC given
	flag = 13 CO ₃ and ALK given
	flag = 14 CO ₃ and DIC given
	flag = 15 ALK and DIC given
	flag = 21 pCO ₂ and pH given
	flag = 22 pCO ₂ and HCO ₃ given
	flag = 23 pCO ₂ and CO ₃ given
	flag = 24 pCO ₂ and ALK given
	flag = 25 pCO ₂ and DIC given
var1	Value of the first variable in mol/kg except for pH and for pCO ₂ in μatm
var2	Value of the second variable in mol/kg except for pH
pCO _{2s}	Partial pressure of the high CO ₂ component in μatm
wf	Weight fraction of the high CO ₂ seawater per kg seawater
S	Salinity
T	Temperature in degrees Celsius
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg
Sit	Concentration of total silicate in mol/kg
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickon (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale
b	"l10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "l10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

comment	The initial or final state water
S	Salinity
T	Temperature in degrees Celsius
P	Pressure in bar
pH	pH
CO2	CO2 concentration (mol/kg)
pCO2	pCO2, CO2 partial pressure (μatm)
fCO2	fCO2, CO2 fugacity (μatm)
HCO3	HCO3 concentration (mol/kg)
CO3	CO3 concentration (mol/kg)
DIC	DIC concentration (mol/kg)
ALK	ALK, total alkalinity (mol/kg)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state

Author(s)

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References

- Dickson A. G. and Riley J. P., 1979 The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water. *Marine Chemistry* **7**, 89-99.
- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.
- Gattuso J.-P. and Lavigne H., 2009. Perturbation experiments to investigate the impact of ocean acidification: approaches and software tools. *Biogeosciences* **6**, 4413-4439.
- Khoo H. K., Ramette R. W., Culbertson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.
- Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.
- Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.

Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

```
pmix(flag=24, var1=384, var2=2302e-6, pCO2s=1e6, wf=0.003, S=34.3,
T=16, P=0, pHscale="T", kf="pf", k1k2="1", ks="d", b="110")
```

pH

ppH

Description

Calculates the carbonate chemistry after pH manipulations through addition of acid or base

Usage

```
ppH(flag, sys, var1, var2, pCO2a, vol, N, S=35, T=20, P=0, Pt=0,
Sit=0, pHscale="T", k1k2="x", kf="x", ks="d")
```

Arguments

flag Select the couple of variables available. The flags which can be used are:

flag = 1 pH and CO₂ given

flag = 2 CO₂ and HCO₃ given

flag = 3 CO₂ and CO₃ given

flag = 4 CO₂ and ALK given

flag = 5 CO₂ and DIC given

flag = 6 pH and HCO₃ given

flag = 7 pH and CO₃ given

flag = 8 pH and ALK given

flag = 9 pH and DIC given

flag = 10 HCO₃ and CO₃ given

flag = 11 HCO₃ and ALK given

flag = 12 HCO₃ and DIC given

flag = 13 CO₃ and ALK given

flag = 14 CO₃ and DIC given

flag = 15 ALK and DIC given

flag = 21 pCO₂ and pH given

	flag = 22 pCO ₂ and HCO ₃ given
	flag = 23 pCO ₂ and CO ₃ given
	flag = 24 pCO ₂ and ALK given
	flag = 25 pCO ₂ and DIC given
sys	0 if the manipulation is carried out in a system closed to the atmosphere or 1 if it is carried out in a system open to the atmosphere
var1	Value of the first variable in mol/kg, except for pH and for pCO ₂ in μatm
var2	Value of the second variable in mol/kg, except for pH
pCO _{2a}	CO ₂ partial pressure in the atmosphere pCO ₂ in μatm . It is only used in systems open to the atmosphere (i.e. when sys=1)
vol	Volume of acid or base added in liter. By convention, it is given a negative sign for acid additions and a positive sign for base additions. The acid must be fortified with NaCl in order to have the same salinity than seawater.
N	Normality of the acid or base in mol/kg
S	Salinity
T	Temperature in degrees Celsius
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg
Sit	Concentration of total silicate in mol/kg
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickson (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	choice of pH scale: "T" for using the total scale, "F" for using the free scale and "SWS" for using the seawater scale, default is total scale

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.

- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

comment	The initial or final state water
S	Salinity
T	Temperature in degrees Celsius
P	Pressure in bar
pH	pH

CO2	CO2 concentration (mol/kg)
pCO2	pCO2, CO2 partial pressure (μatm)
fCO2	fCO2, CO2 fugacity (μatm)
HCO3	HCO3 concentration (mol/kg)
CO3	CO3 concentration (mol/kg)
DIC	DIC concentration (mol/kg)
ALK	ALK, total alkalinity (mol/kg)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state

Author(s)

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References

- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.
- Khoo H. K., Ramette R. W., Culbertson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.
- Gattuso J.-P. and Lavigne H., 2009 Perturbation experiments to investigate the impact of ocean acidification: approaches and software tools. *Biogeosciences* **6**, 4413-4439.
- Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.
- Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

See Also

[buffer](#).

Examples

```
ppH(flag=24, sys=0, var1=384, var2=2302e-6, pCO2a=384, vol=-12e-3,
N=0.01, S=34.3, T=16, P=0, pHscale="T", kf="pf", k1k2="1", ks="d")
```

```
ppH(flag=24, sys=1, var1=384, var2=2302e-6, pCO2a=384, vol=-12e-3,
N=0.01, S=34.3, T=16, P=0, pHscale="T", kf="pf", k1k2="1", ks="d")
```

psi

*Molar ratio of CO₂ released vs CaCO₃ precipitated***Description**

Returns the molar ratio of CO₂ released vs CaCO₃ precipitated described by Frankignoulle et al. (1994).

Usage

```
psi(flag, var1, var2, S=35, T=20, P=0, Pt=0, Sit=0, pHscale="T",
kf="x", k1k2="x", ks="d")
```

Arguments

flag	select the couple of variables available. The flags which can be used are: flag = 1 pH and CO ₂ given flag = 2 CO ₂ and HCO ₃ given flag = 3 CO ₂ and CO ₃ given flag = 4 CO ₂ and ALK given flag = 5 CO ₂ and DIC given flag = 6 pH and HCO ₃ given flag = 7 pH and CO ₃ given flag = 8 pH and ALK given flag = 9 pH and DIC given flag = 10 HCO ₃ and CO ₃ given flag = 11 HCO ₃ and ALK given flag = 12 HCO ₃ and DIC given flag = 13 CO ₃ and ALK given flag = 14 CO ₃ and DIC given flag = 15 ALK and DIC given flag = 21 pCO ₂ and pH given flag = 22 pCO ₂ and HCO ₃ given flag = 23 pCO ₂ and CO ₃ given flag = 24 pCO ₂ and ALK given flag = 25 pCO ₂ and DIC given
var1	enter value of the first variable in mol/kg, except for pH and for pCO ₂ in μ atm
var2	enter value of the second variable in mol/kg, except for pH
S	Salinity
T	Temperature in degrees Celsius
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg; set to 0 if NA

Sit	Concentration of total silicate in mol/kg; set to 0 if NA
pHscale	choice of pH scale: "T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickson (1990), "k" for using Ks from Khoo et al. (1977), default is "d"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For Kf:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

psi ratio of CO₂ released vs CaCO₃ precipitated (mol/mol)

Author(s)

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References

- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO₄ in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.
- Khoo H. K., Ramette R. W., Culbertson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.
- Frankignoulle M., 1994 A complete set of buffer factors for acid/base CO₂ system in seawater. *Journal of Marine Systems* **5**, 111-118.
- Frankignoulle M., Canon C. and Gattuso J.P., 1994 Marine calcification as a source of carbon dioxide- Positive feedback of increasing atmospheric CO₂. *Limnology and Oceanography* **2**, 458-462.
- Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.
- Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.

See Also

[speciation.](#)

Examples

```
## Calculation using the numerical example given in Frankignoulle et al. (1994)
psi(flag=24, var1=350, var2=2400e-6, S=35, T=25, P=0, Pt=0,
Sit=0, pHscale="T", kf="pf", k1k2="1", ks="d")
```

pTA

pTA

Description

Calculates the carbonate chemistry following addition of CO_3^{2-} or HCO_3^-

Usage

```
pTA(flag, sys=0, var1, var2, pCO2a, co3, hco3, S=35, T=20, P=0,
Pt=0, Sit=0, k1k2="x", kf="x", ks="d", pHscale="T", b="110")
```

Arguments

flag	select the couple of variables available. The flags which can be used are:
	flag = 1 pH and CO2 given
	flag = 2 CO2 and HCO3 given
	flag = 3 CO2 and CO3 given
	flag = 4 CO2 and ALK given
	flag = 5 CO2 and DIC given
	flag = 6 pH and HCO3 given
	flag = 7 pH and CO3 given
	flag = 8 pH and ALK given
	flag = 9 pH and DIC given
	flag = 10 HCO3 and CO3 given
	flag = 11 HCO3 and ALK given
	flag = 12 HCO3 and DIC given
	flag = 13 CO3 and ALK given
	flag = 14 CO3 and DIC given
	flag = 15 ALK and DIC given
	flag = 21 pCO2 and pH given
	flag = 22 pCO2 and HCO3 given
	flag = 23 pCO2 and CO3 given
	flag = 24 pCO2 and ALK given
	flag = 25 pCO2 and DIC given

sys	0 if the manipulation is carried out in a system closed to the atmosphere or 1 if it is carried out in a system open to the atmosphere
var1	Value of the first variable in mol/kg, except for pH and for pCO ₂ in μatm
var2	Value of the second variable in mol/kg, except for pH
pCO _{2a}	CO ₂ partial pressure in the atmosphere pCO ₂ in μatm . It is only used in systems open to the atmosphere (i.e. when sys=1)
co3	Amount of CO_3^{2-} added in mol kg^{-1}
hco3	Amount of HCO_3^{-} added in mol kg^{-1}
S	Salinity
T	Temperature in degrees Celsius
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg
Sit	Concentration of total silicate in mol/kg
k1k2	"l" for using K1 and K2 from Lueker et al. (2000), "m06" from Millero et al. (2006), "m10" from Millero (2010) and "r" from Roy et al. (1993). "x" is the default flag; the default value is then "l", except if T is outside the range 2 to 35oC and/or S is outside the range 19 to 43. In these cases, the default value is "m10".
kf	"pf" for using Kf from Perez and Fraga (1987) and "dg" for using Kf from Dickson and Riley (1979 in Dickson and Goyet, 1994). "x" is the default flag; the default value is then "pf", except if T is outside the range 9 to 33oC and/or S is outside the range 10 to 40. In these cases, the default is "dg".
ks	"d" for using Ks from Dickson (1990), "k" for using Ks from Khoo et al. (1977), default is "d"
pHscale	"T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale, default is "T" (total scale)
b	"l10" for computing boron total from the Lee et al. (2010) formulation or "u74" for using the Uppstrom (1974) formulation, default is "l10"

Details

The Lueker et al. (2000) constants for K1 and K2, the Perez and Fraga (1987) constant for Kf and the Dickson (1990) constant for Ks are recommended by Dickson et al. (2007). It is, however, critical to consider that each formulation is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2006): S ranging between 0.1 and 50 and T ranging between 1 and 50oC.
- Millero (2010): S ranging between 1 and 50 and T ranging between 0 and 50oC. Millero (2010) provides a K1 and K2 formulation for the seawater, total and free pH scales. Therefore, when this method is used and if P=0, K1 and K2 are computed with the formulation corresponding to the pH scale given in the flag "pHscale".

For K0:

- Perez and Fraga (1987): S ranging between 10 and 40 and T ranging between 9 and 33oC.
- Dickson and Riley (1979 in Dickson and Goyet, 1994): S ranging between 0 and 45 and T ranging between 0 and 45oC.

For Ks:

- Dickson (1990): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Khoo et al. (1977): S ranging between 20 and 45 and T ranging between 5 and 40oC.

The arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It is recommended to use either vectors with the same dimension or one vector for one argument and numbers for the other arguments.

Pressure corrections and pH scale:

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs and Ksi, the pressure correction was applied on the seawater scale. Hence, if needed, values were first transformed from the total scale to the seawater scale, the pressure correction applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kf, the pressure correction was applied on the free scale. The formulation of Dickson and Riley (1979 in Dickson and Goyet, 1994) provides Kf on the free scale but that of Perez and Fraga (1987) provides it on the total scale. Hence, in that case, Kf was first transformed from the total scale to the free scale. With both formulations, the pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Ks, the pressure correction was applied on the free scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).
- For Kn, The pressure correction was applied on the seawater scale. The pressure correction was applied as described by Millero (1995), and the value was transformed back to the required scale (T, F or SWS).

Value

The function returns a data frame containing the following columns:

comment	The initial or final state water
S	Salinity
T	Temperature in degrees Celsius
P	Pressure in bar
pH	pH
CO2	CO2 concentration (mol/kg)
pCO2	pCO2, CO2 partial pressure (μatm)
fCO2	fCO2, CO2 fugacity (μatm)

HCO3	HCO3 concentration (mol/kg)
CO3	CO3 concentration (mol/kg)
DIC	DIC concentration (mol/kg)
ALK	ALK, total alkalinity (mol/kg)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state

Author(s)

Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

- Dickson A. G. and Riley J. P., 1979 The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water. *Marine Chemistry* **7**, 89-99.
- Dickson A. G., 1990 Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113-127.
- Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.
- Gattuso J.-P. and Lavigne H., 2009 Perturbation experiments to investigate the impact of ocean acidification: approaches and software tools. *Biogeosciences* **6**, 4413-4439.
- Khoo H. K., Ramette R. W., Culbertson C. H. and Bates R. G., 1977 Determination of Hydrogen Ion Concentration in Seawater from 5 to 40°C: Standard Potentials at Salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.
- Lee K., Tae-Wook K., Byrne R.H., Millero F.J., Feely R.A. and Liu Y-M, 2010 The universal ratio of the boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta* **74** 1801-1811.
- Millero F. J., 1995 Thermodynamics of the carbon dioxide system in the oceans. *Geochimica Cosmochimica Acta* **59**: 661-677.
- Millero F. J., 2010 Carbonate constant for estuarine waters. *Marine and Freshwater Research* **61**: 139-142.
- Millero F. J., Graham T. B., Huang F., Bustos-Serrano H. and Pierrot D., 2006 Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Marine Chemistry* **100**, 80-84.
- Uppstrom L.R., 1974 The boron/chlorinity ratio of the deep-sea water from the Pacific Ocean. *Deep-Sea Research I* **21** 161-162.

Examples

```
pTA(flag=24, sys=0, var1=384, var2=2302e-6, pCO2a=384, co3=260e-6,
hco3=1000e-6, S=34.3, T=16, P=0, pHscale="T", kf="pf", k1k2="1", ks="d", b="110")
```

```
pTA(flag=24, sys=1, var1=384, var2=2302e-6, pCO2a=384, co3=260e-6,
hco3=1000e-6, S=34.3, T=16, P=0, pHscale="T", kf="pf", k1k2="1", ks="d", b="110")
```

rho	<i>Density of seawater (kg/m³)</i>
-----	---

Description

Calculates the density of seawater ($kg\ m^{-3}$)

Usage

```
rho(S = 35, T = 25, P = 0)
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0

Value

rho	Density of seawater (kg/m ³)
-----	--

Author(s)

Aurelien Proye and Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Millero F. J. and Poisson A., 1981 International one-atmosphere equation of state of seawater. *Deep-Sea Research* **28A**, 625-629.

Examples

```
rho(35,25,0)
```

seacarb_test_P0	<i>Test data file (at P=0) to test the use of the carb function</i>
-----------------	---

Description

The variables are:

- Flag indicating which couple of variables is used
- Value of the first variable in mol/kg, except for pH and for pCO₂ in μatm
- Value of the second variable in mol/kg, except for pH
- Salinity
- Temperature in degrees Celsius
- Hydrostatic pressure in bar (surface = 0)
- Value of the concentration of total phosphate in mol/kg
- Value of the total silicate in mol/kg

Usage

seacarb_test_P0

Format

A data frame with 20 rows and 8 variables

Source

None, these data were invented for this purpose. The input variables were chosen in order to check that the carbonate chemistry is identical for all flags.

seacarb_test_P300 *Test data file (at P=300) to test the use of the carb function*

Description

The variables are:

- Flag indicating which couple of variables is used
- Value of the first variable in mol/kg, except for pH and for pCO₂ in μatm
- Value of the second variable in mol/kg, except for pH
- Salinity
- Temperature in degrees Celsius
- Hydrostatic pressure in bar (P=300)
- Value of the concentration of total phosphate in mol/kg
- Value of the total silicate in mol/kg

Usage

seacarb_test_P300

Format

A data frame with 20 rows and 8 variables

Source

None, these data were invented for this purpose. The input variables were chosen in order to check that the carbonate chemistry is identical for all flags.

speciation	<i>ionic forms as a function of pH</i>
------------	--

Description

Estimates the concentration of the various ionic forms of a molecule as a function of pH

Usage

```
speciation(K1=K1(), K2=NULL, K3=NULL, pH, conc=1)
```

Arguments

K1	First dissociation constant
K2	Second dissociation constant, default is NULL
K3	Third dissociation constant, default is NULL
pH	pH value, default is 8
conc	concentration of molecule in mol/kg, default is 1 mol/kg

Value

The function returns a data frame containing the following concentrations (in mol/kg if conc is given in mol/kg):

C1	ionic form 1, univalent, bivalent and trivalent molecules
C2	ionic form 2, univalent, bivalent and trivalent molecules
C3	ionic form 3, bivalent and trivalent molecules
C4	ionic form 4, trivalent molecules

Author(s)

Karline Soetaert <K.Soetaert@nioo.knaw.nl>

References

Zeebe R. E. and Wolf-Gladrow D. A., 2001 *CO₂ in seawater: equilibrium, kinetics, isotopes*. Amsterdam: Elsevier, 346 pp.

See Also

[bjerrum](#).

Examples

```
## Speciation of divalent species; example to estimate the various ionic forms
## of dissolved inorganic carbon (DIC = 0.0021 mol/kg) at a salinity of 35,
## a temperature of 25oC and an hydrostatic pressure of 0:
spec <- speciation (K1(35, 25, 0), K2(35, 25, 0), pH=8, conc=0.0021)
## where (spec$C1=[CO2], spec$C2=[HCO3-], spec$C3=[CO3--])

## Speciation of trivalent species (e.g., H3PO4, H2PO4-, HP04--, P04---)
speciation(K1p(), K2p(), K3p(), conc=0.001)

## Effect of temperature on pCO2 - Figure 1.4.18 of Zeebe and Wolf-Gladrow (2001)
Tseq <- seq(0, 30, by=0.5)
pHseq <- carb(flag=15, var1=2300e-6, var2=1900e-6, S=35, T=Tseq, P=0)$pH
CO2 <- speciation(K1(T=Tseq), K2(T=Tseq), conc=1900, pH=pHseq)$C1
pCO2 <- CO2/K0(T=Tseq)
plot(Tseq, pCO2, xlab="Temperature (oC)", ylab="pCO2 (uatm)", type="l",
main="effect of temperature on pCO2")
legend("topleft", c(expression(sum(CO[2])=1900~umol~kg^-1"),
expression(TA=2300~umol~kg^-1")))
```

tris

pH value of the TRIS buffer

Description

pH value of the TRIS buffer (on the total scale in mol/kg)

Usage

```
tris(S=35,T=25)
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC

Details

Note that the arguments can be given as a unique number or as vectors. If the lengths of the vectors are different, the longer vector is retained and only the first value of the other vectors is used. It can therefore be critical to use vectors of the same length.

Value

tris pH value of the TRIS buffer (on the total scale in mol/kg)

Author(s)

Jean-Pierre Gattuso <gattuso@obs-vlfr.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R., 2007 Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

See Also

[amp](#), [pHs1ope](#), [pH](#).

Examples

```
##Example from Dickson et al. (2007)
tris(S=35,T=25)
```

vapress	<i>Computes vapor pressure of seawater</i>
---------	--

Description

Computes vapor pressure of seawater (atm) from temperature and salinity

Usage

```
vapress(S=35, T=25, form="d2007")
```

Arguments

S	Salinity on the practical salinity scale, default is 35
T	Temperature in degrees Celsius, default is 25oC
form	choose either "d2007" for the best-practices formulation to compute vapor pressure of seawater from Dickson et al. (2007) or "wp1980" for the formulation from weiss and Price (1980).

Details

Computes the vapor pressure of seawater p_{H2O} following best practices (Dickson et al., 2007). That computed p_{H2O} is identical, when rounded to the 4th decimal place, with that computed by the equation from Weiss and Price (1980).

Value

vapress Vapor pressure of seawater in atm

Author(s)

James Orr <james.orr@lsce.ipsl.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R. (2007) Guide to best practices for ocean CO₂ measurements. *PICES Special Publication* **3**, 1-191.

Weiss, R. F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, **2**, 203-215.

Weiss, R. F. and Price, B. A. (1980) Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347-359.

See Also

[x2pCO2](#), and [p2xCO2](#).

Examples

```
pH20 <- vapress(S=35, T=25, form="d2007")
```

x2pCO2

Converts mole fraction to partial pressure of CO2

Description

Converts xCO₂ (mole fraction of CO₂) into pCO₂ (partial pressure of CO₂)

Usage

```
x2pCO2(S=35, T=25, Patm=1.0, xCO2=400)
```

Arguments

S	Salinity on the practical salinity scale, default is 35
T	Temperature in degrees Celsius, default is 25oC
Patm	Atmospheric pressure in atmospheres, default is 1.0
xCO2	Mole fraction of CO ₂ in ppm, default is 400

Details

The mole fraction x_{CO_2} (ppm) is computed from p_{CO_2} (μatm) using the following equation: $p_{CO_2} = x_{CO_2}(P_{atm} - p_{H_2O})$, where p_{H_2O} is the vapor pressure of seawater computed following best practices (Dickson et al., 2007). That computed p_{H_2O} is identical, when rounded to the 4th decimal place, with that computed by the equation from Weiss and Price (1980).

Value

pCO2 Partial pressure of CO2 in μatm .

Author(s)

James Orr <james.orr@lsce.ipsl.fr>

References

Dickson A. G., Sabine C. L. and Christian J. R. (2007) Guide to best practices for ocean CO2 measurements. *PICES Special Publication* **3**, 1-191.

Weiss, R. F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, **2**, 203-215.

Weiss, R. F. and Price, B. A. (1980) Nitrous oxide solubility in water and seawater, *Mar. Chem.*, **8**, 347-359.

See Also

[p2xCO2](#) and [vapress](#)

Examples

```
## Atmospheric pressure is rarely equal to 1 atm exactly
## Over the Southern Ocean Patm=0.97 is more realistic
pCO2_socn <- x2pCO2(S=35, T=0, Patm=0.97, xCO2=400.0)
print(pCO2_socn)
## The result (385.6322 uatm) is 12 uatm less than if it was wrongly assumed that Patm=1.0

## Show effect of temperature on pCO2 computed from xCO2, and on resulting variables from "carb"
S <- 35
ALK <- 2300e-6
T <- seq(0,30,5)
xCO2 <- 400
pCO2 <- x2pCO2(S=35, T=T, Patm=1, xCO2=400)
results <- carb(flag=24, var1=pCO2, var2=ALK, S=S, T=T, P=0, Pt=0, Sit=0,
  pHscale="T", kf="pf", k1k2="1", ks="d", b="110")
print(results)
```

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