Package 'seacarb'

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

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Contents

`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 <jean-pierre.gattuso@imev-mer.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)
```

`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="Relative concentration (%)", 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]~PO[4]),
expression(H[2]~PO[4]^"-"),
expression(HPO[4]^"2-"),expression(PO[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	"l10" for using the formulation of Lee et al. (2010), "u74" for using the Uppstrom (1974), or "k18" for using the Kulinski et al. (2018), default is "u74"

Details

Note that the formulation of Kulinski et al. (2018) is specifically designed for the Baltic Sea. Three formulations are described in their paper:

- based on their measurements: TB = [umol/kg] = 10.838 * S + 13.821
- based on Kremling (1970 and 1972): TB [umol/kg] = 11.44 * S + 12.6; R2 = 0.95
- consensus regression (Kremling + their data): TB [umol/kg] = 11.405 * S + 11.869; R2 = 0.97s

The latter formulation is used here.

Value

bor	total boron concentration ($mol\ kg^{-1}$))

Author(s)

Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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.

Kulinski K., Szymczycha B., Koziorowska K., Hammer K. & Schneider B., 2018. Anomaly of total boron concentration in the brackish waters of the Baltic Sea and its consequence for the CO2 system calculations. *Marine Chemistry*. doi:10.1016/j.marchem.2018.05.007.

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, "l10")
```

`buffderiv` *Analytic partial derivatives of the Bolin sensitivity Be*

Description

Computes, in closed form, the four partial derivatives of the Bolin sensitivity $B_e = \partial DIC/\partial[CO_2^*]$ (at constant total alkalinity, temperature and salinity) with respect to temperature, salinity, DIC and total alkalinity.

Usage

```
buffderiv(flag, var1, var2, S = 35, T = 25, Patm = 1, Pt = 0, Sit = 0,
          NH4t = 0, HSt = 0, k1k2 = "l", kf = "dg", ks = "d",
          pHscale = "T", b = "u74", warn = "y", npolish = 3)
```

Arguments

`flag`	select the pair of variables available, as in `carb`
`var1`	value of the first variable in mol/kg, except for pH, and for pCO2 in μatm
`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 is 1 atm
`Pt`	concentration of total dissolved inorganic phosphorus (mol/kg)
`Sit`	concentration of total dissolved inorganic silicon (mol/kg)
`NH4t`	concentration of total dissolved inorganic ammonia (mol/kg)

HSt	concentration of total dissolved inorganic hydrogen sulfide (mol/kg)
k1k2	formulation of K1 and K2. **Must be "l"** (Lueker et al., 2000). See Details.
kf	formulation of Kf. **Must be "dg"** (Dickson and Riley, 1979). See Details.
ks	formulation of Ks. Must be "d" (Dickson, 1990).
pHscale	choice of pH scale. Must be "T" (total scale).
b	formulation of total boron. Must be "u74" (Uppstrom, 1974).
warn	"y" to show warnings when T or S go beyond the valid range
npolish	number of Newton refinement steps applied to [H+] (default 3). See Details.

Details

Surface only (P = 0).

Method. The proton concentration h is fixed implicitly by the total alkalinity constraint

$$F(h; T, S, C_T, A_T) = A_c(h, C_T) + A_{nc}(h) - A_T = 0$$

and B_e is then an explicit algebraic function $G(h, C_T, T, S)$, the same one evaluated by buffsun. For any Y in $\{T, S, C_T, A_T\}$, the implicit function theorem gives

$$\frac{dB_e}{dY} = G_Y + G_h \left(-\frac{F_Y}{F_h} \right)$$

Every term is closed form. The only nonlinear solve is the single call to carb (or carbfull) that supplies h. This makes the routine roughly two orders of magnitude cheaper than differencing carb() numerically, and free of step-size error.

Acid-base systems. Carbonate, borate, water, phosphate, silicate, fluoride, and (on the carbfull path) ammonia and sulfide. Sulfate and the free proton are carried exactly as in SolveSAPHE. The alkalinity is precisely the one that seacarb itself inverts; alk_residual is returned so this can be checked at every point.

Silicate follows the solver. When NH4t = HSt = 0 the routine calls carb, whose alkalinity treats silicate as *monoprotic* (K1si only). Otherwise it calls carbfull, which is *diprotic*. K2si is set to zero on the first path, which reduces the diprotic expressions to the monoprotic ones exactly.

Constants are not optional. The analytic dK/dT and dK/dS (in dlnK.R) are the exact derivatives of specific formulations, so buffderiv stops rather than silently returning derivatives of the wrong function. Two of the guards matter in practice: k1k2 = "x" silently switches to Waters et al. (2014) when T < 2 or T > 35 or S < 19 or S > 43, which is exactly where polar surface waters lie; and kf = "x" silently switches between Perez and Fraga and Dickson and Riley by T and S range, changing the SWS-to-total conversion and hence Kw, Ksi, K1p, K2p and K3p by 0.5 to 0.9 percent. Neither switch warns.

Newton refinement. carb() returns h converged to roughly 1e-10 relative. B_e is steep in h and its derivatives steeper still, so buffderiv applies npolish Newton steps to $F(h) = 0$ using F_h, which it needs anyway. Speciation, B_e and all four derivatives then follow from the same h to machine precision. Set npolish = 0 to use carb()'s h untouched.

Value

A data frame containing:

Be	Bolin sensitivity, dimensionless
dBe_dT	derivative of Be with respect to temperature, per degree Celsius
dBe_dS	derivative of Be with respect to salinity, per practical salinity unit
dBe_dCT	derivative of Be with respect to DIC, per (mol/kg)
dBe_dAT	derivative of Be with respect to total alkalinity, per (mol/kg)
dh_dT	derivative of [H+] with respect to temperature, (mol/kg) per degree Celsius
dh_dS	derivative of [H+] with respect to salinity, (mol/kg) per psu
dh_dCT	derivative of [H+] with respect to DIC, dimensionless
dh_dAT	derivative of [H+] with respect to total alkalinity, dimensionless
alk_residual	Ac(h) + Anc(h) - ALK (mol/kg). A diagnostic. It must vanish to machine precision; if it does not, the alkalinity being differentiated is not the one seacarb solved, and every derivative above is suspect.

Author(s)

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References

Bolin, B. and Eriksson, E., 1959 Changes in the carbon dioxide content of the atmosphere and sea due to fossil fuel combustion. *The Atmosphere and the Sea in Motion*, Rossby Memorial Volume, Rockefeller Institute Press, 130-142.

Munhoven, G., 2013 Mathematics of the total alkalinity-pH equation - pathway to robust and universal solution algorithms: the SolveSAPHE package v1.0.1. *Geoscientific Model Development* **6**, 1367-1388.

Orr, J. C., Epitalon, J.-M. and Gattuso, J.-P., 2015 Comparison of ten packages that compute ocean carbonate chemistry. *Biogeosciences* **12**, 1483-1510.

See Also

buffsun, buffer, buffesm, buffzwg, carb, carbfull, derivnum.

Examples

```
##  Bolin sensitivity and its four partial derivatives,
##  from total alkalinity (2300 umol/kg) and DIC (2000 umol/kg)
buffderiv(flag = 15, var1 = 2300e-6, var2 = 2000e-6, S = 35, T = 20,
          Pt = 0.2e-6, Sit = 3e-6,
          k1k2 = "l", kf = "dg", ks = "d", pHscale = "T", b = "u74")

##  Vectorised over a field. The single carb() call is the only nonlinear solve.
n   <- 1000
S   <- runif(n, 30, 37)
T   <- runif(n, -1.8, 30)
```

```
AT  <- runif(n, 2100, 2400) * 1e-6
CT  <- AT * runif(n, 0.85, 0.97)
d   <- buffderiv(15, AT, CT, S = S, T = T, k1k2 = "l", kf = "dg", ks = "d",
                 pHscale = "T", b = "u74", warn = "n")
summary(d[, c("Be", "dBe_dT", "dBe_dS", "dBe_dCT", "dBe_dAT")])

##  The alkalinity residual must be at machine precision
max(abs(d$alk_residual) / AT)
```

---

buffer *Buffer parameters of the seawater carbonate system*

Description

Returns the eleven buffer factors of the seawater carbonate system defined by Frankignoulle (1994). For each of four possible chemical perturbations – input or output of dissolved CO2 (D), bicarbonate (B), carbonate (C), or strong acid H_3O^+ (H) – Frankignoulle (1994) defines a chemical buffer factor Φ (pH change per unit input/output; $\Phi_H = -dpH/d|Talk|$ for the H case, $\Phi_{D,B,C} = dpH/d|\Sigma CO_2|$ otherwise) and a further buffer factor Π describing the accompanying pCO2 change, in μatm ($\Pi_H = -dpCO_2/d|Talk|$; $\Pi_{D,B,C} = dpCO_2/d|\Sigma CO_2|$). For the D, B, and C cases only, a third, dimensionless factor β is also returned ($\beta_{D,B,C} = dln(pCO_2)/dln|\Sigma CO_2|$). β_D (`BetaD`) is the classical Revelle factor, termed the "homogeneous buffer factor" by Frankignoulle (1994); that terminology, and the underlying quantity itself, trace back to Sundquist et al. (1979). This implementation follows Frankignoulle (1994) for the borate- and water-inclusive ("practical alkalinity") case, extended here to also account for phosphoric and silicic acid systems when Pt and Sit are nonzero, as well as NH3 and H2S acid-base systems when NH4t and HSt are nonzero, and has since been cross-validated against seacarb's `buffesm` (Egleston et al., 2010) and `buffzwg` (Zeebe and Wolf-Gladrow, 2001, corrected): `BetaD` agrees with `buffesm`'s `R` and `buffzwg`'s `RF` to floating-point precision. Its input arguments are identical to those in the `buffesm` and `carb` functions of seacarb.

Usage

```
buffer(flag, var1, var2, S = 35, T = 25, Patm = 1, P = 0, Pt = 0, Sit = 0,
 NH4t = 0, HSt = 0, k1k2 = "x", kf = "x", ks = "d", pHscale = "T", b = "u74", warn = "y",
  eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

`flag`	select the pair 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` enter value of the first variable in mol/kg, except for pH and for pCO2 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

`NH4t` Concentration of total ammonium in mol/kg; set to 0 if NA; when nonzero (or when `HSt` is nonzero), `carbfull()` is used internally instead of `carb()`

`HSt` Concentration of total hydrogen sulfide in mol/kg; set to 0 if NA; when nonzero (or when `NH4t` is nonzero), `carbfull()` is used internally instead of `carb()`

`k1k2` "cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

`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` Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"

warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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.

On the non-carbonate buffering term DD:

Writing $h := [H^+]$, $b := [HCO_3^-]$, and $c := [CO_3^{2-}]$, `PhiD/BetaD/PiD` are built from a non-carbonate buffering term `DD`, constructed additively, one acid-base system at a time (the same construction used in `buffzwg` and `buffesm`, there called w and `Segle` respectively):

$DD = w_{bw} + w_{Si} + w_P + w_N + w_S$

with $w_{bw} = 1 + K_w/h^2 + B_T K_B/(K_B + h)^2$ (borate and water), $w_{Si} = Si_T K_{Si}(h^2 + 4K_{2Si}h + K_{Si}K_{2Si})/(h^2 + K_{Si}h + K_{Si}K_{2Si})^2$ (silicic acid, treated as the full diprotic system, using both K_{Si} and K_{2Si}), w_P the analogous contribution from the three-step phosphoric acid system, $w_N = NH_{4t}K_N/(K_N + h)^2$ (ammonia), and $w_S = HS_t K_{HS}/(K_{HS} + h)^2$ (hydrogen sulfide). w_N and w_S are automatically and exactly zero unless `NH4t` or `HSt`, respectively, are nonzero. The same `DD` is reused, unchanged, as `V` for the bicarbonate/carbonate input-output cases (`PhiB/BetaB/PiB`, `PhiC/BetaC/PiC`), and `PhiH/PiH` are computed from the identity $\Phi_H = 1/(h\ln(10)(D - DD))$, which holds regardless of how many non-carbonate systems `DD` includes.

Pressure corrections and pH scale:

- For K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

All eleven factors follow one convention: each is the change in pH (Phi), in ln(fCO2) (Beta), or in fCO2 (Pi), *per mole of the named substance added*. The four substances are dissolved CO2 (D), bicarbonate (B), carbonate (C) and strong acid (H), with

substance	ΔDIC	ΔALK
dissolved CO2	1	0
bicarbonate	1	1
carbonate	1	2
strong acid	0	-1

Two consequences are easy to misread and are stated explicitly:

1. PhiH and PiH are per mole of *strong acid* added, not per mole of alkalinity. Since adding acid removes alkalinity, PhiH = -dpH/d[ALK]. PhiH is therefore negative even though dpH/d[ALK] is positive.
2. The Beta and Pi factors are computed from *fCO2*, not pCO2. The two differ by about 0.3 percent at 20 degrees C. The Pi factors are returned per μmol/kg, not per mol/kg.

Every factor has been verified against finite differences taken through `carb()`, and agrees to better than 1e-6 percent.

Value

The function returns a data frame containing the following columns:

`PhiD`	PhiD, chemical buffer factor for input/output of dissolved CO2: the change in pH per mole of CO2 added (ΔDIC = 1, ΔALK = 0). Units: pH per mol/kg.
`BetaD`	BetaD, homogeneous or Revelle buffer factor for input/output of dissolved CO2: dln(fCO2)/dln(DIC) at constant ALK. Dimensionless.
`PiD`	PiD, chemical buffer factor for input/output of dissolved CO2: the change in fCO2 per mole of CO2 added. Units: μatm per μmol/kg.
`PhiB`	PhiB, chemical buffer factor for input/output of bicarbonate: the change in pH per mole of HCO3- added (ΔDIC = 1, ΔALK = 1). Units: pH per mol/kg.
`BetaB`	BetaB, homogeneous buffer factor for input/output of bicarbonate: dln(fCO2)/dln(DIC) along that perturbation. Dimensionless.
`PiB`	PiB, chemical buffer factor for input/output of bicarbonate: the change in fCO2 per mole of HCO3- added. Units: μatm per μmol/kg.
`PhiC`	PhiC, chemical buffer factor for input/output of carbonate: the change in pH per mole of CO3– added (ΔDIC = 1, ΔALK = 2). Units: pH per mol/kg.
`BetaC`	BetaC, homogeneous buffer factor for input/output of carbonate: dln(fCO2)/dln(DIC) along that perturbation. Dimensionless.
`PiC`	PiC, chemical buffer factor for input/output of carbonate: the change in fCO2 per mole of CO3– added. Units: μatm per μmol/kg.
`PhiH`	PhiH, chemical buffer factor for input/output of strong acid: the change in pH per mole of strong acid added (ΔALK = -1, ΔDIC = 0). Hence PhiH = -dpH/d[ALK], and is NEGATIVE: adding acid lowers pH. Units: pH per mol/kg.
`PiH`	PiH, chemical buffer factor for input/output of strong acid: the change in fCO2 per mole of strong acid added. Units: μatm per μmol/kg.

Note

When `Sit > 0` and `NH4t = HSt = 0`, this function's diprotic treatment of silicate alkalinity (using both `Ksi` and `K2si`) is very slightly inconsistent with the underlying carbonate system state, because that state comes from `carb()`, which internally treats silicate as monoprotic (`K2si = 0`) regardless of `Sit` (see `carb.Rd`). `carbfull()` is only invoked here when `NH4t` or `HSt` are nonzero, so this inconsistency is not corrected for when only `Pt/Sit` are supplied; it is expected to affect results at only the ~1e-6 relative level. See `carb.Rd` and `carbfull.Rd` for further discussion.

Frankignoulle's (1994) own printed equation for Π_H (his Eq. 11) contains an error: as published, Π_H is given as a quotient divided by Φ_H, whereas it should be their product. This was corrected in seacarb's implementation by J.-P. Gattuso, working with M. Frankignoulle. Later, we independently reconfirmed the fix here by rederiving Π_H from scratch and checking it against the Π_H values listed in Frankignoulle's (1994) Table 1. Rederiving each of the other buffer factor equations in the same way turned up no further errors, including for β_D (`BetaD`, the Revelle factor), which matches Frankignoulle's (1994) original formulation exactly.

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Examples

```
## Computation with a pair 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="l", b="u74")

## 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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
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; all rows describe the SAME equilibrium seawater
## state expressed 20 different ways, so results should be (almost)
## identical across rows -- tiny differences reflect solver precision,
## not a real difference in the underlying state.

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)

## BetaD is the Revelle factor (Frankignoulle's "homogeneous buffer factor"):
## cross-check against seacarb's buffesm() R and buffzwg() RF, which should
## agree to floating-point precision
bu <- buffer(flag=15, var1=0.00230, var2=0.00200, S=35, T=18)
es <- buffesm(flag=15, var1=0.00230, var2=0.00200, S=35, T=18)
zw <- buffzwg(flag=15, var1=0.00230, var2=0.00200, S=35, T=18)
bu$BetaD - es$R    # should be ~0 (floating-point precision)
bu$BetaD - zw$RF   # should be ~0 (floating-point precision)

## Effect of adding ammonia and hydrogen sulfide alkalinity (NH4t, HSt);
## when either is nonzero, carbfull() is used internally instead of carb()
buffer(flag=8, var1=8.2, var2=0.00234, S=35, T=25, Pt=0, Sit=0, NH4t=0, HSt=0)
buffer(flag=8, var1=8.2, var2=0.00234, S=35, T=25, Pt=0, Sit=0, NH4t=10e-6, HSt=1e-6)
```

`buffergen` *Buffer factors of the seawater carbonate system as defined by Hagens and Middelburg (2016)*

Description

Returns the suite of buffer factors presented in Table 3 of Hagens and Middelburg (2016), as well as the proton concentration buffer factor (beta.H of Hofmann et al, 2010) and the classic Revelle factor. For practical purposes, this function excludes the nitrate and nitrite acid-base systems presented in this paper, as well as the fully protonoted form of sulfate (H2SO4) and fully deprotonated form of sulfide (S2-), as their contributions to total alkalinity under natural seawater conditions are negligible. Its input arguments are identical to those in the carbfull function of seacarb.

Usage

```
buffergen(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0, k1k2="x", kf="x",
                ks="d", pHscale="T", b="u74", gas="potential", NH4t=0, HSt=0)
```

Arguments

`flag`	select the pair 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 pCO2 in μatm
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 is 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential" and should be a unique value..

NH4t	Concentration of total ammonium in mol/kg; set to 0 if NA
HSt	Concentration of total hydrogen sulfide in mol/kg; set to 0 if NA

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.

- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs, Ksi and K2si, 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 containing the following matrices:

`Carbfull`	Output of the carbfull function that is used within buffergen
`dALK.dH`	Sensitivity of ALK to a change in proton concentration (dimensionless). Species-specific.
`dtotX.dH`	Sensitivity of an acid-base species to a change in proton concentration (dimensionless). Species-specific.
`dALK.dX`	Sensitivity of ALK to a change in an acid-base species (dimensionless). Species-specific.
`dtotX.dX`	Sensitivity of an acid-base species to a change in its total concentration (dimensionless). Species-specific.
`dALK.dpH`	Sensitivity of ALK to a change in pH (mol/kg-soln). Species-specific.
`dtotX.dpH`	Sensitivity of an acid-species to a change in pH (mol/kg-soln). Species-specific.
`dH.dALK`	Sensitivity of proton concentration to a change in ALK (dimensionless). Values are the same for all species and all acid-base systems, except for the fluoride and sulfate acid-base systems, which slightly deviate due to pH scale conversion effects.
`dH.dtotX`	Sensitivity of an acid-species to a change in its total concentration (dimensionless). Values are the same for all species of a specific acid-base system.
`dX.dALK`	Sensitivity of an acid-species to a change in its total concentration (dimensionless). Species-specific.
`dX.dtotX`	Sensitivity of an acid-species to a change in its total concentration (dimensionless). Species-specific.
`dpH.dALK`	Sensitivity of pH due to a change in ALK ((mol/kg-soln)-1). Values are the same for all species and all acid-base systems, except for the fluoride and sulfate acid-base systems, which slightly deviate due to pH scale conversion effects.

dpH.dtotX	Sensitivity of pH due to a change in the total concentration of an acid-base system ((mol/kg-soln)-1). Values are the same for all species of a specific acid-base system.
beta.H	proton concentration buffer factor (Eq.4 of Hagens and Middelburg (2016), dimensionless)
RF	Revelle factor (dimensionless)

If the total concentration of an acid-base system is 0, the values of the buffer factors corresponding to all species of that acid-base system return NA.

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References

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Examples

```
## With a pair of variables
buffergen(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", gas="potential", NH4t=0, HSt=0)

## With a pair of variables and non-zero nutrient concentrations
buffergen(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=5e-6, Sit=2e-6,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", gas="potential", NH4t=10e-6, HSt=0.1e-6)

## 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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
gas <- c("potential")
NH4t <- c(0, 0, 0)
HSt <- c(0, 0, 0)
buffergen(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt, Sit=Sit,
  kf=kf, k1k2=k1k2, pHscale=pHscale, b=b, gas=gas, NH4t=NH4t, HSt=HSt)

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

`buffesm` *Buffer capacities of the seawater carbonate system from Egleston et al. (2010), corrected and enhanced*

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: when input concentrations of Pt and Sit are set to zero, they produce results that are identical to those shown in ESM's Fig. 2. But when Pt and Sit are nonzero, contributions from phosphoric and silicic acid systems are taken into account as well as NH3 and H2S acid-base systems when NH4t and HSt are nonzero, an improvement to the Egleston et al. (2010) approach. This routine was inspired and adapted from seacarb's "buffer" function. Its input arguments are indentical to those in the "buffer" and "carb" functions of seacarb.

Usage

```
buffesm(flag, var1, var2, S = 35, T = 25, Patm = 1, P = 0, Pt = 0, Sit = 0,
 NH4t = 0, HSt = 0, k1k2 = "x", kf = "x", ks = "d", pHscale = "T", b = "u74", warn = "y",
  eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

`flag` select the pair 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` enter value of the first variable in mol/kg, except for pH and for pCO2 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; when nonzero, account for phosphoric acid system, unlike in Egleston et al. (2010).

`Sit` Concentration of total silicate in mol/kg; set to 0 if NA; when nonzero, account for silicic acid system, unlike in Egleston et al. (2010).

`NH4t` Concentration of total ammonium in mol/kg; set to 0 if NA; when nonzero (or when `HSt` is nonzero), accounts for ammonia alkalinity and `carbfull()` is used internally instead of `carb()`

`HSt` Concentration of total hydrogen sulfide in mol/kg; set to 0 if NA; when nonzero (or when `NH4t` is nonzero), accounts for sulfide alkalinity and `carbfull()` is used internally instead of `carb()`

`k1k2` "cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

`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` Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"

warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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.

On the non-carbonate buffering term Segle:

Writing $h := [H^+]$, $b := [HCO_3^-]$, and $c := [CO_3^{2-}]$, the six buffer factors are built from `Segle`, Egleston et al.'s (2010) S (their Table 1, corrected here as noted above), which is constructed additively, one acid-base system at a time (the same construction used in `buffzwg` and `buffer`, there called w and `DD` respectively):

$Segle = b + 4c + h\,w$, with $w = w_{bw} + w_{Si} + w_P + w_N + w_S$

where $w_{bw} = 1 + K_w/h^2 + B_T K_B/(K_B + h)^2$ (borate and water), $w_{Si} = Si_T K_{Si}(h^2 + 4K_{2Si}h + K_{Si}K_{2Si})/(h^2 + K_{Si}h + K_{Si}K_{2Si})^2$ (silicic acid, treated as the full diprotic system, using both K_{Si} and K_{2Si}), w_P the analogous contribution from the three-step phosphoric acid system, $w_N = NH_{4t}K_N/(K_N + h)^2$ (ammonia), and $w_S = HS_t K_{HS}/(K_{HS} + h)^2$ (hydrogen sulfide). w_N and w_S (correspondingly, `SegleN` and `SegleS`) are automatically and exactly zero unless `NH4t` or `HSt`, respectively, are nonzero.

Pressure corrections and pH scale:

- For K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Value

The function returns a data frame containing the following columns:

gammaDIC	γ_{DIC}, ocean's capacity to buffer changes in [CO2] due to accumulation of CO2 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 CO2 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 CO2 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 [CO2] 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 $(\partial ln[CO_2]/\partial lnDIC)^{-1}$ (unitless)

Note

When `Sit > 0` and `NH4t = HSt = 0`, this function's diprotic treatment of silicate alkalinity (using both `Ksi` and `K2si`) is very slightly inconsistent with the underlying carbonate system state, because that state comes from `carb()`, which internally treats silicate as monoprotic (`K2si = 0`) regardless of `Sit` (see `carb.Rd`). `carbfull()` is only invoked here when `NH4t` or `HSt` are nonzero, so this inconsistency is not corrected for when only `Pt/Sit` are supplied; it is expected to affect results at only the ~1e-6 relative level. See `carb.Rd` and `carbfull.Rd` for further discussion.

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Examples

```
## Computation with a pair 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="l", b="u74")

## 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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
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; all rows describe the SAME equilibrium seawater
## state expressed 20 different ways, so results should be (almost)
## identical across rows -- tiny differences reflect solver precision,
```

```
## not a real difference in the underlying state.
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)
be <- buffesm(flag=flag, var1=var1, var2=var2)
be

## Compute 2 additional factors of interest (ratios of relative changes),
## reusing the same 'be' computed just above (same state, 20 flag encodings)
#     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

## Effect of adding ammonia and hydrogen sulfide alkalinity (NH4t, HSt);
## when either is nonzero, carbfull() is used internally instead of carb()
buffesm(flag=8, var1=8.2, var2=0.00234, S=35, T=25, Pt=0, Sit=0, NH4t=0, HSt=0)
buffesm(flag=8, var1=8.2, var2=0.00234, S=35, T=25, Pt=0, Sit=0, NH4t=10e-6, HSt=1e-6)
```

---

buffsun *Bolin sensitivity and Revelle factor via the condensed common-template equation of Sundquist et al. (1979)*

Description

Returns the Bolin sensitivity $B_e = \partial DIC/\partial[CO_2^*]$ and the classical Revelle factor $Rf = DIC/([CO_2^*]B_e)$ at constant total alkalinity, temperature, and salinity, using the condensed closed-form template first proposed by Sundquist, Plummer and Wigley (1979). The routine is named for that paper.

That template predates the other formulations of the Revelle factor / Bolin sensitivity in common use, and Orr et al. (in prep.) show that three later, independently derived formulations – Zeebe and Wolf-Gladrow (2001, corrected); Egleston, Sabine and Morel (2010, corrected); and Frankignoulle (1994, as implemented in seacarb's `buffer`) – each reduce, exactly, to the equation of Sundquist et al. (1979). They differ only in which acid-base systems are collected into the single non-carbonate term X: Sundquist et al. (1979) included borate alone; the other three added water. This routine implements that common equation with the most complete X available in seacarb, adding phosphate, silicate, fluoride, and, when nonzero, ammonia and sulfide.

Note that this equivalence covers only the Revelle factor / Bolin sensitivity result of each source; Frankignoulle (1994) and Egleston et al. (2010) each define several additional buffer factors (see seacarb's `buffer` and `buffesm`) that are not part of this unification.

Unlike `buffzwg` and `buffesm`, this routine needs no explicit K1 or K2: the equation is written directly in terms of the three dissolved inorganic carbon species, $s = [CO_2^*]$, $b = [HCO_3^-]$, and

$c = [CO_3^{2-}]$, taken from carb()/carbfull()'s own speciation output, with all non-carbonate chemistry isolated in X. buffsun was cross-validated against buffzwg, buffesm, and buffer: for any Pt, Sit, NH4t, and HSt, its Be and Rf agree with buffzwg's Be and RF, buffesm's R, and buffer's BetaD to floating-point precision. It was further checked against buffderiv, which computes B_e independently and refines [H+] to machine precision; the two agree to about 2e-8 percent, the residual being the convergence tolerance of carb() itself. The buffsun input arguments are identical to those of buffzwg, buffesm, and carb.

Usage

```
buffsun(flag, var1, var2, S = 35, T = 25, Patm = 1, P = 0, Pt = 0, Sit = 0,
 NH4t = 0, HSt = 0, k1k2 = "x", kf = "x", ks = "d", pHscale = "T", b = "u74", warn = "y",
  eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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	enter value of the first variable in mol/kg, except for pH and for pCO2 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; when nonzero, accounts for the phosphoric acid system as part of the non-carbonate term X.
Sit	Concentration of total silicate in mol/kg; set to 0 if NA; when nonzero, accounts for the silicic acid system (full diprotic treatment) as part of the non-carbonate term X.
NH4t	Concentration of total ammonium in mol/kg; set to 0 if NA; when nonzero (or when HSt is nonzero), accounts for ammonia alkalinity and carbfull() is used internally instead of carb()
HSt	Concentration of total hydrogen sulfide in mol/kg; set to 0 if NA; when nonzero (or when NH4t is nonzero), accounts for sulfide alkalinity and carbfull() is used internally instead of carb()
k1k2	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.

- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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.

On the underlying formula:

Writing $s := [CO_2^*]$, $b := [HCO_3^-]$, $c := [CO_3^{2-}]$, and $h := [H^+]$, the Bolin sensitivity is computed as

$B_e = 1 + c/s + (Xb - 4c^2)/\big(s(b + 4c + X)\big)$

with the Revelle factor $Rf = DIC/(sB_e)$, and $X = hw$, where w is the same non-carbonate buffering term used by `buffzwg` and `buffesm`, built additively, one acid-base system at a time:

$w = w_{bw} + w_{Si} + w_P + w_F + w_N + w_S$

with $w_{bw} = 1 + K_w/h^2 + B_T K_B/(K_B + h)^2$ (borate and water), $w_{Si} = Si_T K_{Si}(h^2 + 4K_{2Si}h + K_{Si}K_{2Si})/(h^2 + K_{Si}h + K_{Si}K_{2Si})^2$ (silicic acid; see the note below on monoprotic versus diprotic treatment), w_P the analogous contribution from the three-step phosphoric acid system, $w_N = NH_{4t}K_N/(K_N + h)^2$ (ammonia), and $w_S = HS_t K_{HS}/(K_{HS} + h)^2$ (hydrogen sulfide), and $w_F = F_T K'_F/(K'_F + h)^2$ (hydrogen fluoride, with $K'_F = K_F(1 + S_T/K_S)$, i.e. Kf placed on

the same pH scale as h). $-[HF]$ is a species in Dickson's total alkalinity and is carried explicitly by SolveSAPHE, which `carb()` inverts, so it must appear in $w = -\partial A_{nc}/\partial h$ as well; it contributes at the ~2e-6 relative level. w_N and w_S are automatically and exactly zero unless `NH4t` or `HSt`, respectively, are nonzero.

Four independent derivations of the Revelle factor / Bolin sensitivity – Sundquist, Plummer and Wigley (1979); Zeebe and Wolf-Gladrow (2001, corrected); Egleston, Sabine and Morel (2010, corrected); and Frankignoulle (1994, as implemented in `buffer`) – were each rearranged algebraically and shown to reduce, exactly, to this same equation, differing only in which terms are included in X: Sundquist et al. (1979) include only borate ($X = \gamma$); the other three include borate and water ($X = \gamma + \delta$, using the notation of Orr et al., in prep.). This routine's X is the most complete version of the three, additionally including phosphate, silicate, ammonia, and sulfide.

Setting $X = 0$ collapses this equation exactly to

$B_e = 1 + bc/(s(b + 4c))$

the result obtained if carbonate alkalinity A_c, rather than total alkalinity A_T, is assumed to remain fixed as CO2 is added to the ocean – physically incorrect for air-sea CO2 exchange, since borate and water alkalinity (and, if included, phosphate, silicate, ammonia, and sulfide alkalinity) are not actually static: A_c rises while the non-carbonate alkalinity terms fall in compensation, keeping A_T fixed. See Orr et al. (in prep.) for a full discussion, including how this collapse relates to the traditional approximation $B_e \approx [CO_3^{2-}]/[CO_2^*]$ used since Broecker and Peng (1974).

Pressure corrections and pH scale:

- For K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Value

The function returns a data frame containing the following columns:

`Be`	B_e, the Bolin sensitivity, $\partial DIC/\partial[CO_2^*]$ at constant total alkalinity, temperature, and salinity (unitless, since both DIC and $[CO_2^*]$ are in mol/kg)
`Rf`	the classic Revelle factor, $DIC/([CO_2^*]B_e)$, equivalently $(\partial ln[CO_2]/\partial lnDIC)^{-1}$ (unitless); agrees with `buffzwg`'s `Be`/`RF`, `buffesm`'s `R`, and `buffer`'s `BetaD` to floating-point precision

Note

Silicate follows the solver. When `NH4t` = `HSt` = `0` this routine calls `carb()`, whose alkalinity treats silicic acid as *monoprotic* (K1si only; see `carb.Rd`), and K_{2Si} is therefore set to zero, which reduces the diprotic w_{Si} above to $Si_T K_{Si}/(K_{Si}+h)^2$ exactly. When `NH4t` or `HSt` is nonzero it calls `carbfull()`, whose alkalinity is *diprotic*, and the full K_{2Si} is used. Earlier versions applied the diprotic form on both paths, which left w_{Si} inconsistent with the alkalinity `carb()` actually solves by about 6e-8 of A_T at Si_T = 60 μmol/kg. That is corrected.

Author(s)

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Examples

```
## Computation with a pair of variables
buffsun(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, P=0, Pt=0,
Sit=0, pHscale="T", kf="pf", k1k2="l", b="u74")

## Using vectors as arguments
flag <- c(15, 15, 15)
var1 <- c(0.00230, 0.00230, 0.00230)
var2 <- c(0.00200, 0.00200, 0.00200)
S <- c(35, 35, 30)
T <- c(18, 25, 18)
P <- c(0, 0, 0)
Pt <- c(0, 5e-6, 5e-6)
Sit <- c(0, 0, 20e-6)
kf <- c("pf", "pf", "pf")
k1k2 <- c("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
buffsun(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt,
Sit=Sit, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)

## Compare against buffzwg, buffesm, and buffer (should all agree to
## floating-point precision, for any Pt and Sit)
o <- buffsun(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, Pt=5e-6, Sit=20e-6)
z <- buffzwg(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, Pt=5e-6, Sit=20e-6)
e <- buffesm(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, Pt=5e-6, Sit=20e-6)
u <- buffer(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, Pt=5e-6, Sit=20e-6)
o$Rf - z$RF     # should be ~0 (floating-point precision)
o$Rf - e$R      # should be ~0 (floating-point precision)
o$Rf - u$BetaD  # should be ~0 (floating-point precision)

## The X=0 (Ac-constant) collapse: an internal, non-exported illustration
## of how buffsun's general result reduces to the constant-carbonate-
## alkalinity special case (see Details); not run as part of normal use.
```

```
## Not run:
cf <- carbfull(flag=15, var1=0.00230, var2=0.00200, S=35, T=18)
h <- 10^(-cf$pH); s <- cf$CO2; bb <- cf$HCO3; cc <- cf$CO3
Be_X0 <- 1 + bb*cc/(s*(bb+4*cc))
Be_X0

## End(Not run)
```

---

buffzwg *Bolin sensitivity and Revelle factor of the seawater carbonate system from Zeebe and Wolf-Gladrow (2001), corrected and enhanced*

Description

Returns the Bolin sensitivity $B_e = \partial DIC/\partial[CO_2^*]$ at constant total alkalinity, temperature, and salinity, following the closed-form expression given by Zeebe and Wolf-Gladrow (2001, Eq. 1.5.88). Egleston et al., (2010) mentioned that their Eq. 1.5.88 contains a typographical error but did not elaborate. To identify the error, we rederived the equation, finding it to be a missing factor of h/s on one of the two numerator terms, as detailed in comments of the buffzwg function. It was later found that this same corrected equation had been given in the errata of the Zeebe and Wolf-Gladow book (in an errata document from 2010, where it was mentioned that the correction had not yet been implemented in more recent editions of the book). In any case, the corrected formula, which in Zeebe and Wolf-Gladrow (2001) already accounted for carbonate, borate, and water alkalinity, has been extended here to also account for phosphoric and silicic acid systems as well as NH3 and H2S acid-base systems, following the same approach used to extend seacarb's buffesm function. The classic Revelle factor is also returned, computed as $RF = (DIC/[CO_2^*])/B_e$. This routine was validated against buffesm: when Pt = Sit = 0, and separately when either is nonzero, buffzwg's RF and buffesm's R agree to within floating-point precision. This cross-validation also led to the correction of an unrelated bug in buffesm's own phosphate term (an R line-continuation parsing error in numPt, fixed in this package version). The buffzwg input arguments are identical to those in the buffesm and carb functions of seacarb.

Usage

```
buffzwg(flag, var1, var2, S = 35, T = 25, Patm = 1, P = 0, Pt = 0, Sit = 0,
 NH4t = 0, HSt = 0, k1k2 = "x", kf = "x", ks = "d", pHscale = "T", b = "u74", warn = "y",
  eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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` enter value of the first variable in mol/kg, except for pH and for pCO2 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; when nonzero, accounts for the phosphoric acid system, unlike in Zeebe and Wolf-Gladrow (2001).

`Sit` Concentration of total silicate in mol/kg; set to 0 if NA; when nonzero, accounts for the silicic acid system, unlike in Zeebe and Wolf-Gladrow (2001).

`NH4t` Concentration of total ammonium in mol/kg; set to 0 if NA; when nonzero (or when `HSt` is nonzero), accounts for ammonia alkalinity and `carbfull()` is used internally instead of `carb()`

`HSt` Concentration of total hydrogen sulfide in mol/kg; set to 0 if NA; when nonzero (or when `NH4t` is nonzero), accounts for sulfide alkalinity and `carbfull()` is used internally instead of `carb()`

`k1k2` "cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

`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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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.

On the underlying formula:

Writing $s := [CO_2^*]$ and $h := [H^+]$, the Bolin sensitivity is computed as

$$B_e = \left(K_1/h + 4K_1K_2/h^2 + K_1^2K_2/h^3 + (h/s)D_s w\right) \Big/ \left(K_1/h + 4K_1K_2/h^2 + (h/s)w\right)$$

where $D_s = 1 + K_1/h + K_1K_2/h^2$ is the ionization fraction ($DIC/[CO_2^*]$, following the terminology of Jones et al. (2014) and Egleston et al. (2010)), and w is a non-carbonate buffering term built additively, one acid-base system at a time:

$w = w_{bw} + w_{Si} + w_P + w_N + w_S$

with $w_{bw} = 1+K_w/h^2+B_TK_B/(K_B+h)^2$ (borate and water; this term alone reproduces the original Zeebe and Wolf-Gladrow (2001) formula), $w_{Si} = Si_TK_{Si}(h^2 + 4K_{2Si}h + K_{Si}K_{2Si})/(h^2 + K_{Si}h+K_{Si}K_{2Si})^2$ (silicic acid, treated as the full diprotic system, i.e. $Si(OH)_4 \rightleftharpoons SiO(OH)_3^- \rightleftharpoons SiO_2(OH)_2^{2-}$, using both K_{Si} and K_{2Si}; this matches seacarb's own `carbfull()` treatment of silicate alkalinity), w_P the analogous, algebraically more involved contribution from the three-step phosphoric acid system, $w_N = NH_{4t}K_N/(K_N + h)^2$ (ammonia), and $w_S = HS_tK_{HS}/(K_{HS} + h)^2$ (hydrogen sulfide). Each additional term was verified to equal $-\partial A_j/\partial h$, where $A_j(h)$ is that system's own contribution to total alkalinity at fixed total concentration, and to be strictly positive over the seawater pH range, as required for a genuine buffering contribution. w_N and w_S are automatically and exactly zero unless `NH4t` or `HSt`, respectively, are nonzero.

Pressure corrections and pH scale:

- For K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred

from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Value

The function returns a data frame containing the following columns:

Be	B_e, the Bolin sensitivity, $\partial DIC/\partial[CO_2^*]$ at constant total alkalinity, temperature, and salinity (unitless, since both DIC and $[CO_2^*]$ are in mol/kg)
RF	the classic Revelle factor, $(DIC/[CO_2^*])/B_e$, equivalently $(\partial ln[CO_2]/\partial lnDIC)^{-1}$ (unitless); agrees with buffesm's R and buffer's BetaD to floating-point precision

Note

When Sit > 0 and NH4t = HSt = 0, this function's diprotic treatment of silicate alkalinity (using both Ksi and K2si) is very slightly inconsistent with the underlying carbonate system state, because that state comes from carb(), which internally treats silicate as monoprotic (K2si = 0) regardless of Sit (see carb.Rd). carbfull() is only invoked here when NH4t or HSt are nonzero, so this inconsistency is not corrected for when only Pt/Sit are supplied; it is expected to affect results at only the ~1e-6 relative level. See carb.Rd and carbfull.Rd for further discussion.

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Zeebe R. E. and Wolf-Gladrow D. A., 2001 CO2 in seawater: equilibrium, kinetics, isotopes. *Elsevier Oceanography Series* **65**, Amsterdam, 346 pp.

Examples

```
## Computation with a pair of variables
buffzwg(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, P=0, Pt=0,
Sit=0, pHscale="T", kf="pf", k1k2="l", b="u74")

## Using vectors as arguments
flag <- c(15, 15, 15)
var1 <- c(0.00230, 0.00230, 0.00230)
var2 <- c(0.00200, 0.00200, 0.00200)
S <- c(35, 35, 30)
T <- c(18, 25, 18)
P <- c(0, 0, 0)
Pt <- c(0, 5e-6, 5e-6)
Sit <- c(0, 0, 20e-6)
kf <- c("pf", "pf", "pf")
k1k2 <- c("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
buffzwg(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt,
Sit=Sit, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)

## Compare against buffesm's classic Revelle factor (should agree to
## floating-point precision, for any Pt and Sit)
e <- buffesm(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, Pt=5e-6, Sit=20e-6)
z <- buffzwg(flag=15, var1=0.00230, var2=0.00200, S=35, T=18, Pt=5e-6, Sit=20e-6)
e$R - z$RF   # should be ~0 (floating-point precision)
```

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="u74", gas="potential",
        warn="y", eos="eos80", long=1.e20, lat=1.e20)
```

Arguments

flag	select the pair 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 pCO2 in μatm
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 is 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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`	"standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (μatm)
`fCO2`	"standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (μatm)
`pCO2pot`	"potential" pCO2, CO2 partial pressure computed at potential temperature and atmospheric pressure (μatm)
`fCO2pot`	"potential" fCO2, CO2 fugacity computed at potential temperature and atmospheric pressure (μatm)
`pCO2insitu`	"in situ" pCO2, CO2 partial pressure computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)
`fCO2insitu`	"in situ" fCO2, CO2 fugacity computed at in situ temperature and total pressure (atm + hydrostatic) (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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr and Epitalon (2015)

Silicate is treated as monoprotic here: unlike `carbfull()`, `carb()` internally sets the second dissociation constant of Si(OH)4 (`K2si`) to zero, regardless of the value of `Sit` supplied. This is a deliberate simplification (not a bug) that keeps `carb()` from requiring `K2si` at all. Because `K2si` is several orders of magnitude smaller than `Ksi` under typical seawater conditions, the resulting effect on pH, DIC, and other outputs is negligible in practice (of order 1e-6 relative). Use `carbfull()` if a fully self-consistent diprotic treatment of silicate is required, e.g. when feeding its output into a buffer-factor calculation that itself uses the diprotic form of silicate alkalinity (see `buffzwg`, `buffesm`, `buffer`).

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Examples

```
## 1. With a pair of variables
carb(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")

## 2. 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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
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)

## 3. Special case: when input pH is on NBS scale (not a standard option in seacarb)
##    -> example for pH-Alk input pair (flag 8) and Cai & Wang (1998) K1,K2
pHNBS <- c(8.2, 8.1, 8.0)
talk <- c(2300, 2350, 2400) * 1e-6
S <- c(35, 32.5, 30)
T <- c(25, 15, 10)
```

```
## 3a. convert pHNBS to pHSWS (using total activity coeff. fH), then use carb with pHscale="SWS"
pHSWS <- pHnbs2sws(pHNBS, S=S, T=T)
carb(flag=8, var1=pHSWS, var2=talk, S=S, T=T, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="SWS", kf="pf", k1k2="cw", ks="d", b="u74")

## 3b. conversely for input pairs without pH,  convert computed pH on SWS scale to NBS scale,
##     with function pHsws2nbs
##    -> example for Alk-DIC input pair (flag 15) and Cai & Wang (1998) K1,K2
dic <- c(2000., 2030., 2060) * 1e-6
output = carb(flag=15, var1=talk, var2=dic, S=S, T=T, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="SWS", kf="pf", k1k2="cw", ks="d", b="u74")
pHNBS  = pHsws2nbs(output$pH, S=S, T=T)

## 4. 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)

## 5. Test using a data frame
data(seacarb_test_P0) #test data set for P=0 (surface)
tab <- seacarb_test_P0[14:19,]

## 5a. 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]])

## 5b. 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)
```

---

carbb *Parameters of the seawater carbonate system with boron addition*

Description

Returns parameters of the seawater carbonate system when boron is added.

Usage

```
carbb(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0,
  k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential", badd=0,
  warn="y", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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 pCO2 in μatm
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 is 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
badd	Amount of boron added in mol/kg.
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.

- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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	"standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (μatm)
fCO2	"standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (μatm)
pCO2pot	"potential" pCO2, CO2 partial pressure computed at potential temperature and atmospheric pressure (μatm)
fCO2pot	"potential" fCO2, CO2 fugacity computed at potential temperature and atmospheric pressure (μatm)
pCO2insitu	"in situ" pCO2, CO2 partial pressure computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)
fCO2insitu	"in situ" fCO2, CO2 fugacity computed at in situ temperature and total pressure (atm + hydrostatic) (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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

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Examples

```
## With a pair of variables
carbb(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", badd=0)
```

carbfull *Parameters of the seawater carbonate system - extension of carb*

Description

Returns parameters of the seawater carbonate system, including the ammonium and sulfide acid-base systems, as well as full acid-base speciation

Usage

```
carbfull(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0,
        k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential",
        NH4t=0, HSt=0)
```

Arguments

flag	select the pair 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-soln, except for pH and for pCO2 in μatm
var2	Value of the second variable in mol/kg-soln, except for pH
S	Salinity
T	Temperature in degrees Celsius
Patm	Surface atmospheric pressure in atm, default is 1 atm

P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg-soln; set to 0 if NA
Sit	Concentration of total silicate in mol/kg-soln; set to 0 if NA
k1k2	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
NH4t	Concentration of total ammonium in mol/kg-soln; set to 0 if NA
HSt	Concentration of total hydrogen sulfide in mol/kg-soln; set to 0 if NA

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".

- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs, Ksi and K2si, 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-soln)
pCO2	"standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (μatm)
fCO2	"standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (μatm)
pCO2pot	"potential" pCO2, CO2 partial pressure computed at potential temperature and atmospheric pressure (μatm)
fCO2pot	"potential" fCO2, CO2 fugacity computed at potential temperature and atmospheric pressure (μatm)
pCO2insitu	"in situ" pCO2, CO2 partial pressure computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)
fCO2insitu	"in situ" fCO2, CO2 fugacity computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)
HCO3	HCO3 concentration (mol/kg-soln)
CO3	CO3 concentration (mol/kg-soln)
DIC	DIC concentration (mol/kg-soln)
ALK	ALK, total alkalinity (mol/kg-soln)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state
NH4	NH4 concentration (mol/kg-soln)
NH3	NH3 concentration (mol/kg-soln)
BOH3	B(OH)3 concentration (mol/kg-soln)
BOH4	B(OH)4 concentration (mol/kg-soln)
H3PO4	H3PO4 concentration (mol/kg-soln)
H2PO4	H2PO4 concentration (mol/kg-soln)
HPO4	HPO4 concentration (mol/kg-soln)
PO4	PO4 concentration (mol/kg-soln)
H2S	H2S concentration (mol/kg-soln)
HS	HS concentration (mol/kg-soln)
SiOH4	SiOH4 concentration (mol/kg-soln)
SiOOH3	SiOOH3 concentration (mol/kg-soln)

SiO2OH2	SiO2OH2 concentration (mol/kg-soln)
HF	HF concentration (mol/kg-soln)
F	F concentration (mol/kg-soln)
HSO4	HSO4 concentration (mol/kg-soln)
SO4	SO4 concentration (mol/kg-soln)
H	H concentration at specified pH scale (mol/kg-soln)
OH	OH concentration (mol/kg-soln)
NH4t	Supplied NHt concentration (mol/kg-soln); values are recycled if necessary
BOR	Calculated total borate concentration (mol/kg-soln)
Pt	Supplied Pt concentration (mol/kg-soln); values are recycled if necessary
HSt	Supplied HSt concentration (mol/kg-soln); values are recycled if necessary
Sit	Supplied Sit concentration (mol/kg-soln); values are recycled if necessary
FLUO	Calculated total fluoride concentration (mol/kg-soln)
ST	Calculated total sulfate concentration (mol/kg-soln)

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr and Epitalon (2015)

Silicate is treated as diprotic here: unlike `carb()`, which internally sets the second dissociation constant of Si(OH)4 (`K2si`) to zero, `carbfull()` uses the true, nonzero `K2si`. `carbfull()` is also the only one of the two functions that accepts `NH4t` and `HSt`. See `carb.Rd` for further discussion of this difference and its (negligible in practice) numerical consequence.

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

Examples

```
## With a pair of variables
carbfull(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", gas="potential", NH4t=0, HSt=0)

## With a pair of variables and non-zero nutrient concentrations
carbfull(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=5e-6, Sit=2e-6,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", gas="potential", NH4t=10e-6, HSt=0.1e-6)

## 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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
gas <- c("potential", "potential", "potential")
NH4t <- c(0, 0, 0)
HSt <- c(0, 0, 0)
carbfull(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt, Sit=Sit,
  kf=kf, k1k2=k1k2, pHscale=pHscale, b=b, gas=gas, NH4t=NH4t, HSt=HSt)

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

---

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

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See Also

p2d

Examples

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

---

derivnum *Numerical derivatives of seawater carbonate system variables*

Description

Returns numerical derivatives of the seawater carbonate system output variables with respect to input variables.

Usage

```
derivnum(varid, flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0,
      k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential", warn="y",
       eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

varid	Variable length, case insensitive, character identificator of variable with respect to which derivatives are requested. Possible values are: '1' or 'var1' : Variable 1 of the input pair (This is TAlk if flag is 15) '2' or 'var2' : Variable 2 of the input pair (This is DIC if flag is 15) 'sil', 'silt', 'tsil' or 'silicate' : Total silicate concentration 'phos', 'phost', 'tphos' or 'phosphate' : Total phosphate concentration 't', 'temp' or 'temperature' : temperature 's', 'sal' or 'salinity' : salinity 'K0','K1','K2','Kb','Kw','Kspa' or 'Kspc' : one of the dissociation constants 'bor' : total boron
flag	select the input pair of carbonate-system variables available by choosing the following flag: 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 pCO2 in μatm

`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 is 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` "cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

`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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

Details

This subroutine has same input parameters as subroutine carb(). For details on these parameters, refer to documentation of 'carb'.

This subroutine computes partial derivatives of each output variable with respect to each of the input variable (including each of the two chosen carbonate system variables, each of the nutrients (total silicon and total phosphorus), temperature, and salinity.

It computes these derivatives (dy/dx) using the method of central differences, i.e.,

- for dx, it adds a positive and negative perturbation, same and equal in magnitude, to each input variable, one at a time, and
- for dy, it then computes the corresponding induced change in output variables

All arguments but the first (varid), can be given as scalers or vectors. If the lengths of the vectors differs, only the longest vector is retained and the other arguments are set equal to the first value of the other vectors are used. Hence users should use either vectors with the same dimension or one vector for one argument and scalars for others; otherwise, results may not be as intended.

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Value

The function returns a data frame containing the following columns:

H	derivative of [H+] concentration (mol/kg/...)
pH	derivative of pH

CO2	derivative of CO2 concentration (mol/kg/...)
pCO2	"standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (μatm/...)
fCO2	"standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (μatm/...)
HCO3	derivative of HCO3 concentration (mol/kg/...)
CO3	derivative of CO3 concentration (mol/kg/...)
DIC	derivative of DIC concentration (mol/kg/...)
ALK	derivative of ALK, total alkalinity (mol/kg/...)
OmegaAragonite	derivative of Omega aragonite, aragonite saturation state
OmegaCalcite	derivative of Omega calcite, calcite saturation state

If all input data have the same 'flag' value, returned data frame does not show derivatives of input pair of carbonate system variables. For example, if all input flags are 15, the input pair is DIC and ALK; hence, derivatives of DIC and ALK are not returned.

Units of derivative dy/dx is unit(y)/unit(x) where unit(x) are as follows:

degree C	when x is Temperature
psu	when x is Salinity
uatm	when x is pCO2
mol/kg	for all other cases

Author(s)

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Examples

```
## 1) For the input pair ALK and DIC (var1 and var2 when flag=15)
##    compute derivatives of all output varialbes
##    with respect to DIC (i.e., var2)
derivnum(varid='var2', flag=15, var1=2300e-6, var2=2000e-6,
         S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
         pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")

## 2) For the input pair pH and ALK (var1 and var2 when flag=8)
##    compute derivatives of all output variables
##    with respect to [H+] concentration
derivnum(varid='var1', flag=8, var1=8.2, var2=0.00234,
         S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
         pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")
```

```
## 3) Using vectors as arguments and compute derivatives of all output
##    variables with respect to temperature
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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("u74", "u74", "u74")
derivnum(varid='T', flag=flag, var1=var1, var2=var2, S=S, T=T, P=P,
         Pt=Pt, Sit=Sit, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)

# For more examples of use of derivnum.R,
# consult the code of seacarb's errors routine.
```

`eos2teos_chem` *Convert temperature and salinity from EOS-80 to TEOS-10*

Description

Converts in situ temperature to conservative temperature and practical to absolute salinity (SA). Salinity conversion depends on total alkalinity as well as the concentrations of dissolved inorganic carbon, nitrate and silicate.

Usage

```
eos2teos_chem(SP, T, P=0, TA=2300e-6, DIC=2000e-6, NO3=0, SIOH4=0)
```

Arguments

SP	Practical salinity on the practical salinity scale
T	In situ temperature in deg. C
P	Sea water pressure in dbar
TA	Total alkalinity, in mol/kg, default is 2300 Âµmol/kg
DIC	Dissolved inorganic carbon concentration in mol/kg, default is 2000 Âµmol/kg
NO3	Total nitrate concentration in mol/kg, default is 0
SIOH4	Total silicate concentration in mol/kg, default is 0

Details

Conversion from practical to absolute salinity depends on carbonate system parameters and ion concentration which mostly affect water density anomalies.

Value

The function returns a data frame containing the following columns:

CT	Conservative temperature (deg C)
SA	Absolute salinity (g/kg)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

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See Also

teos2eos_chem does the reverse, eos2teos_geo, sp2sa_chem

package gsw

Examples

```
# Calculate Conservative Temperature and Absolute Salinity of a sample with
# Practical salinity of 35 psu, in-situ temperature of 18 deg C,
# at 0 dbar and total alkalinity of 0.00234 mol/kg and DIC of 0.00202 mol/kg
f <- eos2teos_chem(SP=35, T=18, P=0, TA=0.00234, DIC=0.00202)
CT <- f$CT     # Conservative Temperature
SA <- f$SA     # Absolute Salinity
```

---

eos2teos_geo *Convert temperature and salinity from EOS-80 to TEOS-10*

Description

Converts in situ to conservative temperature and practical to absolute salinity (SA). Salinity conversion depends on depth and geographic location.

Usage

```
eos2teos_geo(SP, T, P=0, long=1.e20, lat=1.e20)
```

Arguments

SP	Practical salinity on the practical salinity scale
T	In situ temperature in deg. C
P	Sea water pressure in dbar
long	Longitude in decimal degrees [0 ... +360] or [-180 ... +180]
lat	Latitude in decimal degrees [-90 ... 90]

Details

Conversion from practical to absolute salinity depends on water density anomaly which is correlated with silicate concentration. This function relies on silicate concentration taken from WOA (World Ocean Atlas) to evaluate density anomaly.

Value

The function returns a data frame containing the following columns:

CT	Conservative temperature (deg C)
SA	Absolute salinity (g/kg)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

Pawlowicz R., 2013. What every oceanographer needs to know about TEOS-10 (The TEOS-10 Primer). http://www.teos-10.org/

See Also

teos2eos_geo does the reverse, eos2teos_chem, sp2sa_geo, package gsw

Examples

```
# Calculate conservative temperature and absolute salinity of a sample with
# Practical salinity of 35 psu, in situ temperature of 18 deg C,
# depth is 10 dbar and location is 188 degrees East and 4 degrees North.
f <- eos2teos_geo(SP=35, T=18, P=10, long=188, lat=4)
CT <- f$CT     # Conservative temperature
SA <- f$SA     # Absolute salinity
```

`errors` *Uncertainty propagation for computed marine carbonate system variables*

Description

Estimates combined standard uncertainties in computed carbonate system variables by propagating inout uncertainties (standard uncertainties) in six input variables, including (Orr et al., Mar. Chem., in press):

- the input pair of carbonate system variables,
- the 2 input nutrients (silicate and phosphate concentrations),
- temperature and salinity. It also accounts for
- the errors in the key dissociation constants pK0, pK1, pK2, pKb, pKw, pKspa and pKspc
- the error in total boron

Usage

```
errors(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0,
               evar1=0, evar2=0, eS=0.01, eT=0.01, ePt=0, eSit=0,
               epK=c(0.002, 0.0075, 0.015, 0.01, 0.01, 0.02, 0.02),
               eBt=0.02, method = "ga", r=0.0, runs=10000,
               k1k2='x', kf='x', ks="d", pHscale="T", b="u74", gas="potential",
               warn="y", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

`flag` select the pair of carbonate system input variables. The flags to be used are as follows:
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 pCO2 in μatm)
var2	Value of the second variable (in mol/kg, except for pH)
S	Salinity (practical salinity scale)
T	Temperature in degrees Celsius
Patm	Surface atmospheric pressure in atm, default is 1 atm
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total dissolved inorganic phosphorus (mol/kg); set to 0 if NA
Sit	Concentration of total dissolved inorganic silicon (mol/kg); set to 0 if NA
evar1	Standard uncertainty in var1 of input pair of carbonate system variables
evar2	Standard uncertainty in var2 of input pair of carbonate system variables
eS	Standard uncertainty in salinity; default is 0.01
eT	Standard uncertainty in temperature (degree C); default is 0.01
ePt	Standard uncertainty in total dissolved inorganic phosphorus concentration (mol/kg)
eSit	Standard uncertainty in total dissolved inorganic silicon concentration (mol/kg)
epK	Standard uncertainty) in 7 key dissociation constants: pK0, pK1, pK2, pKb, pKw, pKspa and pKspc. This is a vector. The default is c(0.002, 0.0075, 0.015, 0.01, 0.01, 0.02, 0.02).
eBt	Standard uncertainty in total boron, given as a relative fractional error. The default is 0.02, which equates to a 2% error
method	Case insensitive character string to choose the error-propagation method: 1) Gaussian, 2) Method of Moments, or 3) Monte Carlo). These methods are specified using the 2-letter codes "ga", "mo", or "mc", respectively. The default is "ga" (Gaussian).
r	Correlation coefficient between standard uncertainties of var1 and var2 (only useful with method="mo", i.e., ignored for the 2 other methods, the default is r=0.0
runs	Number of random samples (ignored unless method="mc"; the default is runs=10000
k1k2	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

Details

Complete information on routine uncertainty propagation for the marine carbon dioxide system can be found in Orr et al. (in press). This function requires users to specify each input standard uncertainty as either the standard deviation or the standard error of the mean. The latter implies much smaller propagated uncertainties, but is appropriate only when interested in the error in the mean, not the error of a given measurement. Beware that it is easy to fool oneself when using the standard error of the mean rather than the standard deviation.

This function requires different types of standard uncertainties:

- Standard uncertainties for evar1, evar2, eS, eT, ePt, eSit (same units as the input data, e.g., mol/kg);
- Standard uncertainties in pK units for epK; and
- Standard uncertainties in relative fractional units (between 0.0 and 1.0) for eBt.

This function propagates standard uncertainty from input to output variables using one of three methods:

- Gaussian: The Gaussian method is the standard technique for estimating a computed variable's (z) second moment (its variance or standard deviation) based on a first-order approximation to z. More precisely, we use here the basic 1st order, 2nd moment uncertainty analysis (a type of Taylor expansion), assuming no covariance between input variables. This is the approach used by Dickson and Riley (1978). It is the default method.

- Method of moments: The method of moments is a more general form of the Gaussian method. But in addition, it also accounts for covariance between input variables. In this case, the 'errors' routine allows the user to specify a value of the correlation coefficient 'r', having a value between -1.0 and 1.0, to indicate the correlation between standard uncertainties of the input pair of carbonate system variables. That correlation is used to compute the covariance. But by default, it is assumed that there is no covariance (r=0.0).
- Monte Carlo: The Monte Carlo method is a brute-force approach relying on repeated random sampling of input errors, adding those to each input variables, calculating the corresponding output variables for each sample, and finally assessing the standard deviation in each output variables.

This function has many input parameters that are identical to those in the carb function. For their details, refer to the 'carb' documentation.

All parameters may be scalars or vectors except epK, eBt, method, runs, and gas.

- runs and eBt must be scalars
- method and gas must each consist of a character string
- epK may be a vector of 7 values. In that case, it must list errors for pK0, pK1, pK2, pKb, pKw, pKspa and pKspc, respectively. That set of errors is identical for all input data. Alternatively, users may specify 'epK=NULL' or 'epK=0' to set all 7 values to zero and thus neglect errors in the equilibrium constants.

In constrast, for evar1, evar2, r, eS, eT, ePt and eSit:

- if they are vectors, they represent standard uncertainties associated with each data point
- if they are scalars (single real numbers), they represent one standard uncertainty value each associated to all data points

The same remark applies to parameter r (correlation coefficient).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Value

The function returns a 2-dimensional dataframe, with the following columns:

`H`	combined standard uncertainty in [H+] concentration (mol/kg)
`pH`	combined standard uncertainty in pH
`CO2`	combined standard uncertainty in CO2 concentration (mol/kg)
`pCO2`	combined standard uncertainty in "standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (uatm)
`fCO2`	combined standard uncertainty in "standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (uatm)

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

If all input data have the same 'flag' value, the returned data frame does not show combined standard uncertainties on input pair of carbonate system variables. For example, if all input flags are 15, the input pair is DIC and ALK; hence, errors on DIC and ALK are not returned.

Correlation coefficient

By default, 'r' is zero. However, for some pairs the user may want to specify a different value. For example, measurements of pCO2 and pH are often anti-correlated. The same goes for two other pairs: 'CO2 and CO3' and 'pCO2 and CO3'. But even for these cases, care is needed before using non-zero values of 'r'.

When the user wishes to propagate standard uncertainties for an individual measurement, 'r' should ALWAYS be zero if each member of the input pair is measured independently. In this case, we are interested in the correlation between the uncertainties in those measurements, not in the correlation between the measurements themselves. Uncertainties from those measurements are probably not correlated if they come from different instruments. Conversely, if users are interested in the error in the mean of a distribution of measurements (i.e., if they are propagating standard errors instead of standard deviations), one should then also account for the correlation between the measurements of the two variables of the input pair.

For input pairs where one member is pH (flags 1, 6, 7, 8, 9, and 21), this 'errors' function automatically inverses the sign of 'r'. The reason for that is that the associated derivatives are computed in terms of the hydrogen ion concentration (H+), not pH. Therefore for each of these 6 flags, if the user wants to compute their own 'r' that should be done by (1) using the H+ concentration instead of pH, and (2) inversing the sign of that computed 'r' before passing it as an argument to this routine. Usually though (when not calculating r for pH), the user may just use the 'r' in the expected way. For example, to include the covariance term when there is a perfect anticorrelation of pH with pCO2, one would use 'r=-1.0'.

Computation time

Computation time depends on the method chosen; the Monte Carlo method takes much longer to execute. The computational time required for the Monte Carlo method is proportional to the number of runs. More runs, implies improved accuracy: runs = 10000 appears a minimum to obtain an accuracy of less than 1%. Accuracy is inversely proportional to the number of runs.

Computation time also depends on the chosen pair of input variables. For example, with the input pair DIC and Total alkalinity (flag=15), it is much longer than for input pair pH and Total alkalinity (flag=8)

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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.

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Examples

```
## 1) For the input pair ALK and DIC (var1 and var2 when flag=15),
## compute resulting uncertainty from given uncertainty on ALK and DIC (5 umol/kg)
## and default uncertainties in dissociation constants and total boron
## using the default method (Gaussian)
errors(flag=15, var1=2300e-6, var2=2000e-6, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
       evar1=5e-6, evar2=5e-6, eS=0, eT=0, ePt=0, eSit=0,
       pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")
## Typical output:
## H             pH          CO2           fCO2      pCO2      HCO3          ...
## 3.721614e-10  0.01796767  5.441869e-07  19.25338  19.31504  9.170116e-06  ...

## 2) Do the same as in one, but assign a 4% uncertainty to total boron
##    This uncertainty is the amount by which estimates from Lee et al (2010) and
##    Uppstrom (1974) differ. The default for the latter is eBt=0.02.
errors(flag=15, var1=2300e-6, var2=2000e-6, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
       evar1=5e-6, evar2=5e-6, eS=0, eT=0, ePt=0, eSit=0, eBt=0.04,
       pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")

## 3) For the input pair pH and ALK (var1 and var2 when flag=8)
## compute standard errors in output variables from errors in input variables, i.e.,
## for pH (0.005 pH units) and in ALK (5 umol/kg), along with
## errors in total dissolved inorganic phosphorus (0.1 umol/kg) and
## total dissolved inorganic silicon (2 umol/kg) concentrations, while
## assuming no uncertainty in dissociation constants & boron, using the Gaussian method:
errors(flag=8, var1=8.25, var2=2300e-6,  S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
       evar1=0.005, evar2=5e-6, eS=0, eT=0, ePt=0.1, eSit=2, epK=0, eBt=0,
       method="ga", pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")

## 4) For the input pair pCO2 and pH (var1 and var2 when flag=21)
## compute standard errors in output variables from errors in input variables, i.e.,
## for pCO2 (2 uatm) and pH (0.005 pH units), with no uncertainties in Pt and Sit
## nor in the dissociation constants BUT a perfect anticorrelation between pCO2 and pH,
## (the input pair) using the Method of moments:
errors(flag=21, var1=400, var2=8.1,  S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
       evar1=2, evar2=0.005, eS=0, eT=0, ePt=0.0, eSit=0, epK=0, eBt=0,
       method="mo", r=-1.0, pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")

## 5) Use vectors as arguments and compute errors on all output variables
## using Monte Carlo method taking into account input errors on pH, ALK, DIC
## and dissociation constants (pKx)
```

```
flag <- c(8, 15)
var1 <- c(8.2, 0.002394, 8.25)
var2 <- c(0.002343955, 0.002017)
S <- c(35, 35)
T <- c(25, 25)
P <- 0
Pt <- 0
Sit <- 0
evar1 <- c(0.005, 2e-6)
evar2 <- c(2e-6, 2e-6)
epKx <- c(0.002, 0.01, 0.02, 0.01, 0.01, 0.01, 0.01)
eBtx = 0.01
method <- "mc"
kf <- "pf"
k1k2 <- "l"
pHscale <- "T"
b <- "u74"
## NOTE that the following is executable but enclosed in "donttest"
## because it takes too long to run when submiting to CRAN
## and is therefore rejected
errors(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt, Sit=Sit,
       evar1=evar1, evar2=evar2, eS=0, eT=0, ePt=0, eSit=0, epK=epKx, eBt=eBtx,
       method=method, runs=10000, kf=kf, k1k2=k1k2, pHscale=pHscale, b=b)
```

`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, 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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

Author(s)

Heloise Lavigne, Jean-Pierre Gattuso, and James Orr <jean-pierre.gattuso@imev-mer.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.

Orr J. C., Epitalon J.-M. and Gattuso J.-P., 2015. Comparison of seven packages that compute ocean carbonate chemistry. *Biogeosciences* **12**, 1483-1510.

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

See Also

p2fCO2.

Examples

```
f2pCO2(T=25, Patm=1.0, P=0, fCO2=380)
```

---

fCO2insi *fCO2 at in situ temperature*

Description

Correction to compensate for the difference in temperature between the temperature of measurement and in situ temperature.

Usage

```
fCO2insi(fCO2lab = 400, Tlab = 20, SST = 19)
```

Arguments

fCO2lab	Fugacity of CO2 measured in the lab in μatm
Tlab	Temperaure of measurment in the lab in in degrees Celsius, default is 20oC
SST	Temperature in degrees Celsius, default is 19oC

Value

fCO2insi	Fugacity of CO2 at in situ temperature in μatm, the same units as that for the fCO2 input.

Note

The empirical correction applied is from Takahashi (1993) as recommended by Pierrot et al. (2009)

Author(s)

Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Pierrot D., Neill C., Sullivan K., Castle R., Wanninkhof R., LÃ¼ger H., Johannessen T., Olsen A., Feely R. A. and Cosca C. E., 2009. Recommendations for autonomous underway pCO2 measuring systems and data-reduction routines. *Deep-Sea Res. II* **56**, 512-522.

Takahashi T., Olafsson J., Goddard J. G., Chipman D. W. and Sutherland S. C., 1993. Seasonal variation of CO2 and nutrients in the high-latitude surface oceans: a comparative study. *Glob. Biogeochem. Cycles* **7**, 843-878.

See Also

f2pCO2, pCO2insi.

Examples

```
fCO2insi(fCO2lab = 400, SST = 15, Tlab = 16)
```

---

fH *Total activity coefficient for H+*

Description

Compute total hydrogen ion activity coefficient. The activity coefficient (fH) is used to convert from H+ concentration on SWS scale to H+ activity (ah), as used for NBS scale; likewise fH is used to make the conversion in the opposite direction, from the NBS scale to the SWS scale. Here, fH is taken from Takahashi et al (1982, GEOSECS Pacific Expedition, Chap 3, p. 80) who say: fH is the total activity coeff., which includes contributions from HSO4- and HF [as well as H+].

Takahashi et al. (1982) computed a relationship for fH based on the experimental data from Culberson & Pytkowicz (1973), who determined it experimentally as a function of temperature and salinity. The approach is old and full of uncertainty. Newer approaches are more complicated (Pitzer equations) and big uncertainties remain (Marion et al., 2011; Pilson, 2013).

Usage

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

Arguments

S	Salinity on the practical salinity scale, default is 35
T	Temperature in degrees Celsius, default is 25oC

Details

This total activity coefficient appears in the following basic chemistry equation: $ah = fH * hsws$, where ah is the activity of hydrogen ion, fH is the total activity coefficient, and $hsws = [H+] + [HSO4-] + [HF]$. In other words, $hsws$ is the total hydrogen ion conccentration on the seawater scale.

The two pH scales of concern are defined as $pHNBS = -log10(ah)$ and $pHSWS = -log10(hsws)$.

Value

`fH`	Total activity coefficient for H+

Author(s)

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

References

Culberson, C.H., & Pytkowicz, R.M. (1973). Ionization of water in seawater. *Marine Chemistry*, **1(4)**, 309-316.

Marion G.M., Millero F.J., Camoes M.F., Spitzer P., Feistel R., Chen C.T.A. 2011. pH of seawater. *Marine Chemistry* **126** 89-96.

Pilson M.E.Q. (2013) An introduction to the chemistry of the sea, 2 edn. Cambridge, UK: Cambridge University Press.

Takahashi T., Williams R.T., and Ros D.L. (1982) Carbonate chemistry. GEOSECS Pacific Expedition, Volume 3, Hydrographic Data 1973-1974, 77-83.

See Also

pHnbs2sws and pHsws2nbs

Examples

```
## Compute fH
   f = fH(T=25, S=35)
   print(f)
## Check value: The result is 0.7134043
```

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

Description

Henry's constant mol/(kg/atm)

Usage

```
K0(S=35, T=25, P=0, Patm=1, warn="y")
```

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 is 1 atm
warn	"y" to show warnings when T or S go beyond the valid range for K0; "n" to supress warnings. The default is "y".

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.

For pressure corrections: the pressure correction term of Weiss (1974) is used.

Value

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

Author(s)

Jean-Marie Epitalon, Aurelien Proye, and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

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

Examples

```
K0(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

```
K1(S=35, T=25, P=0, k1k2="x", pHscale="T", kSWS2scale="x", ktotal2SWS_P0="x", warn="y")
```

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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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 for all formulations of K1 and K2, nor when the hydrostatic pressure is 0. It is advised to use default value "x", in which case it is computed when required.
ktotal2SWS_P0	Conversion factor from the total scale to the SWS at an hydrostatic pressure of 0. It is not required for all formulations of K1 and K2. It is advised to use default value "x", in which case it is computed when required.
warn	"y" to show warnings when T or S go beyond the valid range for K1; "n" to supress warnings. The default is "y".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): formulation is that of Waters et al (2014). See below.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.

- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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)

Jean-Marie Epitalon and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Cai W. J., and Wang Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* **43**, 657-668.

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.

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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., Pierrot D., Lee K., Wanninkhof R., Feely R., Sabine C. L., Key R. M. and Takahashi T., 2002. Dissociation constants for carbonic acid determined from field measurements. Deep Sea Research Part I: Oceanographic Research Papers **49**:1705-1723.

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.

Mojica Prieto F. J. and Millero F. J., 2002. The values of pK1 + pK2 for the dissociation of carbonic acid in seawater. *Geochimica et Cosmochimica Acta* **66**, 2529-2540.

Papadimitriou S., Loucaides S., RÃ©rolle V. M. C., Kennedy P., Achterberg E. P., Dickson A. G., Mowlem M. and Kennedy H., 2018. The stoichiometric dissociation constants of carbonic acid in seawater brines from 298 to 267 K. *Geochimica et Cosmochimica Acta* **220**, 55-70.

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.

Schockman, K.M., Byrne, R.H., 2021. Spectrophotometric determination of the bicarbonate dissociation constant in seawater, *Geochimica et Cosmochimica Acta*..

Sulpis O., Lauvset S. K. and Hagens M., 2020. Current estimates of K1* and K2* appear inconsistent with measured CO2 system parameters in cold oceanic regions. *Ocean Science* **16**, 847-862.

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], *Marine Chemistry* **165**, 66-67.

See Also

K2.

Examples

```
K1(S=35,T=25,P=0,k1k2="l",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="x", warn="y")
```

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. It is advised to use default value "x", in which case it is computed when required.
warn	"y" to show warnings when T or S go beyond the valid range for K1p; "n" to supress warnings. The default is "y".

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, Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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 *Second dissociation constant of carbonic acid (mol/kg)*

Description

Second dissociation constant of carbonic acid (mol/kg)

Usage

```
K2(S=35, T=25, P=0, k1k2="x", pHscale="T", kSWS2scale="x", ktotal2SWS_P0="x", warn="y")
```

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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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 for all formulations of K1 and K2, nor when the hydrostatic pressure is 0. It is advised to use default value "x", in which case it is computed when required.
ktotal2SWS_P0	Conversion factor from the total scale to the SWS at an hydrostatic pressure of 0. It is not required for all formulations of K1 and K2. It is advised to use default value "x", in which case it is computed when required.
warn	"y" to show warnings when T or S go beyond the valid range for K2; "n" to supress warnings. The default is "y".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): S ranging from 19.6 to 41 and T ranging between 15 to 35oC.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.

- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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, Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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) constant is recommended by DOE (1994).

Cai W. J., and Wang Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* **43**, 657-668.

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.

Mojica Prieto F. J. and Millero F. J., 2002. The values of pK1 + pK2 for the dissociation of carbonic acid in seawater. *Geochimica et Cosmochimica Acta* **66**, 2529-2540.

Papadimitriou S., Loucaides S., RÃ©rolle V. M. C., Kennedy P., Achterberg E. P., Dickson A. G., Mowlem M. and Kennedy H., 2018. The stoichiometric dissociation constants of carbonic acid in seawater brines from 298 to 267 K. *Geochimica et Cosmochimica Acta* **220**, 55-70.

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.

Schockman, K.M., Byrne, R.H., 2021. Spectrophotometric determination of the bicarbonate dissociation constant in seawater, *Geochimica et Cosmochimica Acta*..

Sulpis O., Lauvset S. K. and Hagens M., 2020. Current estimates of K1* and K2* appear inconsistent with measured CO2 system parameters in cold oceanic regions. *Ocean Science* **16**, 847-862.

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], *Marine Chemistry* **165**, 66-67.

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="x", warn="y")
```

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. It is advised to use default value "x", in which case it is computed when required.
warn	"y" to show warnings when T or S go beyond the valid range for K2p; "n" to supress warnings. The default is "y".

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, Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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)
```

K2si *Second dissociation constant of Si(OH)4*

Description

Second dissociation constant of Si(OH)4 (mol/kg)

Usage

```
K2si(S=35, T=25, P=0, pHscale="T", kSWS2scale="x", ktotal2SWS_P0="x")
```

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. It is advised to use default value "x", in which case it is computed when required.
ktotal2SWS_P0	Conversion factor from the total scale to the SWS at an hydrostatic pressure of 0. It is advised to use default value "x", in which case it is computed when required.

Details

This equation is modified from Wischmeyer et al. (2003), who fitted the temperature-dependent K2si from Nordstrom et al. (1990) for freshwater to a value of 12.56 for T=25 and an ionic strength of 0.5 mol/kg. The temperature and salinity ranges in which it is valid are not well constrained.

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

K2si	Second dissociation constant of Si(OH)4 (mol/kg)

Note

`K2si` is only used internally by seacarb's carbonate-system solver when `fullresult=TRUE`, i.e. from within `carbfull()`. `carb()` itself (`fullresult=FALSE`) always sets `K2si` to zero internally, treating silicic acid as a monoprotic system regardless of the value of `Sit` supplied. See `carb.Rd` and `carbfull.Rd`. Because `K2si` is several orders of magnitude smaller than `Ksi` under typical seawater conditions, this simplification has a negligible (~1e-6 relative) effect on computed carbonate system variables.

Author(s)

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

References

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

Nordstrom D. K., L. N. Plummer, D. Langmuir, E. Busenberg, H. M. May, B. F. Jones, D. L. Parkhurst, 1990 Revised chemical equilibrium data from major mineral reactions and their limitations. In: Melchior, D.C., R. L. Bassett (Eds.) Chemical Modeling of Aqueous Systems. *IIACS Series* **416**. American Chemical Society, Washington, DC.

Wischmeyer A. G., Y. Del Amo, M. Brzezinski, D. A. Wolf-Gladrow, 1995 Theoretical constraints on the uptake of silicic acid species by marine diatoms. *Marine Chemistry* **82**: 13-29.

Examples

```
K2si(S=35, T=25, P=0, pHscale="T")
```

`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="x", warn="y")
```

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. It is advised to use default value "x", in which case it is computed when required.
`warn`	"y" to show warnings when T or S go beyond the valid range for K3p; "n" to supress warnings. The default is "y".

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, Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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="x", ktotal2SWS_P0="x", warn="y")
```

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. It is advised to use default value "x", in which case it is computed when required.
ktotal2SWS_P0	Conversion factor from the total scale to the SWS at an hydrostatic pressure of 0. It is advised to use default value "x", in which case it is computed when required.
warn	"y" to show warnings when T or S go beyond the valid range for Kb; "n" to supress warnings. The default is "y".

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, Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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* **375**, 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, warn="y")
```

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
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".

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, K2si, 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 6 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
kfree2total	to convert from the free scale to total scale
kSWS2total	to convert from the seawater scale to the total scale
kSWS2free	to convert from the seawater scale to the free 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="x", Ks_p="x", warn="y")
```

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 or set to "x", it is computed; if given, computation speed is increased
Ks_p	Stability constant of hydrogen sulfate (mol/kg) at chosen pressure; if not given or set to "x", it is computed; if given, computation speed is increased
warn	"y" to show warnings when T or S go beyond the valid range for Kf; "n" to supress warnings. The default is "y".

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, Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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 *variable for internal use*

Description

nothing

Khs *Dissociation constant of hydrogen sulfide (mol/kg)*

Description

Dissociation constant of hydrogen sulfide (mol/kg)

Usage

```
Khs(S=35, T=25, P=0, pHscale="T", kSWS2scale="x", ktotal2SWS_P0="x", warn="y")
```

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	Optional conversion factor from the seawater pH scale to the chosen pH scale. Supply the value already computed for the other constants in the same calculation (as calculate_carb does for Kw, Ksi, K1p, K2p and K3p), so that every constant is placed on the same pH scale by the same route. If omitted, the factor is recomputed here with kconv using its default kf="x"; a caller who requested kf="dg" would then silently receive a constant built on a different Kf, an inconsistency of up to 0.9 percent.
ktotal2SWS_P0	Optional conversion factor from the total pH scale to the seawater pH scale at atmospheric pressure. Khs is native to the total pH scale, so like Kb it requires both conversion factors. Same rationale as kSWS2scale.
warn	"y" to show warnings when T or S go beyond the valid range for Khs; "n" to supress warnings. The default is "y".

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", kSWS2scale="x", warn="y")
```

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	Optional conversion factor from the seawater pH scale to the chosen pH scale. Supply the value already computed for the other constants in the same calculation (as `calculate_carb` does for `Kw`, `Ksi`, `K1p`, `K2p` and `K3p`), so that every constant is placed on the same pH scale by the same route. If omitted, the factor is recomputed here with `kconv` using its default `kf="x"`; a caller who requested `kf="dg"` would then silently receive a constant built on a different `Kf`, an inconsistency of up to 0.9 percent.
warn	"y" to show warnings when T or S go beyond the valid range for Kn; "n" to supress warnings. The default is "y".

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")
```

`Ks` *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", warn="y")
```

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"
`warn`	"y" to show warnings when T or S go beyond the valid range for Ks; "n" to supress warnings. The default is "y".

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 as described by Millero (1995), and the value transformed back to the required scale (T, F or SWS).

Value

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

Author(s)

Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Dickson A. G., 1990 Standard potential of the reaction: AgCI(s) + 1/2H2(g) = Ag(s) + HCI(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 40oC: standard potentials at salinities from 20 to 45. *Analytical Chemistry* **49**, 29-34.

Examples

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

`Ksi` *Dissociation constant of Si(OH)4*

Description

Dissociation constant of Si(OH)4 on total scale (mol/kg)

Usage

```
Ksi(S=35, T=25, P=0, pHscale="T", kSWS2scale="x", warn="y")
```

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. It is advised to use default value "x", in which case it is computed when required.
`warn`	"y" to show warnings when T or S go beyond the valid range for Ksi; "n" to supress warnings. The default is "y".

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

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

Note

Si(OH)4 is a diprotic acid: it has both a first dissociation constant (`Ksi`, this function) and a second (`K2si`). seacarb's `carb()` function, however, internally sets `K2si` to zero (treating silicate as if it were monoprotic), regardless of the value of `Sit` supplied; only `carbfull()` uses the true, nonzero `K2si`. See `carb.Rd`, `carbfull.Rd`, and `K2si.Rd`.

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, warn="y")
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0
warn	"y" to show warnings when T or S go beyond the valid range for Kspa; "n" to supress warnings. The default is "y".

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.

Pressure coorection was performed as described by Millero (1995).

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 <jean-pierre.gattuso@imev-mer.fr>

References

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

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` *Solubility product of calcite (mol/kg)*

Description

Solubility product of calcite (mol/kg)

Usage

```
Kspc(S=35, T=25, P=0, warn="y")
```

Arguments

`S`	Salinity, default is 35
`T`	Temperature in degrees Celsius, default is 25oC
`P`	Hydrostatic pressure in bar (surface = 0), default is 0
`warn`	"y" to show warnings when T or S go beyond the valid range for Kspc; "n" to supress warnings. The default is "y".

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.

The pressure coorection was performed as described by Millero (1995).

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 <jean-pierre.gattuso@imev-mer.fr>

References

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

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="x", warn="y")
```

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. It is advised to use default value "x", in which case it is computed when required.
warn	"y" to show warnings when T or S go beyond the valid range for Kw; "n" to supress warnings. The default is "y".

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, 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).

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 (mol2/kg2)

Author(s)

Heloise Lavigne, Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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")
```

---

oa *Perturbation of the seawater carbonate system*

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="u74", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

`flag`	select the pair of variables available to describe the initial seawater. 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 available to describe the initial seawater, in mol/kg except for pH and for pCO2 in uatm
`var2`	Value of the second variable available to describe the initial seawater, in mol/kg except for pH
`pCO2f`	pCO2 target value, in uatm
`pCO2s`	pCO2s is the pCO2, in uatm, of the "high-CO2" seawater that will be mixed with "normal seawater". The default value is 10^6 uatm, that is seawater bubbled with pure CO2 gas and saturated with CO2.
`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`	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
`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 pCO2 isoclines are drawn in the back. Default is false.
`b`	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74".
`eos`	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
`long`	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
`lat`	latitude of data point, used when eos parameter is "teos10".

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). Beware that each formulation for a constant is only valid for specific ranges of temperature and salinity:

For K1 and K2:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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 pCO2. Note that if a vector is given in argument only the first value is used.

`perturbation` Table providing key parameters for the following methods:

CO2 bubbling: high-CO2 air is bubbled in seawater. The first parameter is the value of the pCO2 in the air required to bubble the seawater (in uatm).

SW mixing: mixing of "normal" and "high-CO2" seawater. The fist parameter, "Weight fraction high-CO2 SW" or wf, is the weight fraction of the high-CO2 seawater per kg seawater.

Addition of acid: 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 mimic natural ocean acidification, which increases dissolved inorganic carbon and does not change total alkalinity; rather, acid addition reduces total alkalinity while not changing dissolved inorganic carbon.

- 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" (Riebesell et al, 2010).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Author(s)

Heloise Lavigne and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

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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.

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

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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.

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Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], Marine Chemistry 165, 66-67.

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="l", ks="d", plot=TRUE, b="u74")
```

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="u74")
```

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 pair 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 pCO2 in μatm

`var2` Value of the second variable in mol/kg, except for pH

`k1k2` "cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

`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) 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` Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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)

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References

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

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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="u74")
```

---

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 <jean-pierre.gattuso@imev-mer.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, P=0, pCO2)
```

Arguments

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

Value

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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

Author(s)

Heloise Lavigne, Jean-Pierre Gattuso, and James Orr <jean-pierre.gattuso@imev-mer.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.

Orr J. C., Epitalon J.-M. and Gattuso J.-P., 2015. Comparison of seven packages that compute ocean carbonate chemistry. *Biogeosciences* **12**, 1483-1510.

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, *Marine Chemistry*, **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 atmospheric pCO2 (partial pressure of CO2) into atmospheric xCO2 (mole fraction of CO2)

Usage

```
p2xCO2(S=35, T=25, Patm=1, 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 pH20 is the vapor pressure of seawater computed following best practices (Dickson et al., 2007). That computed pH20 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. and Price, B. A. (1980) Nitrous oxide solubility in water and seawater, Marine Chemistry, **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 = p2xCO2(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="u74", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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 pCO2 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

Author(s)

Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

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.

Cai W. J., and Wang Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* **43**, 657-668.

Dickson A. G., 1990 Standard potential of the reaction: AgCI(s) + 1/2H2(g) = Ag(s) + HCI(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 40oC: 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 Atlantoc 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.

Orr J. C., Epitalon J.-M. and Gattuso J.-P., 2015. Comparison of seven packages that compute ocean carbonate chemistry. *Biogeosciences* **12**, 1483-1510.

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

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], Marine Chemistry 165, 66-67.

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="l", ks="d", b="u74") # 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="l", ks="d", b="u74") # with 0.5 * Ca concentration
```

---

pCO2insi *pCO2 at in situ temperature*

Description

Correction to compensate for the difference in temperature between the temperature of measurement and in situ temperature.

Usage

```
pCO2insi(pCO2lab = 400, Tlab = 20, SST = 19)
```

Arguments

pCO2lab	Partial pressure of CO2 measured in the lab in μatm
Tlab	Temperature of measurement in the lab in in degrees Celsius, default is 20oC
SST	Temperature in degrees Celsius, default is 19oC

Value

pCO2insi	Partial pressure of CO2 at in situ temperature in μatm, the same units as that for the pCO2 input.

Note

The empirical correction applied is from Takahashi (1993) as recommended by Pierrot et al. (2009)

Author(s)

Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Pierrot D., Neill C., Sullivan K., Castle R., Wanninkhof R., LÃ¼ger H., Johannessen T., Olsen A., Feely R. A. and Cosca C. E., 2009. Recommendations for autonomous underway pCO2 measuring systems and data-reduction routines. *Deep-Sea Res. II* **56**, 512-522.

Takahashi T., Olafsson J., Goddard J. G., Chipman D. W. and Sutherland S. C., 1993. Seasonal variation of CO2 and nutrients in the high-latitude surface oceans: a comparative study. *Glob. Biogeochem. Cycles* **7**, 843-878.

See Also

`f2pCO2`, `fCO2insi`.

Examples

```
pCO2insi(pCO2lab = 400, SST = 15, Tlab = 16)
```

`Pcoeffs` *Coefficients used for pressure-correcting the equilibrium constants*

Description

Pressure corrections are based on the following equations:

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

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 15 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="x", kconv2Scale="x", warn="y")
```

Arguments

`Kvalue`	Value of the constant at P=0 (hydrostatic pressure in bar, surface = 0)
`Ktype`	Name of the constant,

- 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 sufide(mol/kg)
- Kn Dissociation constant of ammonium (mol/kg)
- Ksi Dissociation constant of Si(OH)4 (mol/kg)
- K2si Second dissociation constant of Si(OH)4 (mol/kg)

`T`	Temperature in degrees Celsius, default is 25oC
`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 advised to use default value "x", in which case it is computed when required. (may slow 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 advised to use default value "x", in which case it is computed when required. (may slow down the computation)
`warn`	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".

Details

- The pressure correction is applied on the seawater scale for K1, K2, K1p, K2p, K3p, Kb, Khs, Kn, Ksi, K2si 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="u74", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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 pCO2 in μatm
var2	Value of the second variable in mol/kg, except for pH
pCO2g	CO2 partial pressure of the gas used for bubbling in μatm
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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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)
b	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.

- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

Author(s)

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References

Cai W. J., and Wang Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* **43**, 657-668.

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: AgCI(s) + 1/2H2(g) = Ag(s) + HCI(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.

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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.

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., 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.

Orr J. C., Epitalon J.-M. and Gattuso J.-P., 2015. Comparison of seven packages that compute ocean carbonate chemistry. *Biogeosciences* **12**, 1483-1510.

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

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], Marine Chemistry 165, 66-67.

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="l", ks="d", b="u74")
```

---

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 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

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

Author(s)

Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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 <jean-pierre.gattuso@imev-mer.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: AgCI(s) + 1/2H2(g) = Ag(s) + HCI(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 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 and pressure*

Description

pH at in situ temperature and pressure

Usage

```
pHinsi(pH=8.2, ALK=2.4e-3, Tinsi=20, Tlab=25, Pinsi=0, S=35, Pt=0, Sit=0,
  k1k2 = "x", kf = "x", ks="d", pHscale = "T", b="u74", eos = "eos80",
  long = 1e+20, lat = 1e+20)
```

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
Pinsi	In situ hydrostatic pressure in bar (surface = 0)
S	Salinity
Pt	value of the concentration of total phosphate in mol/kg
Sit	the value of the total silicate in mol/kg

k1k2	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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 "u74"
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.

- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Value

pH pH at in situ temperature and pressure

Author(s)

Jean-Pierre Gattuso, <jean-pierre.gattuso@imev-mer.fr>

References

Cai W. J., and Wang Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* **43**, 657-668.

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.

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], Marine Chemistry 165, 66-67.

Examples

```
pHinsi(pH=8.2,ALK=2.4e-3,Tinsi=25,Tlab=25,Pinsi=200,S=35,Pt=0,Sit=0)
```

---

pHnbs2sws *Converts pH from NBS to SWS scale*

Description

Converts pH on NBS scale to pH on SWS scale pCO2. The NBS-to-SWS conversion is done with the total activity coefficient fH (combined activity coeff for H+, HSO4-, and HF) from Takahashi et al. (1982) based on data from Culberson and Pytkowicz (1973). The approach is old and full of uncertainty. Newer approaches are more complicated (Pitzer equations) and big uncertainties remain (Marion et al., 2011; Pilson, 2013).

Usage

```
pHnbs2sws(pHNBS, S=35, T=25)
```

Arguments

pHNBS	pH on NBS scale
S	Salinity on the practical salinity scale, default is 35
T	Temperature in degrees Celsius, default is 25oC

Details

The pHSWS is computed from pHNBS using the total activity coefficient and relying on the following basic chemistry equation: $ah = fH * hsws$, where ah is the activity of hydrogen ion, fH is the total activity coefficient, and $hsws = [H+] + [HSO4-] + [HF]$. In other words, $hsws$ is the hydrogen ion concentration on the seawater scale.

The two pH scales are defined as $pHNBS = -log10(ah)$ and $pHSWS = -log10(hsws)$.

Value

pHSWS	pH on SWS scale

Author(s)

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

References

Culberson, C.H., & Pytkowicz, R.M. (1973). Ionization of water in seawater. *Marine Chemistry*, **1(4)**, 309-316.

Marion G.M., Millero F.J., Camoes M.F., Spitzer P., Feistel R., Chen C.T.A. 2011. pH of seawater. *Marine Chemistry* **126** 89-96.

Pilson M.E.Q. (2013) An introduction to the chemistry of the sea, 2 edn. Cambridge, UK: Cambridge University Press.

Takahashi T., Williams R.T., and Ros D.L. (1982) Carbonate chemistry. GEOSECS Pacific Expedition, Volume 3, Hydrographic Data 1973-1974, 77-83.

See Also

fH and pHsws2nbs

Examples

```
## Convert pHNBS to pHSWS
   pHNBS = 8.0                          # pH on the NBS scale
   pHSWS = pHnbs2sws(pHNBS, T=25, S=35) # pH on the SWS scale
   print(pHSWS)
## Check value: the result should be 7.853336
```

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 <jean-pierre.gattuso@imev-mer.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)
```

pHspec *Calculates pHT from results of spectrophotometric measurements*

Description

Calculates pH of a water sample from absorbance ratios R, obtained from spectrophotometric measurements with pH indicator dyes (on the total scale in mol/kg-soln)

Usage

```
pHspec(S=35, T=25, R=1, d="mCP", k="m18", warn="y")
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
R	Absorbance ratio, default is 1
d	Dye used for spectrophotometric measurement, default is "mCP"
k	"m18" for using mCP characterization by Mueller and Rehder (2018)
warn	"y" to show warnings when S and/or T go beyond the valid range for the chosen d and k; "n" to supress warnings. The default is "y".

Details

The model used to calculate the return value of this function is based on experimental data. It is critical to consider that the formulation refers to the conditions studied during the characterization experiment and is only valid for the studied ranges of temperature and salinity:

- Mueller and Rehder (2018): S ranging between 0 and 40, T ranging between 5 and 35oC, and the dye used being m-Cresol purple (mCP) with R referring to the ratio of absorbances at wavelengths 578 and 434 nm.

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

pHspec	The function returns the pH value of a water sample from absorbance ratios R, obtained from spectrophotometric measurements with pH indicator dyes (on the total scale in mol/kg-soln)

Author(s)

Jens Daniel Mueller <jens.mueller@io-warnemuende.de> Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Mueller, J. D. and Rehder, G., 2018 Metrology for pH Measurements in Brackish Waters - Part 2: Experimental Characterization of Purified meta-Cresol Purple for Spectrophotometric pHT Measurements. *Frontiers in Marine Science* **5:177**, 1-9.doi:10.3389/fmars.2018.00177

See Also

amp, pHslope, pH. tris,

Examples

```
##Example should give test value pHT = 7.6713
 pHspec(S=35, T=25, R=1, d="mCP", k="m18", warn="y")
```

---

pHsws2nbs *Converts pH from SWS to NBS scale*

Description

Converts pH on SWS scale to pH on NBS scale pCO2. The SWS-to-NBS conversion is done with the total activity coefficient fH (combined activity coeff for H+, HSO4-, and HF) from Takahashi et al. (1982) based on data from Culberson and Pytkowicz (1973). The approach is old and full of uncertainty. Newer approaches are more complicated (Pitzer equations) and big uncertainties remain (Marion et al., 2011; Pilson, 2013).

Usage

```
pHsws2nbs(pHSWS, S=35, T=25)
```

Arguments

pHSWS	pH on SWS scale
S	Salinity on the practical salinity scale, default is 35
T	Temperature in degrees Celsius, default is 25oC

Details

The pHNBS is computed from pHSWS using the total activity coefficient and relying on the following basic chemistry equation: $ah = fH * hsws$, where ah is the activity of hydrogen ion, fH is the total activity coefficient, and $hsws = [H+] + [HSO4-] + [HF]$. In other words, $hsws$ is the hydrogen ion concentration on the seawater scale.

The two pH scales are defined as $pHNBS = -log10(ah)$ and $pHSWS = -log10(hsws)$.

Value

pHNBS	pH on NBS scale

Author(s)

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

References

Culberson, C.H., & Pytkowicz, R.M. (1973). Ionization of water in seawater. *Marine Chemistry*, **1(4)**, 309-316.

Marion G.M., Millero F.J., Camoes M.F., Spitzer P., Feistel R., Chen C.T.A. 2011. pH of seawater. *Marine Chemistry* **126** 89-96.

Pilson M.E.Q. (2013) An introduction to the chemistry of the sea, 2 edn. Cambridge, UK: Cambridge University Press.

Takahashi T., Williams R.T., and Ros D.L. (1982) Carbonate chemistry. GEOSECS Pacific Expedition, Volume 3, Hydrographic Data 1973-1974, 77-83.

See Also

fH and pHnbs2sws

Examples

```
## Convert pHSWS to pHNBS
   pHSWS = 7.853336                    # pH on the SWS scale
   pHNBS = pHsws2nbs(pHSWS, T=25, S=35) # pH on the NBS scale
   print(pHNBS)
## Check value: the result should be 8.0
```

---

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="u74", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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 pCO2 in μatm
`var2`	Value of the second variable in mol/kg except for pH
`pCO2s`	Partial pressure of the high CO2 component in μatm
`wf`	Weight fraction of the high CO2 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`	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
`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`	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74".

eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

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Dickson A. G., 1990 Standard potential of the reaction: AgCI(s) + 1/2H2(g) = Ag(s) + HCI(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.

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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.

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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="l", ks="d", b="u74")
```

---

ppH *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", eos = "eos80",
long = 1e+20, lat = 1e+20)
```

Arguments

flag	Select the pair 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 its is carried out in a system open to the atmosphere
var1	Value of the first variable in mol/kg, except for pH and for pCO2 in μatm

var2	Value of the second variable in mol/kg, except for pH
pCO2a	CO2 partial pressure in the atmosphere pCO2 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

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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.

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.

Orr J. C., Epitalon J.-M. and Gattuso J.-P., 2015. Comparison of seven packages that compute ocean carbonate chemistry. *Biogeosciences* **12**, 1483-1510.

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], Marine Chemistry 165, 66-67.

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="l", 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="l", 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, Patm, P=0, Pt=0, Sit=0, pHscale="T",
kf="x", k1k2="x", ks="d", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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	enter value of the first variable in mol/kg, except for pH and for pCO2 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 is 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
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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

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"
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
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- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

Value

The function returns a data frame containing the following columns:

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

Author(s)

Jean-Pierre Gattuso and Heloise Lavigne <jean-pierre.gattuso@imev-mer.fr>

References

Cai W. J., and Wang Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* **43**, 657-668.

Dickson A. G., 1990 Standard potential of the reaction: AgCI(s) + 1/2H2(g) = Ag(s) + HCI(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 40oC: 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.

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], Marine Chemistry 165, 66-67.

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="l", 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="u74",
eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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 its is carried out in a system open to the atmosphere
var1	Value of the first variable in mol/kg, except for pH and for pCO2 in μatm
var2	Value of the second variable in mol/kg, except for pH
pCO2a	CO2 partial pressure in the atmosphere pCO2 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^{2-} 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".

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)
b	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr et al. (2015)

Author(s)

Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Cai W. J., and Wang Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology and Oceanography* **43**, 657-668.

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: AgCI(s) + 1/2H2(g) = Ag(s) + HCI(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.

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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.

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

Waters, J., Millero, F. J., and Woosley, R. J., 2014. Corrigendum to "The free proton concentration scale for seawater pH", [MARCHE: 149 (2013) 8-22], Marine Chemistry 165, 66-67.

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

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="l", ks="d", b="u74")

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="l", ks="d", b="u74")
```

---

rho *Density of seawater (kg/m3)*

Description

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

Usage

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

Arguments

S	Practical Salinity (PSS-78), default is 35
T	Temperature in degrees Celsius (ITS-90), default is 25oC
P	Hydrostatic pressure in bar (surface = 0), default is 0

Value

rho	Density of seawater (kg/m3)

Author(s)

Aurelien Proye and Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.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)
```

`sa2sp_chem` *From absolute to practical salinity*

Description

Converts from absolute to practical salinity (SP). Salinity conversion depends on total alkalinity as well as the concentrations of dissolved inorganic carbon, nitrate and silicate.

Usage

```
sa2sp_chem(SA, TA=2300e-6, DIC=2000e-6, NO3=0, SIOH4=0)
```

Arguments

`SA`	Absolute salinity in g/kg
`TA`	Total alkalinity, in mol/kg, default is 2300 Âµmol/kg
`DIC`	Dissolved inorganic carbon concentration in mol/kg, default is 2000 Âµmol/kg
`NO3`	Total nitrate concentration in mol/kg, default is 0
`SIOH4`	Total silicate concentration in mol/kg, default is 0

Details

Convert from absolute to practical salinity from carbon system parameters and ion concentration which most affect water density anomalies.

Value

`SP`	Practical salinity (in psu)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

Pawlowicz R., Wright D. G. and Millero F. J., 2011. The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater. *Ocean Science* **7**, 363-387.

Pawlowicz R., 2013. What every oceanographer needs to know about TEOS-10 (The TEOS-10 Primer). http://www.teos-10.org/

See Also

sp2sa_chem does the reverse, sa2sp_geo

Examples

```
# Calculate the practical salinity of a sample with Absolute Salinity of 35 g/kg,
# Total Alkalinity of 0.00234 mol/kg and DIC of 0.00202 mol/kg
SP <- sa2sp_chem(SA=35, TA=0.00234, DIC=0.00202)
```

`sa2sp_geo` *From absolute to practical salinity*

Description

Converts from absolute to practical salinity based on depth and geographic location.

Usage

```
sa2sp_geo(SA, P=0, long=1.e20, lat=1.e20)
```

Arguments

`SA`	Absolute salinity in g/kg
`P`	Sea water pressure in dbar
`long`	Longitude in decimal degrees [0 ... +360] or [-180 ... +180]
`lat`	Latitude in decimal degrees [-90 ... 90]

Details

This function is almost an alias of subroutine gsw_SP_from_SA from gsw package on which it relies. The only difference is in that depth and location are optional. If location is not given, or incomplete (either longitude or latitude missing), an arbitrary location is chosen: the mid equatorial atlantic ocean. Note that this implies an error on computed SA ranging from 0 up to 0.02 g/kg.

Value

`SP`	Practical salinity (psu)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

Pawlowicz R., 2013. What every oceanographer needs to know about TEOS-10 (The TEOS-10 Primer). http://www.teos-10.org/

See Also

sp2sa_geo does the reverse, sa2sp_chem

Examples

```
# Calculate the practical salinity of a sample whose absolute Salinity is 35,
# depth is 10 dbar and location is 188 degrees East and 4 degrees North.
SP <- sa2sp_geo(35, 10, 188, 4)
```

---

seacarb_test_P0 *Test data file (at P=0) to test the use of the carb function*

Description

The variables are:

- Flag indicating which pair 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 pair 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.

seaFET *Test seaFET data file*

Description

Short test file for using with functions sf_calc and sf_calib. It is an excerpt of a file produced by a SeaFET pH sensor.

Usage

```
seaFET
```

Format

A data frame with 8 variables (datetime, Eint, Eext, Salinity, Temperature, pHspectro, E0int25, E0ext25) and 10 rows

sf_calc *Calculation of calibrated pH for seaFET sensor*

Description

The function sf_calc() calculates pH time series (pHint_tot and pHext_tot) for SeaFET pH sensors, using calibration coefficients E0int25 and E0ext25 from the function sf_calib(). Both functions are R-adaptations from MATLAB scripts published by Bresnahan et al. (2014).

Usage

```
sf_calc(calEint=0.0865, calEext= -0.93, E0int25 =-0.39,
  E0ext25=-1.46, calT=16.2, calSal=35.6)
```

Arguments

calEint	EINT (V), default is 0.0865
calEext	EEXT (V), default is -0.93
E0int25	Coeficient of calibration related to the internal sensor and obtained via sf_calib function, default is -0.39. If time-serie, we use the mean per periode of deployement
E0ext25	Coeficient of calibration related to the external sensor and obtained via sf_calib function, default is -1.46. If time-serie, we use the mean per periode of deployement
calT	Temperature in degrees Celsius, default is 16.2
calSal	Salinity, default is 35.6

Details

Input values should be vectors of equal length. E0int25 and E0ext25 should be constant throughout the time series. When multiple reference samples are available for one SeaFET deployment, mean E0int25 and mean E0ext25 should be calculated and used in sf_calc(). Each unique SeaFET deployment requires a new calculation of mean E0int25 and mean E0ext25 based on reference pH samples (total hydrogen ion scale). For detailed SeaFET calibration instructions and recommendations see Bresnahan et al. (2014) and Rivest et al. (2016).

Value

This function returns a dataframe comprising 2 variables:

pHint_tot	Calibrated pH of the internal sensor at in situ temperature.
pHext_tot	Calibrated pH of the external sensor at in situ temperature.

Author(s)

Samir Alliouane, Lydia Kapsenberg, Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Bresnahan, P. J. J., Martz, T. R., Takeshita, Y., Johnson, K. S., and LaShomb, M., 2014. Best practices for autonomous measurement of seawater pH with the Honeywell Durafet. *Methods Oceanogr.* **9**, 44-60.

Martz, T.R., Connery, J.G., and Johnson, K.S., 2010. Testing the Honeywell Durafet for seawater pH applications. *Limnol. Oceanogr. Meth.* **8**, 172-184.

Rivest, E.B., O'Brien, M., Kapsenberg, L., Gotschalk, C.C., Blanchette, C.A., Hoshijima, U., and Hofmann, G.E., 2016. Beyond the benchtop and the benthos: dataset management planning and design for time series of ocean carbonate chemistry associated with Durafet(c)-based pH sensors. *Ecological Informatics* **36**, 209-220.

See Also

sf_calib.

Examples

```
sf_calc(calEint=0.0865, calEext= -0.93, E0int25 =-0.39,
  E0ext25=-1.46, calT=16.2, calSal=35.6)

## Using the test file seaFET
sf_calc(calEint=seaFET$Eint, calEext=seaFET$Eext,
  E0int25=seaFET$E0int25, E0ext25=seaFET$E0ext25,
  calT=seaFET$Temperature, calSal=seaFET$Salinity)
```

---

sf_calib *Calibration coefficients for seaFET sensor*

Description

Calibration coefficients E0INT,25, E0EXT,25

Usage

```
sf_calib(calEint=0.0865, calEext=-0.93, calpH=8.132, calT=16.2, calSal=35.6)
```

Arguments

calEint	EINT (V), default is 0.0865
calEext	EEXT (V), default is -0.93
calpH	spectrophotometric pH in Total scale, default is 8.132
calT	Temperature in degrees Celsius, default is 16.2
calSal	Salinity, default is 35.6

Details

Outputs E0INT25 and E0EXT25 must be calculated for each reference sample collected during a SeaFET deployment. Multiple E0INT25 and E0EXT25 may be calculated if there is more than one reference sample for a given deployment. As such, arguments can be given as unique numbers or as vectors (vectors should be of the same length).

It is critical that Eint (calEint) and Eext (calEext) recorded by the SeaFET match reference sample measurements of temperature (calT), salinity (calSal), and spectrophotometric pH (calpH, total hydrogen ion scale) taken at the same time. Note that SeaFET temperature measurements may require calibration via an applied offset. When possible, calibrated CTD temperature and salinity measurements may be used, while spectrophotometric pH measurements always require discrete 'reference' water samples (unless in situ, certified, seawater-based, Tris pH buffer is used). The accepted time offset between collection of reference samples and SeaFET measurements depends on the hydrology and pH variability of the location. For detailed SeaFET calibration instructions and recommendations see Bresnahan et al. (2014) and Rivest et al. (2016).

Value

This function returns a dataframe comprising 2 variables:

`E0int25`	Calibration coefficients of the internal sensor at 25oC.
`E0ext25`	Calibration coefficients of the external sensor at 25oC.

Author(s)

Samir Alliouane, Lydia Kapsenberg, Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr>

References

Bresnahan, P. J. J., Martz, T. R., Takeshita, Y., Johnson, K. S., and LaShomb, M., 2014. Best practices for autonomous measurement of seawater pH with the Honeywell Durafet. *Methods Oceanogr.* **9**, 44-60.

Martz, T.R., Connery, J.G., and Johnson, K.S., 2010. Testing the Honeywell Durafet for seawater pH applications. *Limnol. Oceanogr. Meth.* **8**, 172-184.

Rivest, E.B., O'Brien, M., Kapsenberg, L., Gotschalk, C.C., Blanchette, C.A., Hoshijima, U., and Hofmann, G.E., 2016. Beyond the benchtop and the benthos: dataset management planning and design for time series of ocean carbonate chemistry associated with Durafet(c)-based pH sensors. *Ecological Informatics* **36**, 209-220.

See Also

`sf_calc`.

Examples

```
sf_calib(calEint=0.0865, calEext=-0.93, calpH=8.132, calT=16.2, calSal=35.6)

## Using the test file seaFET
sf_calib(calEint=seaFET$Eint, calEext=seaFET$Eext,
```

```
calpH=seaFET$pHspectro, calT=seaFET$Temperature,
calSal=seaFET$Salinity)
```

`sir` *Parameters of the seawater carbonate system including the substrate-inhibitor-ratio (SIR)*

Description

This function is a modification of *carb*. It returns parameters of the seawater carbonate system, as well as additional parameters relevant to the substrate-inhibitor-ratio (SIR).

Usage

```
sir(flag, var1, var2, S = 35, T = 25, Patm = 1, P = 0,
               Pt = 0, Sit = 0, k1k2 = "x", kf = "x", ks = "d", pHscale = "T",
               b = "u74", gas = "potential", warn = "y", eos = "eos80",
               long = 1e+20, lat = 1e+20)
```

Arguments

`flag`	select the pair 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 pCO2 in μatm
`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 is 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

Details

Calculates the "substrate-inhibitor ratio (SIR)" (i.e. [HCO3-]/[H+]) which is used as a metric to predict carbonate chemistry dependency of biotic calcium carbonate formation (Bach, 2015). Please note that hydrogen ion concentrations in the output [HCO3-]/[H+] are on the *free scale*, regardless

of the input pH scale. We have included pH and [H+] outputs on multiple scales as a teaching exercise to show how calculating the SIR on different scales changes its meaning.

The function is based on *carb* and therefore also returns parameters of the seawater carbonate system.

***carb* 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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- 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.
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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".
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.

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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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`	"standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (μatm)
`fCO2`	"standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (μatm)
`pCO2pot`	"potential" pCO2, CO2 partial pressure computed at potential temperature and atmospheric pressure (μatm)
`fCO2pot`	"potential" fCO2, CO2 fugacity computed at potential temperature and atmospheric pressure (μatm)
`pCO2insitu`	"in situ" pCO2, CO2 partial pressure computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)

fCO2insitu	"in situ" fCO2, CO2 fugacity computed at in situ temperature and total pressure (atm + hydrostatic) (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
SIR	substrate inhibitor ratio: [HCO3]/[H_free] (mol:μmol)
H_free	H ion concentration on free scale (μmol/kg)
H_sws	H ion concentration on seawater scale (μmol/kg)
H_t	H ion concentration on total scale (μmol/kg)
pH_free	pH calculated on the free scale
pH_sws	pH calculated on the seawater scale
pH_t	pH calculated on the total scale

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr and Epitalon (2015)

Because `sir()` calls `carb()` rather than `carbfull()`, it inherits `carb()`'s treatment of silicic acid as monoprotic (the second dissociation constant `K2si` is internally set to zero) and does not include ammonia or hydrogen sulfide alkalinity at all. See `carb.Rd`. Use `sir_full()` for the complete treatment of all these systems.

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Examples

```
## With a pair of variables
sir(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74")

## 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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
sir(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)
sir(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[14:19,]

## method 1 using the column numbers
sir(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
sir(flag=tab$flag, var1=tab$var1, var2=tab$var2, S=tab$S, T=tab$T,
P=tab$P, Sit=tab$Sit, Pt=tab$Pt)
```

`sir_b` *Parameters of the seawater carbonate system with boron addition, including the substrate-inhibitor-ratio (SIR)*

Description

This function is a modification of *carbb*. It returns parameters of the seawater carbonate system when boron is added, as well as additional parameters relevant to the SIR.

Usage

```
sir_b(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0,
  k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential", badd=0,
  warn="y", eos = "eos80", long = 1e+20, lat = 1e+20)
```

Arguments

flag	select the pair 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 pCO2 in μatm
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 is 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	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
badd	Amount of boron added in mol/kg.
warn	"y" to show warnings when T or S go beyond the valid range for constants; "n" to supress warnings. The default is "y".
eos	"teos10" to specify T and S according to Thermodynamic Equation Of Seawater - 2010 (TEOS-10); "eos80" to specify T and S according to EOS-80.
long	longitude of data point, used when eos parameter is "teos10" as a conversion parameter from absolute to practical salinity.
lat	latitude of data point, used when eos parameter is "teos10".

Details

Calculates the "substrate-inhibitor ratio (SIR)" (i.e. [HCO3-]/[H+]) which is used as a metric to predict carbonate chemistry dependency of biotic calcium carbonate formation (Bach, 2015). Please note that hydrogen ion concentrations in the output [HCO3-]/[H+] are on the *free scale*, regardless of the input pH scale. We have included pH and [H+] outputs on multiple scales as a teaching exercise to show how calculating the SIR on different scales changes its meaning.

The function is based on *carbb* and therefore also returns parameters of the seawater carbonate system when boron is added.

***carbb* 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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- Lueker et al. (2000): S ranging between 19 and 43 and T ranging between 2 and 35oC.
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Roy et al. (1993): S ranging between 5 and 45 and T ranging between 0 and 45oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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 K0, the pressure correction term of Weiss (1974) is used.
- 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).

long and lat are used as conversion parameters from absolute to practical salinity: when seawater is not of standard composition, practical salinity alone is not sufficient to compute absolute salinity and vice-versa. One needs to know the density. When long and lat are given, density is inferred from WOA silicate concentration at given location. When they are not, an arbitrary geographic point is chosen: mid equatorial Atlantic. Note that this implies an error on computed salinity up to 0.02 g/kg.

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	"standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (μatm)
fCO2	"standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (μatm)
pCO2pot	"potential" pCO2, CO2 partial pressure computed at potential temperature and atmospheric pressure (μatm)
fCO2pot	"potential" fCO2, CO2 fugacity computed at potential temperature and atmospheric pressure (μatm)
pCO2insitu	"in situ" pCO2, CO2 partial pressure computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)
fCO2insitu	"in situ" fCO2, CO2 fugacity computed at in situ temperature and total pressure (atm + hydrostatic) (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
SIR	substrate inhibitor ratio: [HCO3]/[HCO3]/[H_free] (mol:μmol)
H_free	H ion concentration on free scale (μmol/kg)
H_sws	H ion concentration on seawater scale (μmol/kg)
H_t	H ion concentration on total scale (μmol/kg)
pH_free	pH calculated on the free scale
pH_sws	pH calculated on the seawater scale
pH_t	pH calculated on the total scale

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr and Epitalon (2015).

Because `sir_b()` calls `carbb()` (equivalent to `carb()`, with the additional `badd` argument for boron-addition experiments), it likewise treats silicic acid as monoprotic internally (`K2si` is set to zero) and does not include ammonia or hydrogen sulfide alkalinity. See `carb.Rd`. Use `sir_full()` for the complete treatment of all these systems.

Author(s)

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Examples

```
## With a pair of variables
sir_b(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0,
  Pt=0, Sit=0,pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", badd=0)
```

`sir_full` *Parameters of the seawater carbonate system including the substrate-inhibitor-ratio (SIR) - extension of carb*

Description

This function is a modification of carb. It returns parameters of the seawater carbonate system, including the ammonium and sulfide acid-base systems, as well as full acid-base speciation and additional parameters relevant to the SIR.

Usage

```
sir_full(flag, var1, var2, S=35, T=25, Patm=1, P=0, Pt=0, Sit=0,
        k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential",
        NH4t=0, HSt=0)
```

Arguments

`flag` select the pair 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-soln, except for pH and for pCO2 in μatm
var2	Value of the second variable in mol/kg-soln, except for pH
S	Salinity
T	Temperature in degrees Celsius
Patm	Surface atmospheric pressure in atm, default is 1 atm
P	Hydrostatic pressure in bar (surface = 0)
Pt	Concentration of total phosphate in mol/kg-soln; set to 0 if NA
Sit	Concentration of total silicate in mol/kg-soln; set to 0 if NA
k1k2	"cw" for using K1 and K2 from Cai & Wang (1998), "l" from Lueker et al. (2000), "m02" from Millero et al. (2002), "m06" from Millero et al. (2006), "m10" from Millero (2010), "mp2" from Mojica Prieto et al. (2002), "p18" from Papadimitriou et al. (2018), "r" from Roy et al. (1993), "sb21" from Shockman & Byrne (2021), "s20" from Sulpis et al. (2020), and "w14" from Waters et al. (2014). "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 "w14".
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) 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	Concentration of total boron. "l10" for the Lee et al. (2010) formulation or "u74" for the Uppstrom (1974) formulation, default is "u74"
gas	used to indicate the convention for INPUT pCO2, i.e., when it is an input variable (flags 21 to 25): "insitu" indicates it is referenced to in situ pressure and in situ temperature; "potential" indicates it is referenced to 1 atm pressure and potential temperature; and "standard" indicates it is referenced to 1 atm pressure and in situ temperature. All three options should give identical results at surface pressure. This option is not used when pCO2 is not an input variable (flags 1 to 15). The default is "potential".
NH4t	Concentration of total ammonium in mol/kg-soln; set to 0 if NA
HSt	Concentration of total hydrogen sulfide in mol/kg-soln; set to 0 if NA

Details

Calculates the "substrate-inhibitor ratio (SIR)" (i.e. [HCO3-]/[H+]) which is used as a metric to predict carbonate chemistry dependency of biotic calcium carbonate formation (Bach, 2015). Please note that hydrogen ion concentrations in the output [HCO3-]/[H+] are on the *free scale*, regardless of the input pH scale. We have included pH and [H+] outputs on multiple scales as a teaching exercise to show how calculating the SIR on different scales changes its meaning.

The function is based on *carbfull* and therefore also returns parameters of the seawater carbonate system, including the ammonium and sulfide acid- base systems, as well as full acid-base speciation.

***carbfull* 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:

- Cai and Wang (1998): S ranging between 0 and 40 and T ranging between 0.2 and 30oC.
- 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.
- Mojica Prieto et al. (2002): S ranging from 5 to 42 and T ranging between 0 and 45oC.
- Millero et al. (2002): S ranging from 34 to 37 and T ranging between -1.6 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".
- Waters et al.(2014): S ranging between 1 and 50 and T ranging between 0 and 50oC. Waters (2014) 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".
- Papadimitriou et al. (2018): S ranging from 33 to 100 and T ranging between -6 to 25oC.
- Sulpis et al. (2020): S ranging from 30.7 to 37.6 and T ranging between -1.7 to 31.8oC.
- Shockman & Byrne (2021): for K2, S ranging from 19.6 to 41 and T ranging between 15 to 35oC. For K1, formulation is that of Waters et al.

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 K0, the pressure correction term of Weiss (1974) is used.
- For K1, K2, pK1, pK2, pK3, Kw, Kb, Khs, Ksi and K2si, 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-soln)
`pCO2`	"standard" pCO2, CO2 partial pressure computed at in situ temperature and atmospheric pressure (μatm)
`fCO2`	"standard" fCO2, CO2 fugacity computed at in situ temperature and atmospheric pressure (μatm)
`pCO2pot`	"potential" pCO2, CO2 partial pressure computed at potential temperature and atmospheric pressure (μatm)
`fCO2pot`	"potential" fCO2, CO2 fugacity computed at potential temperature and atmospheric pressure (μatm)
`pCO2insitu`	"in situ" pCO2, CO2 partial pressure computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)

fCO2insitu	"in situ" fCO2, CO2 fugacity computed at in situ temperature and total pressure (atm + hydrostatic) (μatm)
HCO3	HCO3 concentration (mol/kg-soln)
CO3	CO3 concentration (mol/kg-soln)
DIC	DIC concentration (mol/kg-soln)
ALK	ALK, total alkalinity (mol/kg-soln)
OmegaAragonite	Omega aragonite, aragonite saturation state
OmegaCalcite	Omega calcite, calcite saturation state
NH4	NH4 concentration (mol/kg-soln)
NH3	NH3 concentration (mol/kg-soln)
BOH3	B(OH)3 concentration (mol/kg-soln)
BOH4	B(OH)4 concentration (mol/kg-soln)
H3PO4	H3PO4 concentration (mol/kg-soln)
H2PO4	H2PO4 concentration (mol/kg-soln)
HPO4	HPO4 concentration (mol/kg-soln)
PO4	PO4 concentration (mol/kg-soln)
H2S	H2S concentration (mol/kg-soln)
HS	HS concentration (mol/kg-soln)
SiOH4	SiOH4 concentration (mol/kg-soln)
SiOOH3	SiOOH3 concentration (mol/kg-soln)
SiO2OH2	SiO2OH2 concentration (mol/kg-soln)
HF	HF concentration (mol/kg-soln)
F	F concentration (mol/kg-soln)
HSO4	HSO4 concentration (mol/kg-soln)
SO4	SO4 concentration (mol/kg-soln)
H	H concentration at specified pH scale (mol/kg-soln)
OH	OH concentration (mol/kg-soln)
NH4t	Supplied NHt concentration (mol/kg-soln); values are recycled if necessary
BOR	Calculated total borate concentration (mol/kg-soln)
Pt	Supplied Pt concentration (mol/kg-soln); values are recycled if necessary
HSt	Supplied HSt concentration (mol/kg-soln); values are recycled if necessary
Sit	Supplied Sit concentration (mol/kg-soln); values are recycled if necessary
FLUO	Calculated total fluoride concentration (mol/kg-soln)
ST	Calculated total sulfate concentration (mol/kg-soln)
SIR	substrate inhibitor ratio: [HCO3]/[H_free] (mol:μmol)
H_free	H ion concentration on free scale (μmol/kg)
H_sws	H ion concentration on seawater scale (μmol/kg)
H_t	H ion concentration on total scale (μmol/kg)
pH_free	pH calculated on the free scale
pH_sws	pH calculated on the seawater scale
pH_t	pH calculated on the total scale

Note

Warning: pCO2 estimates below 100 m are subject to considerable uncertainty. See Weiss (1974) and Orr and Epitalon (2015)

Unlike `sir()` and `sir_b()`, `sir_full()` calls `carbfull()` and therefore uses the full diprotic treatment of silicic acid (both `Ksi` and `K2si`) and includes ammonia and hydrogen sulfide alkalinity via `NH4t` and `HSt`. See `carb.Rd` for discussion of the (small, ~1e-6 relative) resulting difference from `sir()`/`sir_b()`.

Author(s)

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

Examples

```
## With a pair of variables
sir_full(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=0, Sit=0,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", gas="potential", NH4t=0, HSt=0)

## With a pair of variables and non-zero nutrient concentrations
sir_full(flag=8, var1=8.2, var2=0.00234, S=35, T=25, P=0, Patm=1.0, Pt=5e-6, Sit=2e-6,
pHscale="T", kf="pf", k1k2="l", ks="d", b="u74", gas="potential", NH4t=10e-6, HSt=0.1e-6)

## 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("l", "l", "l")
pHscale <- c("T", "T", "T")
b <- c("l10", "l10", "l10")
gas <- c("potential", "potential", "potential")
NH4t <- c(0, 0, 0)
HSt <- c(0, 0, 0)
sir_full(flag=flag, var1=var1, var2=var2, S=S, T=T, P=P, Pt=Pt, Sit=Sit,
  kf=kf, k1k2=k1k2, pHscale=pHscale, b=b, gas=gas, NH4t=NH4t, HSt=HSt)

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

---

sp2sa_chem *From Practical to absolute salinity*

Description

Converts from practical to absolute salinity based on total alkalinity as well as on the concentrations of dissolved inorganic carbon, nitrate and silicate.

Usage

```
sp2sa_chem(SP, TA=2300e-6, DIC=2000e-6, NO3=0, SIOH4=0)
```

Arguments

SP	Practical salinity on the practical salinity scale
TA	Total alkalinity, in mol/kg, default is 2300 Âµmol/kg
DIC	Dissolved inorganic carbon concentration in mol/kg, default is 2000 Âµmol/kg
NO3	Total nitrate concentration in mol/kg, default is 0
SIOH4	Total silicate concentration in mol/kg, default is 0

Details

Converts from practical to absolute salinity from carbonate system parameters and ion concentration which mostly affect water density anomalies.

Value

SA	Absolute salinity (g/kg)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

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See Also

sa2sp_chem does the reverse, sp2sa_geo

Examples

```
# Calculate the absolute salinity of a sample with practical Salinity of 35,
# Total Alkalinity of 0.00234 mol/kg and DIC of 0.00202 mol/kg
SA <- sp2sa_chem(SP=35, TA=0.00234, DIC=0.00202)
```

---

sp2sa_geo *From practical to absolute salinity*

Description

Converts from practical to absolute salinity based on depth and geographic location.

Usage

```
sp2sa_geo(SP, P=0, long=1.e20, lat=1.e20)
```

Arguments

SP	Practical salinity on the practical salinity scale
P	Sea water pressure in dbar
long	Longitude in decimal degrees [0 ... +360] or [-180 ... +180]
lat	Latitude in decimal degrees [-90 ... 90]

Details

This function is almost an alias of function gsw_SA_from_SP of the gsw package on which it relies. The only difference is in that depth and location are optional. If location is not given, or incomplete (either longitude or latitude missing), an arbitrary location is chosen: the mid equatorial atlantic ocean. Note that this implies an error on computed SA ranging from 0 up to 0.02 g/kg.

Value

SA	Absolute salinity (g/kg)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

Pawlowicz R., 2013. What every oceanographer needs to know about TEOS-10 (The TEOS-10 Primer). http://www.teos-10.org/

See Also

sa2sp_geo does the reverse, sp2sa_chem

Examples

```
# Calculate the absolute salinity of a sample whose practical Salinity is 35,
# depth is 10 dbar and location is 188 degrees East and 4 degrees North.
SA <- sp2sa_geo(35, 10, 188, 4)     # 34.711778344814114
```

---

speciation *ionic forms as a function of pH*

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

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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

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-, HPO4--, PO4---)
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")))
```

---

teos2eos_chem *Convert temperature and salinity from TEOS-10 to EOS-80*

Description

Converts conservative temperature to in situ temperature and absolute salinity to practical salinity (SP). Salinity conversion depends on total alkalinity as well as on the concentrations of dissolved inorganic carbon, nitrate and silicate.

Usage

```
teos2eos_chem(SA, CT, P=0, TA=2300e-6, DIC=2000e-6, NO3=0, SIOH4=0)
```

Arguments

SA	Absolute salinity in g/kg
CT	Conservative temperature in degrees C
P	Sea water pressure in dbar
TA	Total alkalinity, in mol/kg, default is 2300 Âµmol/kg
DIC	Dissolved inorganic carbon concentration in mol/kg, default is 2000 Âµmol/kg
NO3	Total nitrate concentration in mol/kg, default is 0
SIOH4	Total silicate concentration in mol/kg, default is 0

Details

Conversion from absolute to practical salinity depends on carbonate system parameters and ion concentration which mostly affect water density anomalies.

Value

The function returns a data frame containing the following columns:

T	In situ temperature (deg C)
SP	Practical salinity (psu)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

Pawlowicz R., Wright D. G. and Millero F. J., 2011. The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater. *Ocean Science* **7**, 363-387.

Pawlowicz R., 2013. What every oceanographer needs to know about TEOS-10 (The TEOS-10 Primer). http://www.teos-10.org/

See Also

eos2teos_chem, teos2eos_geo, sa2sp_cham, package gsw

Examples

```
# Calculate in situ temperature and practical salinity of a sample with
# Absolute salinity of 35 g/kg, Conservative temperature of 18 deg C,
# at 0 dbar and Total alkalinity of 0.00234 mol/kg and DIC of 0.00202 mol/kg
f <- teos2eos_chem(SA=35, CT=18, P=0, TA=0.00234, DIC=0.00202)
T <- f$T     # insitu temperature
SP <- f$SP     # Practical salinity
```

`teos2eos_geo` *Convert temperature and salinity from TEOS-10 to EOS-80*

Description

Converts conservative temperature to in situ temperature and absolute salinity to practical salinity (SP). Salinity conversion depends on depth and geographic location.

Usage

```
teos2eos_geo(SA, CT, P=0, long=1.e20, lat=1.e20)
```

Arguments

`SA`	Absolute salinity in g/kg
`CT`	Conservative temperature in degrees C
`P`	Sea water pressure in dbar
`long`	Longitude in decimal degrees [0 ... +360] or [-180 ... +180]
`lat`	Latitude in decimal degrees [-90 ... 90]

Details

Conversion from absolute to practical salinity depends on water density anomaly which is correlated with silicate concentration. This function relies on silicate concentration taken from WOA (World Ocean Atlas) to evaluate the density anomaly.

Value

The function returns a data frame containing the following columns:

`T`	In situ temperature (deg C)
`SP`	Practical salinity (psu)

Author(s)

Jean-Marie Epitalon

References

McDougall T. J., Jackett D. R., Millero F. J., Pawlowicz R. and Barker P. M., 2012. A global algorithm for estimating Absolute Salinity. *Ocean Science* **8**, 1123-1134.

Pawlowicz R., Wright D. G. and Millero F. J., 2011. The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater. *Ocean Science* **7**, 363-387.

Pawlowicz R., 2013. What every oceanographer needs to know about TEOS-10 (The TEOS-10 Primer). http://www.teos-10.org/

See Also

eos2teos_geo does the reverse, teos2eos_chem, sa2sp_geo, package gsw

Examples

```
# Calculate in situ temperature and practical salinity of a sample with
# Absolute salinity of 35 g/kg, conservative temperature of 18 deg C,
# depth is 10 dbar and location is 188 degrees East and 4 degrees North.
f <- teos2eos_geo(SA=35, CT=18, P=10, long=188, lat=4)
T <- f$T     # in situ temperature
SP <- f$SP     # Practical salinity
```

---

theta *Potential temperature of seawater*

Description

Computes theta, the potential temperature of seawater given original temperature, salinity, pressure, and reference pressure

Usage

```
theta(S=35, T=25, P=0, Pref=0)
```

Arguments

S	Salinity on the practical salinity scale, default is 35
T	Temperature in degrees Celsius, default is 25oC
P	Hydrostatic pressure in bar (surface = 0; 1000 db = 100 bar), default is 0
Pref	Reference hydrostatic pressure in bar, default is 0

Details

Computes the potential temperature of seawater relative to a chosen reference pressure following Fofonoff and Millard (1983). The potential temperature θ is the temperature that a water parcel would have if were moved adiabatically to another pressure level Pref. Typically, the potential temperature is referenced to the surface ($Pref = 0$). The potential teperature depends on the original salinity S, *in-situ* temperature T and pressure P.

This routine is essentially a wrapper for the swTheta routine of the 'oce' package. Unlike the latter, pressure units here are given in bars and method="unesco" is prescribed.

Value

theta	potential temperature of seawater (C)

Author(s)

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

References

Fofonoff, P. and R. C. Millard Jr, 1983. Algorithms for computation of fundamental properties of seawater. *Unesco Technical Papers in Marine Science*, **44**, 53 pp.

See Also

swTheta.

Examples

```
#Calculate the potential temperature for a sample at 1000 db referenced to the surface
theta <- theta(S=35, T=25, P=100, Pref=0)
```

---

tris *pH of TRIS buffer*

Description

Calculates the pH value of TRIS buffered artificial seawater solutions (on the total scale in mol/kg-soln)

Usage

```
tris(S=35,T=25,b=0.04,k="d98",warn="y")
```

Arguments

S	Salinity, default is 35
T	Temperature in degrees Celsius, default is 25oC
b	Molality if TRIS/TRISH+ in moles per kg of water, default is 0.04 mol/kg-H20
k	"d98" for DelValls and Dickson 1998, "m18" for using tris characterization by Mueller et al (2018), default is "d98"
warn	"y" to show warnings when S,T and/or b go beyond the valid range for the chosen k; "n" to supress warnings. The default is "y".

Details

The models used to calculate the return value of this function are based on experimental data. It is critical to consider that each formulation refers to the artificial seawater solution applied during the characterization experiment and is only valid for the studied ranges of temperature and salinity:

- DelValls and Dickson (1998): S ranging between 20 and 40, T ranging between 0 and 45oC, and b being 0.04 mol/kg-H20.
- Mueller et al. (2018): S ranging between 5 and 40, T ranging between 5 and 45oC, and b ranging between 0.01 and 0.04 mol/kg-H20.

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`	The function returns the pH value of TRIS buffered artificial seawater solutions (on the total scale in mol/kg-soln)

Author(s)

Jean-Pierre Gattuso <jean-pierre.gattuso@imev-mer.fr> and Jens Daniel Mueller <jens.mueller@io-warnemuende.d

References

DelValls, T. A., and Dickson, A. G., 1998 The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ('tris') in synthetic sea water. *Deep Sea Research Part I: Oceanographic Research Papers* **45(9)**, 1541-1554. doi:10.1016/S09670637(98)000193

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.

Mueller, J. D., Bastkowski, F., Sander, B., Seitz, S., Turner, D. R., Dickson, A. G., and Rehder, G., 2018 Metrology for pH measurements in brackish waters- Part 1: Extending electrochemical pHT measurements of TRIS buffers to salinities 5-20. *Frontiers in Marine Science* **5:176**, 1-12. doi:10.3389/fmars.2018.00176

See Also

`amp`, `pHslope`, `pH`.

Examples

```
##Example from Mueller et al. (2018), should give test value pHT = 8.0703
 tris(S=20,T=25,b=0.04,k="m18")
```

vapress *Computes vapor pressure of seawater*

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 pH20 following best practices (Dickson et al., 2007). That computed pH20 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, Marine Chemistry, **2**, 203-215.

Weiss, R. F. and Price, B. A. (1980) Nitrous oxide solubility in water and seawater, Marine Chemistry, **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 atmospheric xCO2 (mole fraction of CO2) into atmospheric 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 CO2 in ppm, default is 400

Details

The mole fraction xCO2 (ppm) is computed from pCO2 (μatm) using the following equation: $xCO2 = pCO2(Patm - pH2O)$, where pH20 is the vapor pressure of seawater computed following best practices (Dickson et al., 2007). That computed pH20 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. and Price, B. A. (1980) Nitrous oxide solubility in water and seawater, Marine Chemistry, **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="l", ks="d", b="u74")
print(results)
```

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