

Package ‘SolveSAPHE’

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Title Solver Suite for Alkalinity-PH Equations

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Description Universal and robust algorithm for solving the total alkalinity-pH equation presented in G. Munhoven (2013) <doi:10.5194/gmd-6-1367-2013> and G. Munhoven (2021) <doi:10.5194/gmd-2020-447>. The total alkalinity-pH equation relates total alkalinity and pH for a given set of acid-base concentrations in a given water sample, among which carbonic acid. This package is particularly useful in marine chemistry involving dissolved inorganic carbon. Original package in Fortran can be found at <doi:10.5281/zenodo.4328965>.

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Author Jean-Marie Epitalon [aut, cre, cph],
Jean-Pierre Gattuso [cph],
Guy Munhoven [aut]

Maintainer Jean-Marie Epitalon <jean-marie.epitalon@orange.fr>

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ACVT_HSWO_HFREE	<i>Conversion ratio H_SWS/H_free from free pH-scale to SWS scale</i>
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Description

Function returns the ratio H_{SWS}/H_{free} as a function of temperature, salinity and pressure

Usage

ACVT_HSWO_HFREE(t_k , s , p_{bar})

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_{bar}	pressure in bar

Value

ratio	Ratio H_{SWS}/H_{free}
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

Examples

ACVT_HSWO_HFREE($t_k=298, s=35, p_{bar}=0$)

ACVT_HTOT_O_HFREE *Conversion ratio H_Tot/H_free from free pH-scale to Total scale*

Description

Function returns the ratio H_Tot/H_free as a function of temperature, salinity and pressure

Usage

ACVT_HTOT_O_HFREE(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Value

ratio	Ratio H_Tot/H_free
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

Examples

ACVT_HTOT_O_HFREE(t_k=298,s=35, p_bar=0)

AK_AMMO_1_YAMI95 *Dissociation constant of ammonium in sea-water [mol/kg-SW]*

Description

Function returns the dissociation constant of ammonium in sea-water [mol/kg-SW]

Usage

AK_AMMO_1_YAMI95(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS

Value

KNH Dissociation constant of ammonium in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Yao and Millero (1995), Millero (1995) for pressure correction

Examples

AK_AMMO_1_YAMI95(t_k=298, s=35, p_bar=0)

AK_BORA_DICK90

Boric acid dissociation constant KB in mol/kg-SW

Description

Calculates boric acid dissociation constant in mol/kg-SW on the total pH-scale

Usage

AK_BORA_DICK90(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: Total

Value

KB Dissociation constant of boric acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Dickson (1990, eq. 23) – also Handbook (2007, eq. 37), Millero (1979) pressure correction

Examples

AK_BORA_DICK90(t_k=298, s=35, p_bar=0)

AK_CARB_0_WEIS74 *Henry's constant K0 in (mol/kg-SW)/atmosphere*

Description

Calculates Henry's constant (K0) based on Weiss (1979) formulation

Usage

AK_CARB_0_WEIS74(t_k, s)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu

Details

currently no pressure correction

Value

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

Guy Munhoven and Jean-Marie Epitalon

References

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

Examples

AK_CARB_0_WEIS74(t_k=298, s=35)

AK_CARB_1_LUEK00	<i>First dissociation constant of carbonic acid in mol/kg-SW from Luecker et al.</i>
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Description

Calculates first dissociation constant of carbonic acid in mol/kg-SW on the total pH-scale, following Luecker et al. (2000)

Usage

AK_CARB_1_LUEK00(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: Total

Value

K1	First dissociation constant of carbonic acid in mol/kg-SW
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Luecker et al. (2000) – also Handbook (2007), Millero (1979) pressure correction

Examples

AK_CARB_1_LUEK00(t_k=298, s=35, p_bar=0)

AK_CARB_1_MILL95	<i>First dissociation constant of carbonic acid in mol/kg-SW from Millero et al. (1995)</i>
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Description

Calculates first dissociation constant of carbonic acid in mol/kg-SW on the SWS pH-scale.

Usage

AK_CARB_1_MILL95(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS

Value

K1	First dissociation constant of carbonic acid in mol/kg-SW
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Millero (1995, eq 50 – ln K1(COM)), Millero (1982) pressure correction

Examples

AK_CARB_1_MILL95(t_k=298, s=35, p_bar=0)

AK_CARB_1_ROYE93	<i>First dissociation constant of carbonic acid in mol/kg-SW, from Roy et al.</i>
------------------	---

Description

Calculates first dissociation constant of carbonic acid in mol/kg-SW on the total pH-scale, following Roy et al. (1993)

Usage

AK_CARB_1_ROYE93(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: Total

Value

K1	First dissociation constant of carbonic acid in mol/kg-SW
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Roy et al. (1993) – also Handbook (1994), Millero (1979) pressure correction

Examples

AK_CARB_1_ROYE93(t_k=298, s=35, p_bar=0)

AK_CARB_2_LUEK00	<i>Second dissociation constant of carbonic acid in mol/kg-SW from Luecker et al.</i>
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Description

Calculates second dissociation constant of carbonic acid in mol/kg-SW on the total pH-scale, following Luecker et al. (2000)

Usage

AK_CARB_2_LUEK00(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: Total

Value

K2 Second dissociation constant of carbonic acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Luecker et al. (2000) – also Handbook (2007), Millero (1979) pressure correction

Examples

AK_CARB_2_LUEK00(t_k=298, s=35, p_bar=0)

AK_CARB_2_MILL95 *Second dissociation constant of carbonic acid in mol/kg-SW from Millero et al. (1995)*

Description

Calculates second dissociation constant of carbonic acid in mol/kg-SW on the SWS pH-scale.

Usage

AK_CARB_2_MILL95(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS

Value

K2 Second dissociation constant of carbonic acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Millero (1995, eq 51 – ln K2(COM)), Millero (1979) pressure correction

Examples

AK_CARB_2_MILL95(t_k=298, s=35, p_bar=0)

AK_CARB_2_ROYE93	<i>Second dissociation constant of carbonic acid in mol/kg-SW from Roy et al.</i>
------------------	---

Description

Calculates second dissociation constant of carbonic acid in mol/kg-SW on the total pH-scale, following Roy et al. (1993)

Usage

AK_CARB_2_ROYE93(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: Total

Value

K2 Second dissociation constant of carbonic acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Roy et al. (1993) – also Handbook (1994), Millero (1979) pressure correction

Examples

AK_CARB_2_ROYE93(t_k=298, s=35, p_bar=0)

AK_H2S_1_MILL95

Dissociation constant of hydrogen sulfide in sea-water

Description

Function returns the dissociation constant of hydrogen sulfide in sea-water

Usage

```
AK_H2S_1_MILL95(t_k, s, p_bar)
```

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS (according to Yao and Millero, 1995, p. 82: "refitted if necessary")

Total (according to Lewis and Wallace, 1998)

We stick to SWS here for the time being

The fits from Millero (1995) and Yao and Millero (1995) derive from Millero et al. (1988), with all the coefficients multiplied by $-\ln(10)$

Value

KHS	Dissociation constant of hydrogen sulfide in mol/kg-SW
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Millero et al. (1988) (cited by Millero (1995), Millero (1995) for pressure correction

Examples

```
AK_H2S_1_MILL95(t_k=298,s=35, p_bar=0)
```

AK_HF_PEFR87 *Dissociation constant of hydrogen fluoride in sea-water [mol/kg-SW]*

Description

Function returns the dissociation constant of hydrogen fluoride [mol/kg-SW]

Usage

AK_HF_PEFR87(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: Total (according to Handbook, 2007)

Value

KHF	Dissociation constant of hydrogen fluoride in mol/kg-SW
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Perez and Fraga (1987), Millero (1995) for pressure correction

Examples

AK_HF_PEFR87(t_k=298, s=35, p_bar=0)

AK_HSO4_DICK90

Dissociation constant of hydrogen sulfate (bisulfate) in sea-water

Description

Function returns the dissociation constant of hydrogen sulfate [mol/kg-SW]

Usage

AK_HSO4_DICK90(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: Total (according to Handbook, 2007)

Value

KSO	Dissociation constant of hydrogen sulfate in mol/kg-SW
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Dickson (1990) – also Handbook (2007), Millero (1995) for pressure correction

Examples

AK_HSO4_DICK90(t_k=298, s=35, p_bar=0)

AK_PHOS_1_MILL95 *First dissociation constant of phosphoric acid (H₃PO₄) in seawater*

Description

Calculates first dissociation constant of phosphoric acid on the SWS pH-scale

Usage

AK_PHOS_1_MILL95(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS

Value

KP1 First dissociation constant of phosphoric acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Yao and Millero (1995), Millero (1995) for pressure correction

Examples

AK_PHOS_1_MILL95(t_k=298, s=35, p_bar=0)

AK_PHOS_2_MILL95 *Second dissociation constant of phosphoric acid (H₃PO₄) in seawater*

Description

Calculates second dissociation constant of phosphoric acid on the SWS pH-scale

Usage

AK_PHOS_2_MILL95(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS

Value

KP2 Second dissociation constant of phosphoric acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Yao and Millero (1995), Millero (1995) for pressure correction

Examples

AK_PHOS_2_MILL95(t_k=298, s=35, p_bar=0)

AK_PHOS_3_MILL95 *Third dissociation constant of phosphoric acid (H₃PO₄) in seawater*

Description

Calculates third dissociation constant of phosphoric acid on the SWS pH-scale

Usage

AK_PHOS_3_MILL95(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS

Value

KP3 Third dissociation constant of phosphoric acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Yao and Millero (1995), Millero (1995) for pressure correction

Examples

AK_PHOS_3_MILL95(t_k=298, s=35, p_bar=0)

AK_SILI_1_MILL95 *First dissociation constant of sillicic acid (H4SiO4) in seawater*

Description

Calculates first dissociation constant of sillicic acid on the SWS pH-scale

Usage

AK_SILI_1_MILL95(t_k, s)

Arguments

t_k temperature in Kelvin

s Salinity in psu

Details

pH scale: SWS (according to Dickson et al, 2007)

No pressure correction available

Value

KSi First dissociation constant of sillicic acid in mol/kg-SW

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Yao and Millero (1995) cited by Millero (1995)

Examples

AK_SILI_1_MILL95(t_k=298, s=35)

AK_W_MILL95	<i>Water dissociation constant Kw in (mol/kg-SW)^2</i>
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Description

Calculates water dissociation constant Kw in (mol/kg-SW)² on the SWS pH-scale

Usage

AK_W_MILL95(t_k, s, p_bar)

Arguments

t_k	temperature in Kelvin
s	Salinity in psu
p_bar	pressure in bar

Details

pH scale: SWS

Value

Kw	Dissociation constant of water in (mol/kg-SW) ²
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Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

Millero (1995) for value at p_bar = 0, Millero (pers. comm. 1996) for pressure correction

Examples

AK_W_MILL95(t_k=298, s=35, p_bar=0)

solve_pH_from_AT *Solver for the total alkalinity-pH equations*

Description

Determines [H+] from Total alkalinity and dissolved total elements in sea water. Universal and robust algorithm from Munhoven (2013) with Newton- Raphson iterations

Usage

```
solve_pH_from_AT(p_alktot, p_dicvar, p_bortot, p_po4tot, p_siltot,
                 p_nh4tot, p_h2stot, p_so4tot, p_flutot, p_pHscale, p_dicsel,
                 p_askVal=FALSE, p_dissoc, p_temp=18, p_sal=35, p_pres=0, p_hini)
```

Arguments

p_alktot	Total alkalinity (mol/kg)
p_dicvar	Value of a carbonate system related variable : DIC, [CO2*], [HCO3-] or [CO3-] (mol/kg) See below parameter p_dicsel
p_bortot	Total boron concentration (mol/kg)
p_po4tot	Total phosphate concentration (mol/kg)
p_siltot	Total silicate concentration (mol/kg)
p_nh4tot	Total ammonia concentration (mol/kg)
p_h2stot	Total sulfide concentration (mol/kg)
p_so4tot	Total sulphate concentration (mol/kg)
p_flutot	Total fluor concentration (mol/kg)
p_pHscale	Chosen pH scale: "T" for the total scale, "F" for the free scale and "SWS" for using the seawater scale
p_dicsel	Carbonate variable selector (default = DIC). See parameter p_dicvar above. Values are: "DIC" : p_dicvar = DIC (Dissolved Inorganic Carbon) "CO2" : p_dicvar = [CO2*] "HCO3" : p_dicvar = [HCO3-] "CO3" : p_dicvar = [CO3-]
p_askVal	Optional boolean - set to TRUE if you want this function to return error on alkalinity, along with [H+] concentration value. Default is FALSE
p_dissoc	Named list of all dissociation constants. The list is optional but, if given, it should contain all members listed below excepted K2_Sil, which is itself optional. Member names are : K1_DIC : First dissociation constant of carbonic acid (mol/kg) on chosen scale

	K2_DIC : Second dissociation constant of carbonic acid (mol/kg) on chosen scale
	K_BT : Dissociation constant of boric acid (mol/kg) on chosen scale
	K1_PO4 : First dissociation constant of phosphoric acid (mol/kg) on chosen scale
	K2_PO4 : Second dissociation constant of phosphoric acid (mol/kg) on chosen scale
	K3_PO4 : third dissociation constant of phosphoric acid (mol/kg) on chosen scale
	K_Sil : First dissociation constant of sillicic acid (mol/kg) on chosen scale
	K2_Sil : Second dissociation constant of sillicic acid (mol/kg) on chosen scale. It is optional. If K2_Sil is absent from the list, then SiO2(OH)2 ion is not considered in the alkalinity equation. Only SiO(OH)3 ion is.
	K_NH4 : Dissociation constant of ammonium (mol/kg) on chosen scale
	K_H2S : Dissociation constant of hydrogen sulfide (mol/kg) on chosen scale
	K_HSO4 : Dissociation constant of hydrogen sulfate (mol/kg) on free scale
	K_HF : Dissociation constant of hydrogen fluoride (mol/kg) on free scale
	K_H2O : Dissociation constant of water (mol/kg) on chosen scale
	Note that all dissociation constants shall be expressed in chosen pH scale except K_HF and K_HSO4 which shall be in free scale.
	If the list is not given, these constants, excepted K2_Sil, will be calculated.
p_temp	Temperature in degree Celsius, to compute dissociation constants when p_dissoc is not given
p_sal	Salinity, in practical salinity unit (psu), to compute dissociation constants when p_dissoc is not given
p_pres	Pressure, in bars, to compute dissociation constants when p_dissoc is not given
p_hini	Optional initial value of [H+] concentration If p_dicse1 = "CO3", a vector of two initial values are expected since there may be two solutions for pH. Else, one initial value is expected

Details

Formulations used when calculating dissociation constants:

- Carbonate if Total pH scale: Luecker et al. (2000) – also Handbook (2007)
- Carbonate if SWS or Free pH scale: Millero et al. (1995) – also Handbook (2007)
- Boric acid: Dickson (1990, eq. 2 3) – also Handbook (2007, eq. 37)
- Phosphoric acid: Yao and Millero (1995)
- Silicic acid: Yao and Millero (1995) cited by Millero (1995)
- Ammonium: Yao and Millero (1995)
- Hydrogen sulfide: Millero et al. (1988) (cited by Millero (1995))
- Hydrogen sulfate: Dickson (1990) – also Handbook (2007)
- Fluoric acid if Total pH scale: Perez and Fraga (1987)

- Fluoric acid if SWS or Free pH scale: Dickson and Riley (1979)
- Water: Millero (1995)

This function does not support vectors as arguments, only scalar values.

Value

If `p_dicssel` is "CO3", there may be one or two solutions for [H+], else there is only one. In case there are two solutions, both are returned.

- If you set `p_askVal` to TRUE, the function returns a data frame containing the following columns:
 - zh : [H+] concentration value(s) in the chosen pH scale
 - val : Error(s) on total alkalinity, that is the deviation between total alkalinity calculated from [H+] and given total alkalinity
- If you set `p_askVal` to FALSE (default), the function returns only [H+] concentration value(s) in the chosen pH scale.

Author(s)

Guy Munhoven and Jean-Marie Epitalon

References

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

Examples

```
## Compute [H+] from Alkalinity total and DIC, on total pH scale
p_dissoc <- list()
p_dissoc$K1_DIC <- 1.421828e-06
p_dissoc$K2_DIC <- 1.081555e-09
p_dissoc$K_BT <- 2.526573e-09
p_dissoc$K1_P04 <- 0.02408434
p_dissoc$K2_P04 <- 1.076024e-06
p_dissoc$K3_P04 <- 1.600484e-09
p_dissoc$K_Sil <- 4.071935e-10
p_dissoc$K_NH4 <- 5.380823e-10
p_dissoc$K_H2S <- 3.087264e-07
p_dissoc$K_HS04 <- 0.1003021 # on free scale
p_dissoc$K_HF <- 0.00176441 # on free scale
p_dissoc$K_H2O <- 5.97496e-14
solve_pH_from_AT(p_alktot=2.5e-3, p_dicvar=2e-3, p_bortot=0.0004157, p_po4tot=0, p_siltot=0,
  p_nh4tot=0, p_h2stot=0, p_so4tot=0.0282, p_flutot=6.832e-05, p_pHscale="T",
  p_dicssel="DIC", p_dissoc=p_dissoc)

## Giving initial [H+] value and asking for final error on alkalinity, on seawater pH scale
result <- solve_pH_from_AT(p_alktot=0.00234, p_dicvar=0.001936461, p_bortot=0.0004157, p_po4tot=0,
```

```
        p_siltot=0, p_nh4tot=0, p_h2stot=0, p_so4tot=0.0282, p_flutot=6.832e-05,
        p_pHscale="SWS",p_dicsel="DIC", p_dissoc=p_dissoc, p_askVal=TRUE, p_hini=1.e-8)
H <- result$zh
error <- result$val

## Compute [H+] from Alkalinity total and CO3, on total free scale
H <- solve_pH_from_AT(p_alktot=0.00240, p_dicvar=2.775481e-04, p_bortot=0.0004157, p_po4tot=0,
        p_siltot=0, p_nh4tot=0, p_h2stot=0, p_so4tot=0.0282, p_flutot=6.832e-05,
        p_pHscale="F", p_dicsel="CO3", FALSE, p_dissoc=p_dissoc)
H1 <- H[1]
if (H[2] != 1) print ( c("Second solution : ", H[2]))
```

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