Package 'SolveSAPHE'

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Title Solver Suite for Alkalinity-PH Equations

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Imports stats

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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R topics documented:

ACVT_HSWS_O_HFREE *Conversion ratio H_SWS/H_free from free pH-scale to SWS scale*

Description

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

Usage

```
ACVT_HSWS_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_SWS/H_free

Author(s)

Guy Munhoven and Jean-Marie Epitalon

Examples

```
ACVT_HSWS_O_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

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)

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 *First dissociation constant of carbonic acid in mol/kg-SW from Luecker et al.*

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

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

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

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 *First dissociation constant of carbonic acid in mol/kg-SW, from Roy et al.*

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

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 *Second dissociation constant of carbonic acid in mol/kg-SW from Luecker et al.*

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 *Second dissociation constant of carbonic acid in mol/kg-SW from Roy et al.*

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

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

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

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 *Water dissociation constant Kw in (mol/kg-SW)^2*

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

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 pratical salinty 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_dicsel = "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_dicsel 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_PO4 <- 0.02408434
p_dissoc$K2_PO4 <- 1.076024e-06
p_dissoc$K3_PO4 <- 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_HSO4 <- 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_dicsel="DIC", p_dissoc=p_dissoc)

## Giving inital [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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