MIKE ECO Lab

pH Calculation

Scientific Documentation

PLEASE NOTE

COPYRIGHT

This document refers to proprietary computer software, which is protected by copyright. All rights are reserved. Copying or other reproduction of this manual or the related programmes is prohibited without prior written consent of DHI. For details please refer to your 'DHI Software Licence Agreement'.

LIMITED LIABILITY

The liability of DHI is limited as specified in your DHI Software License Agreement:

In no event shall DHI or its representatives (agents and suppliers) be liable for any damages whatsoever including, without limitation, special, indirect, incidental or consequential damages or damages for loss of business profits or savings, business interruption, loss of business information or other pecuniary loss arising in connection with the Agreement, e.g. out of Licensee's use of or the inability to use the Software, even if DHI has been advised of the possibility of such damages.

This limitation shall apply to claims of personal injury to the extent permitted by law. Some jurisdictions do not allow the exclusion or limitation of liability for consequential, special, indirect, incidental damages and, accordingly, some portions of these limitations may not apply.

Notwithstanding the above, DHI's total liability (whether in contract, tort, including negligence, or otherwise) under or in connection with the Agreement shall in aggregate during the term not exceed the lesser of EUR 10,000 or the fees paid by Licensee under the Agreement during the 12 months' period previous to the event giving rise to a claim.

Licensee acknowledge that the liability limitations and exclusions set out in the Agreement reflect the allocation of risk negotiated and agreed by the parties and that DHI would not enter into the Agreement without these limitations and exclusions on its liability. These limitations and exclusions will apply notwithstanding any failure of essential purpose of any limited remedy.

CONTENTS

MIKE ECO Lab
pH Calculations
Scientific Documentation

APPENDICES

APPENDIX A – Chemical and physical parameters
Literature values and estimations

1 Introduction

MIKE ECO Lab provides a series of functions to calculate pH and related chemical properties. This document describes the calculations behind these functions. The functions are:

$$\text{pH} = \text{SOLVE\_PH}(A_{tot}, \gamma_C, sal, t, d, \gamma_P, \gamma_{Si})$$

$$[\text{OH}^-] = \text{CONC\_OH}(\text{pH}, sal, t, d)$$

$$[\text{H}^+]_{Free} = \text{CONC\_H\_FREE}(\text{pH}, sal, t, d)$$

$$\gamma_{C\{CO_2\}} = \text{CONC\_CO2}(\gamma_C, \text{pH}, sal, t, d)$$

$$\gamma_{C\{HCO_3\}} = \text{CONC\_HCO3}(\gamma_C, \text{pH}, sal, t, d)$$

$$\gamma_{C\{CO_3\}} = \text{CONC\_CO3}(\gamma_C, \text{pH}, sal, t, d)$$

$$fug_{CO_2} = \text{FUGACITY\_CO2}(\gamma_C, \text{pH}, sal, t, d)$$

$$p_{CO_2} = \text{PP\_CO2}(\gamma_C, \text{pH}, sal, t, d)$$

$$Flux_{CO_2} = \text{FLUX\_CO2}(p_{CO_2}^{air}, p_{CO_2}^{water}, sal, t, u_{10})$$

The input and output values are:

pH	pH value
$[\text{OH}^-]$	concentration of hydroxide in $\mu\text{mol/kg-sw}$
$[\text{H}^+]_{Free}$	concentration of free hydrogen ions in $\mu\text{mol/kg-sw}$
$\gamma_{C\{CO_2\}}$	carbon mass concentration of CO_2 in mg/L
$\gamma_{C\{HCO_3\}}$	carbon mass concentration of HCO_3 in mg/L
$\gamma_{C\{CO_3\}}$	carbon mass concentration of CO_3 in mg/L
fug_{CO_2}	equilibrium fugacity of CO_2 in Pa
p_{CO_2}	equilibrium partial pressure of CO_2 in Pa
$Flux_{CO_2}$	CO_2 flux in $\text{g-C/(m}^2\text{ d)}$
sal	salinity of water in psu
t	water temperature in $°\text{C}$
d	water depth in m
γ_C	total carbon concentration in mg/L
γ_P	total phosphorus concentration in mg/L
γ_{Si}	total silicon concentration in mg/L
A_{tot}	alkalinity in $\mu\text{mol/kg-sw}$
$p_{CO_2}^{water}$	partial pressure of CO_2 in water in Pa
$p_{CO_2}^{air}$	partial pressure of CO_2 in air in Pa
u_{10}	average wind speed 10m above water surface in m/s

Except for the function FLUX_CO2, the pH calculation functions in MIKE ECO Lab are based on the CO2SYS Program **Error! Reference source not found.**. The functions do not replicate the CO2SYS Program **Error! Reference source not found.**, but the calculations behind the functions use the equation system from the CO2SYS Program **Error! Reference source not found.**. This equation system is described in detail in c

hapters 3-5. For some of the input/output arguments the MIKE ECO Lab functions use other units than the CO2SYS Program **Error! Reference source not found.**. This n ecessitates some conversions, which are described in chapter 2. MIKE ECO Lab offers the same settings as the CO2SYS Program **Error! Reference source not found.**. These s ettings and their effects on the calculations are the topic of chapter 6. The calculations for the FLUX_CO2 function are based on Wanninkhof (2014) /4/, see chapter 7.

2 Conversion of input and output

Some of the input arguments for the MIKE ECO Lab functions must be converted before they are ready to be used in the calculations. Similarly, some of the results are converted before they are returned. The conversions of alkalinity, fugacity and partial pressure are simple unit conversions. The conversions of concentrations and between water depth and hydrostatic pressure, however, are more complicated.

2.1 Alkalinity

The calculations use $\mathrm{mol/kg\text{-}sw}$ for alkalinity A_{tot} whereas the MIKE ECO Lab functions use $\mathrm{\mu mol/kg\text{-}sw}$ for input/output values of alkalinity. (The CO2SYS Program **Error! R eference source not found.** also uses $\mathrm{\mu mol/kg\text{-}sw}$ for input/output values of alkalinity.) The unit conversion for alkalinity follows the rule

$$1\ \frac{\mu\mathrm{mol}}{\mathrm{kg\text{-}sw}} = 10^{-6}\frac{\mathrm{mol}}{\mathrm{kg\text{-}sw}}. \tag{2.1}$$

2.2 Concentrations

The calculations use molal concentrations in $\mathrm{mol/kg\text{-}sw}$ for all chemical species, whereas the input/output for MIKE ECO Lab functions use either molal concentration in $\mathrm{\mu mol/kg\text{-}sw}$ or mass concentrations in $\mathrm{mg/L}$. (The CO2SYS Program **Error! Reference s ource not found.** uses molal concentrations in $\mathrm{\mu mol/kg\text{-}sw}$ for input/output.) The MIKE ECO Lab functions return the
molal concentrations $[\mathrm{OH^-}]$ and $[\mathrm{H^+}]_{Free}$ in $\mathrm{\mu mol/kg\text{-}sw}$. Their unit is converted according to eq. (2.1). The MIKE ECO Lab functions take the mass concentrations γ_C, γ_P and γ_{Si} of total carbon, total phosphorus and total silicon as input in $\mathrm{mg/L}$ and convert them to their molal concentrations C_{tot}, P_{tot} and Si_{tot}. The molal concentrations $[\mathrm{CO_2^*}]$, $[\mathrm{HCO_3^-}]$ and $[\mathrm{CO_3^{2-}}]$ are converted to carbon mass concentrations $\gamma_{C\{CO_2\}}$, $\gamma_{C\{HCO_3\}}$ and $\gamma_{C\{CO_3\}}$ in $\mathrm{mg/L}$ before they are returned by the MIKE ECO Lab functions.

The concentration of a species X can be represented as a mass concentration γ_X expressing species mass per solution volume, a molar concentration c_X expressing species amount per solution volume or a molal concentration b_X expressing species amount per solution mass. The mass and molar concentrations are related by the molar mass M_X of the species:

$$\gamma_X = c_X\,M_X. \tag{2.2}$$

The molar and molal concentrations are related by the density ρ_{sol} of the solution:

$$c_X = b_X\,\rho_{sol}. \tag{2.3}$$

Combining eqs. (2.2)-(2.3) gives a relation between molal and mass concentrations:

$$\gamma_X = b_X\,M_X\,\rho_{sol}. \tag{2.4}$$

Rewriting the equation to convert the other way gives:

$$b_X = \frac{\gamma_X}{M_X\,\rho_{sol}}. \tag{2.5}$$

For eqs. (2.4)-(2.5), if the molar mass M_X is in $\mathrm{g/mol}$, the density ρ_{sol} is in $\mathrm{kg\text{-}sw/m^3}$ and the molal concentration b_X is in $\mathrm{mol/kg\text{-}sw}$, then the mass concentration γ_X will be in $\mathrm{g/m^3}$, which is equivalent to $\mathrm{mg/L}$ (since $1\mathrm{g} = 1000\mathrm{mg}$ and $1\mathrm{m^3} = 1000\mathrm{L}$).

In the calculations, the notations X_{tot} and $[X]$ both represent molal concentrations b_X of species X. The mass concentrations of total carbon, total phosphorus and total silicon are converted to their molal concentrations using

$$C_{tot} = \frac{\gamma_C}{M_C\,\rho_{sol}}, \tag{2.6}$$

$$P_{tot} = \frac{\gamma_P}{M_P\,\rho_{sol}}, \tag{2.7}$$

$$Si_{tot} = \frac{\gamma_{Si}}{M_{Si}\,\rho_{sol}}. \tag{2.8}$$

The concentrations $\gamma_{C\{CO_2\}}$, $\gamma_{C\{HCO_3\}}$ and $\gamma_{C\{CO_3\}}$ represent the mass concentrations of CO_2, HCO_3 and CO_3, but only counting the mass of carbon. Since each of these molecules has one carbon atom, this corresponds to using M_C in eq. (2.4).

$$\gamma_{C\{CO_2\}} = [CO_2^*]\,M_C\,\rho_{sol} \tag{2.9}$$

$$\gamma_{C\{HCO_3\}} = [HCO_3^-]\,M_C\,\rho_{sol} \tag{2.10}$$

$$\gamma_{C\{CO_3\}} = [CO_3^{2-}]\,M_C\,\rho_{sol} \tag{2.11}$$

The concentration conversions require the solution density ρ_{sol} and the molar mass M_X of the species. The density of seawater is calculated from salinity sal and temperature t using the MIKE ECO Lab function GET_WATER_DENSITY:

$$\rho_{sol} = GET\_WATER\_DENSITY(sal, t). \tag{2.12}$$

This has the unit $\mathrm{kg/m^3}$. The molar masses are listed in appendix A.1.

2.3 Depth and hydrostatic pressure

The calculations use the hydrostatic pressure p in bar. (The CO2SYS Program **Error! R eference source not found.** uses dbar for input values of hydrostatic pressure.) The MIKE ECO Lab functions take the water depth d in m as input and use this to derive the hydrostatic pressure. The hydrostatic pressure p at a given water depth d depends on the additional parameters, salinity sal and temperature t.

The depth is converted to pressure using the calculations behind the MIKE ECO Lab function GET_DEPTH_PRESSURE, see reference manual. The GET_DEPTH_PRESSURE function calculates the total pressure in bar from water depth d in m, salinity sal in psu and temperature t in $°C$. The total pressure is calculated as the sum of the hydrostatic pressure and the atmospheric pressure (approximately $1\mathrm{bar}$). Therefore, the hydrostatic pressure in bar corresponds to

$$p = GET\_DEPTH\_PRESSURE(d, sal, t) - 1. \tag{2.13}$$

2.4　Fugacity and partial pressure

The calculations use atm for fugacity fug_{CO_2} and partial pressures p_{CO_2}, $p_{CO_2}^{water}$, $p_{CO_2}^{air}$. The MIKE ECO Lab functions use Pa for input/output values of these pressures. (The CO2SYS Program uses $\mathrm{\mu atm}$ for input/output values of fugacity and partial pressure.) The unit conversion between pressure in Pa and in atm is given by

$$1\ \mathrm{atm} = 101\,325\ \mathrm{Pa}. \tag{2.14}$$

3 Equation system

The equation system for the pH calculations is based on carbon chemistry and a description of alkalinity. It is assumed that the chemical reactions of the system are in equilibrium, which allows the use of equilibrium equations. Many of the parameters for the equations are calculated from physical conditions, such as salinity, temperature and pressure. The pH value enters the equations through the hydrogen ion concentration as pH is defined directly from $[\text{H}^+]$, see section 4 on pH scales.

3.1 Carbon equations

This section presents the chemistry of CO_2 dissolved in water. For a more detailed description, see the PICES Guide /1/ (Ch. 2), which is the basis for this section. In equilibrium, the reactions for CO_2 can be described with the following set of equations (PICES Guide /1/):

$$K_0 = \frac{[\text{CO}_2^*]}{fug_{CO_2}} \tag{3.1}$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2^*]} \tag{3.2}$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \tag{3.3}$$

On the left-hand sides are the equilibrium constants K_0, K_1 and K_2; K_0 is the solubility coefficient of carbon dioxide, and K_1, K_2 are the dissociation constants for carbonic acid. On the right-hand sides are expressions with the concentrations of chemical species and the fugacity fug_{CO_2} of carbon dioxide. The concentration $[\text{CO}_2^*]$ represents the sum of $[\text{CO}_2]$ and $[\text{H}_2\text{CO}_3]$, which is common practice (PICES Guide /1/). An additional expression is obtained by writing the mass conservation equation (PICES Guide /1/):

$$C_{tot} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}], \tag{3.4}$$

where C_{tot} is the total dissolved inorganic carbon (DIC).

These equations are rewritten to express fugacity and the carbon species in terms of the total carbon C_{tot}, the hydrogen ion concentration $[\text{H}^+]$ and the equilibrium constants K_0, K_1, K_2:

$$fug_{CO_2} = C_{tot} \frac{1}{K_0} \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1\,[\text{H}^+] + K_1\,K_2} \tag{3.5}$$

$$[\text{CO}_2^*] = C_{tot} \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1\,[\text{H}^+] + K_1\,K_2} \tag{3.6}$$

$$[\text{HCO}_3^-] = C_{tot} \frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + K_1\,[\text{H}^+] + K_1\,K_2} \tag{3.7}$$

$$[\text{CO}_3^{2-}] = C_{tot} \frac{K_1 K_2}{[\text{H}^+]^2 + K_1\,[\text{H}^+] + K_1\,K_2} \tag{3.8}$$

The carbon alkalinity is defined in equation (3.12) as $A_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$ and this can be written as

$$A_C = C_{tot} \frac{K_1([\text{H}^+] + 2\,K_2)}{[\text{H}^+]^2 + K_1\,[\text{H}^+] + K_1\,K_2} \,. \tag{3.9}$$

The equilibrium constants K_0, K_1 and K_2 depend on salinity, temperature and pressure and are calculated as described in chapter 5. The values of K_1 and K_2 are calculated with respect to the pH scale chosen in options. This implies, the above equations apply to $[\text{H}^+]$ on this scale; that is, $[\text{H}^+]$ refers to $[\text{H}^+]_{opt}$. When the equilibrium constants and the total carbon C_{tot} are given, the only unknown on the right-hand sides of eqs. (3.5)-(3.9) is the hydrogen ion concentration $[\text{H}^+]_{opt}$.

3.1.1 Fugacity and partial pressure

The fugacity of a gas is an effective partial pressure that accounts for non-ideal effects of the gas. The fugacity fug_i of a gas i is related to the partial pressure p_i through a fugacity coefficient φ_i; for carbon dioxide: This is written

$$fug_{CO_2} = \varphi_{CO_2}\, p_{CO_2}. \tag{3.10}$$

The fugacity coefficient φ_{CO_2} is dimensionless and depends on temperature. It is estimated in appendix A.3.1.

3.2 Alkalinity expression

The alkalinity A_{tot} is expressed as a sum of species concentrations. The terms in the alkalinity expression varies with the **Set of constants** setting. (See chapter 6 for more information on settings.)

3.2.1 Set of constants: 1-5, 9-14 Standard

The standard expression for alkalinity is defined according to the CO2SYS Program **Error! Reference source not found.** as:

$$A_{tot} = A_C + A_P + A_{Si} + A_B + [\text{OH}^-] - [\text{H}^+]_{Free} - [\text{HSO}_4^-] - [\text{HF}] \tag{3.11}$$

where, A_C is the carbon alkalinity, A_P is the phosphorus alkalinity, A_{Si} is the silicon alkalinity and A_B is the boron alkalinity. The various terms are defined as:

$$A_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \tag{3.12}$$

$$A_P = 2[\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] - [\text{H}_3\text{PO}_4] \tag{3.13}$$

$$A_{Si} = [\text{SiO(OH)}_3^-] \tag{3.14}$$

$$A_B = [\text{B(OH)}_4^-] \tag{3.15}$$

Additionally, $[\text{H}^+]_{Free}$ denotes the concentration of free hydrogen ions.

3.2.2 Set of constants: 6 GEOSECS

Following the calculations in the CO2SYS Program **Error! Reference source not found.**, the GEOSECS alkalinity is expressed as

$$A_{tot}^{GEOSECS} = A_C + A_B^{GEOSECS} - [\text{H}^+]_{Free} - [\text{HSO}_4^-] - [\text{HF}]. \tag{3.16}$$

where

$$A_B^{GEOSECS} = [\text{H}_2\text{BO}_3^-]. \tag{3.17}$$

Note that in the documentation to the CO2SYS Program **Error! Reference source not found.**, the GEOSECS alkalinity is reported as in eq. (3.16), but without the terms $[\text{H}^+]_{Free}$, $[\text{HSO}_4^-]$ and $[\text{HF}]$. This is also consistent with the alkalinity used in Takahashi et al. /39/. However, the additional terms should be negligible for sufficiently small hydrogen ion concentrations, see the discussion in section 3.3.2.

3.2.3 Set of constants: 7 Peng

Following the calculations in the CO2SYS Program **Error! Reference source not found.**, the Peng alkalinity is expressed as

$$A_{tot}^{Peng} = A_C + A_P^{Peng} + A_{Si}^{Peng} + A_B^{Peng} + [\text{OH}^-] - [\text{H}^+]_{Free} - [\text{HSO}_4^-] - [\text{HF}]. \tag{3.18}$$

where

$$A_P^{Peng} = 3[\text{PO}_4^{3-}] + 2[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-], \tag{3.19}$$

$$A_{Si}^{Peng} = [\text{H}_3\text{SiO}_4^-], \tag{3.20}$$

$$A_B^{Peng} = A_B^{GEOSECS} = [\text{H}_2\text{BO}_3^-]. \tag{3.21}$$

The Peng expression for phosphorus alkalinity relates to standard expression (3.13) as

$$A_P^{Peng} = A_P + P_{tot}, \tag{3.22}$$

where P_{tot} is the total phosphorus concentration, see eq. (3.32).

Note, the alkalinity expression in Peng et al. (1987) /34/ is defined as in eq. (3.18), but without the terms $[\text{HSO}_4^-]$ and $[\text{HF}]$. Again, the deviating terms are supposedly small.

3.2.4 Set of constants: 8 Freshwater

Following the calculations in the CO2SYS Program **Error! Reference source not found.**, the freshwater alkalinity is expressed as

$$A_{tot}^{Freshwater} = A_C + [\text{OH}^-] - [\text{H}^+]_{Free}. \tag{3.23}$$

3.3 Alkalinity terms

The derivation of the alkalinity terms follows the PICES Guide /1/, and the resulting equations are equivalent with the CO2SYS Program **Error! Reference source not f ound.**. The various alkalinity terms can be rewritten using equilibrium equations for the reactions and mass conservation equations. This has already been done for the carbon alkalinity A_C, resulting in equation (3.9). The other alkalinity terms can be rewritten in a similar way. For the standard alkalinity expression, the equilibrium equations for the relevant reactions are as below (PICES Guide /1/):

$$K_{P1} = \frac{[\text{H}^+]\,[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \tag{3.24}$$

$$K_{P2} = \frac{[\text{H}^+]\,[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \tag{3.25}$$

$$K_{P3} = \frac{[\text{H}^+]\,[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \tag{3.26}$$

$$K_{Si} = \frac{[\text{H}^+][\text{SiO(OH)}_3^-]}{[\text{Si(OH)}_4]} \tag{3.27}$$

$$K_B = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]} \tag{3.28}$$

$$K_W = [\text{H}^+][\text{OH}^-] \tag{3.29}$$

$$K_S = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \tag{3.30}$$

$$K_F = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} \tag{3.31}$$

On the left-hand sides are dissociation constants, and on the right-hand sides are the concentrations of the reacting species. The mass conservation equations for total phosphorus P_{tot}, total silicon Si_{tot}, total boron B_{tot}, total sulphur S_{tot} and total fluorine F_{tot} are as below (PICES Guide /1/):

$$P_{tot} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \tag{3.32}$$

$$Si_{tot} = [\text{Si(OH)}_4] + [\text{SiO(OH)}_3^-] \tag{3.33}$$

$$B_{tot} = [\text{B(OH)}_3] + [\text{B(OH)}_4^-] \tag{3.34}$$

$$S_{tot} = [\text{HSO}_4^-] + [\text{SO}_4^{2-}] \tag{3.35}$$

$$F_{tot} = [\text{HF}] + [\text{F}^-] \tag{3.36}$$

The equilibrium equations and mass conservation equations are used to rewrite the terms (without carbon) in the standard alkalinity expression (3.11)-(3.15):

$$A_P = P_{tot}\,\frac{K_{P1}K_{P2}[\text{H}^+] + 2K_{P1}K_{P2}K_{P3} - [\text{H}^+]^3}{[\text{H}^+]^3 + K_{P1}[\text{H}^+]^2 + K_{P1}K_{P2}[\text{H}^+] + K_{P1}K_{P2}K_{P3}} \tag{3.37}$$

$$A_{Si} = Si_{tot} \frac{K_{Si}}{[\text{H}^+] + K_{Si}} \tag{3.38}$$

$$A_B = B_{tot} \frac{K_B}{[\text{H}^+] + K_B} \tag{3.39}$$

$$[\text{OH}^-] = \frac{K_W}{[\text{H}^+]} \tag{3.40}$$

$$[\text{HSO}_4^-] = S_{tot} \frac{[\text{H}^+]}{[\text{H}^+] + K_S} \tag{3.41}$$

$$[\text{HF}] = F_{tot} \frac{[\text{H}^+]}{[\text{H}^+] + K_F} \tag{3.42}$$

These expressions were derived according to the PICES Guide /1/ and correspond to the calculations in the CO2SYS Program **Error! Reference source not found.**.

The non-standard alkalinity terms are defined from the standard terms. The Peng expression for phosphorus alkalinity is calculated using eq. (3.13), repeated here:

$$A_P^{Peng} = A_P + P_{tot} \tag{3.43}$$

where the standard phosphorus alkalinity A_P is calculated according to eq. (3.37). The Peng expression for silicon alkalinity has the same form as the standard expression (3.38):

$$A_{Si}^{Peng} = A_{Si}. \tag{3.44}$$

The boron alkalinity used for GEOSECS and Peng has the same form as the standard expression (3.39):

$$A_B^{Peng} = A_B^{GEOSECS} = A_B. \tag{3.45}$$

Though these expressions use the standard expressions, they can yield different results as the non-standard cases use different estimates for the dissociation constants.

The alkalinity terms are now expressed as functions of the dissociation constants, the total concentration of species and the concentration of hydrogen ions. The total concentrations are determined from input arguments, see section 3.3.1. The dissociation constants depend on salinity, temperature and pressure and are calculated as described in section 5. This leaves $[\text{H}^+]$ as the only variable in the alkalinity terms.

3.3.1   Concentrations

The total concentrations in eqs. (3.32)-(3.36) are all resolved from input arguments. The concentrations for total boron B_{tot}, total sulphur S_{tot} and total fluorine F_{tot} are estimated from a typical composition of seawater. Hence, they are calculated from salinity sal, see appendix A.2. The concentrations for total phosphorus P_{tot} and total silicon Si_{tot} must be given directly as input.

3.3.2 Details of calculations

This section explains how the concept of different pH scales affects the calculation of alkalinity terms (3.37)-(3.42). Converting from one pH scale to another pH scale corresponds to changing the value of $[H^+]$. Since the dissociation constants in eqs. (3.24)-(3.31) are related to the H^+ concentration, they change with the pH scale. The pH scales are described in section 4, and the details of calculating dissociation constants are described in section 5. Most of the alkalinity terms are defined using a general notion of hydrogen ion concentration, $[H^+]$. The different values of $[H^+]$ corresponding to different pH scales are distinguished by a subscript; for example, $[H^+]_{opt}$ is the hydrogen ion concentration corresponding to the pH scale chosen in the settings.

The dissociation constants K_B, K_W, K_{P1}, K_{P2}, K_{P3} and K_{Si} are calculated with respect to the pH scale chosen in options. This implies that the hydrogen ion concentration in eqs. (3.37)- (3.40) must be on this scale; that is $[H^+]$ refers to $[H^+]_{opt}$. The dissociation constants K_F and K_S are calculated with respect to the free pH scale, and hence the H^+ concentration in eqs. (3.41)-(3.42) must be on the free scale; that is $[H^+]$ refers to $[H^+]_{Free}$.

The alkalinity terms using $[H^+]_{Free}$ are rewritten to be expressed in terms of $[H^+]_{opt}$ instead. The concentration $[H^+]_{Free}$ appears both as a separate alkalinity term and in the expressions (3.41)-(3.42). The H^+ concentration can be converted from the chosen scale to the free scale by multiplying a conversion factor:

$$[H^+]_{Free} = [H^+]_{opt} \, \text{pH}conv_{opt\ to\ Free}. \tag{3.46}$$

See section 4.5 for pH scale conversions. In accordance with the calculations from the CO2SYS Program **Error! Reference source not found.**, the conversion is instead c alculated as

$$[H^+]_{Free} = [H^+]_{opt} \, \text{pH}conv_{Total\ to\ Free} \tag{3.47}$$

regardless of the chosen scale. This conversion is used for all occurrences of $[H^+]_{Free}$ in the alkalinity terms. If the H^+ concentration is small, the terms using $[H^+]_{Free}$ are small compared to the other alkalinity terms. Therefore, the deviation in the conversion factor has no noticeable effect when it is used to calculate alkalinity. The CO2SYS Program **Error! Reference source not found.** has these comments for calculating alkalinity:

"*Though it is coded for H on the total pH scale, for the pH values occurring in seawater (pH > 6) it will be equally valid on any pH scale (H terms negligible) as long as the K constants are on that scale.*"

To summarize, the alkalinity terms in eqs. (3.37)-(3.42), and thereby also the non-standard alkalinity terms in eqs. (3.43)-(3.45), are all expressed using $[H^+]_{opt}$ for the H^+ concentration.

3.4 Solve equations

The MIKE ECO Lab functions based on the CO2SYS Program are calculated using the equation system described in this chapter. Conversion of input and output arguments are not considered here; they are discussed in chapter 2. In all cases, the conditions salinity sal, temperature t and pressure p are supplied from input arguments. This makes it possible to calculate several parameters for the equation system. The total concentrations B_{tot}, S_{tot} and F_{tot} are estimated from salinity, see section 3.3.1. The equilibrium constants

K_i are calculated from the conditions as described in chapter 5. The pH scale conversions $\text{pH}conv_{i\,to\,j}$ can also be calculated from the conditions, see chapter 4. The fugacity coefficient φ_{CO_2} is determined from temperature, see section 3.1.1. The settings can influence how the parameters are calculated. It is not necessary to calculate all parameters for all functions. If pH is given as input, it is defined to be pH_{opt} and is used to calculate the corresponding hydrogen ion concentration $[H^+]_{opt}$.

The MIKE ECO Lab functions CONC_CO2, CONC_HCO3, CONC_CO3, FUGACITY_CO2 and PP_CO2 are based solely on the carbon system in section 3.1. The concentrations $[CO_2^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ are calculated from eqs. (3.6)-(3.8). The fugacity fug_{CO_2} of CO2 is calculated from eq. (3.5). The partial pressure p_{CO_2} of CO2 is calculated from eq. (3.10) by first calculating the fugacity fug_{CO_2}. In these equations, $[H^+]$ refers to $[H^+]_{opt}$, and the value of C_{tot} is required.

The MIKE ECO Lab function CONC_OH calculates the concentration $[OH^-]$ using eq. (3.40), where $[H^+]$ refers to $[H^+]_{opt}$. Note, that option 6 Peng for the **Set of constants** setting does not use the concentration of hydroxide, and for this option it is assumed that $[OH^-] = 0$.

The MIKE ECO Lab function CONC_H_FREE calculates the concentration $[H^+]_{Free}$ using the correct conversion from $[H^+]_{opt}$ in eq. (3.46) (not the approximate conversion in eq. (3.47)).

The MIKE ECO Lab function SOLVE_PH uses the alkalinity expression to define an equation for pH_{opt}. The carbon alkalinity is expressed as function of $[H^+]_{opt}$ using eq. (3.9) and C_{tot}. The other alkalinity terms are also written as functions of $[H^+]_{opt}$ as described in section 3.3. This requires the values of P_{tot} and Si_{tot}, in addition to the parameters calculated from the conditions. The alkalinity terms are inserted into the alkalinity expression determined by the settings. Equating the alkalinity expression with the alkalinity value A_{tot} gives an equation for $[H^+]_{opt}$ and thereby pH_{opt}. The equation is solved numerically with a Newton-Raphson method as implemented in the CO2SYS Program **Error! Reference source not found.**. The value of pH_{opt} is determined with an a ccuracy of four decimals.

4   pH scales

Basically, pH is a dimensionless value defined from the concentration of hydrogen ions as

$$pH = -\log_{10}[H^+]. \tag{4.1}$$

Strictly speaking, the logarithm needs a dimensionless argument. However, to ease notation, when taking the logarithm of a concentration, it will be assumed that the concentration has the dimension of mol/kg and the value without the dimension is used in the logarithm.

There are different ways to define and measure the concentration of H^+, and this has led to different pH scales. Four different pH scales are used in the calculations:

- The total scale (Total)
- The seawater scale (SWS)
- The free scale (Free)
- The NBS scale (NBS)

The value of pH on each scale has a corresponding notion of H+ concentration. The different pH scales are indicated with the same index for pH and $[H^+]$:

$$pH_i = -\log_{10}[H^+]_i \text{ where } i = Total, SWS, Free, NBS. \tag{4.2}$$

4.1   The free scale

pH on the free scale is simply defined from the concentration of free hydrogen ions, $[H^+]_{Free}$:

$$pH_{Free} = -\log_{10}[H^+]_{Free}. \tag{4.3}$$

4.2   The total scale

pH on the total scale is linked to a corresponding hydrogen ion concentration $[H^+]_{Total}$:

$$pH_{Total} = -\log_{10}[H^+]_{Total}. \tag{4.4}$$

The total scale is defined as in the CO2SYS Program **Error! Reference source not found.**:

$$[H^+]_{Total} = [H^+]_{Free}\left(1 + \frac{S_{tot}}{K_S}\right) \tag{4.5}$$

The dissociation constant K_S is for the free scale. See section 5 for how dissociation constants are related to pH scales.

4.3   The seawater scale

pH on the seawater scale is linked to a corresponding hydrogen ions concentration $[H^+]_{SWS}$:

$$pH_{SWS} = -\log_{10}[H^+]_{SWS}. \tag{4.6}$$

The seawater scale is defined as in the CO2SYS Program **Error! Reference source not found.**:

$$[H^+]_{SWS} = [H^+]_{Free} \left(1 + \frac{S_{tot}}{K_S} + \frac{F_{tot}}{K_F} \right).$$

(4.7)

The dissociation constants K_S and K_F are for the free scale. See section 5 for how dissociation constants are related to pH scales.

4.4   The NBS scale

pH on the NBS scale is defined from the activity a_H of hydrogen ions rather than the concentration (the CO2SYS Program **Error! Reference source not found.**):

$$pH_{NBS} = -\log_{10} a_H.$$

(4.8)

To use the same notation across pH scales, the notation $[H^+]_{NBS} = a_H$ is used even though the activity is a dimensionless quantity and strictly speaking not a concentration.

The activity a_H of hydrogen ions is related to the concentration through an activity coefficient f_H. Here, the activity is related to the seawater scale concentration (the CO2SYS Program **Error! Reference source not found.**):

$$a_H = f_H \, [H^+]_{sws}.$$

(4.9)

By convention, the activity coefficient is considered a dimensionless quantity and eq. (4.9) uses the value of $[H^+]_{sws}$ without unit. The hydrogen activity coefficient f_H depends on salinity and temperature but is assumed to be independent of pressure (the CO2SYS Program **Error! Reference source not found.**). For estimations of the activity coefficient fH, see appendix A.3.2.

4.5   Conversion between scales

The conversion between pH scales corresponds to the conversion of the H^+ concentration. In general, the conversion from scale i to scale j can be written using a conversion factor $pHconv_{i \, to \, j}$:

$$[H^+]_j = [H^+]_i \, pHconv_{i \, to \, j}.$$

(4.10)

For example, eq. (4.7) indicates that the conversion factor from the free scale to the seawater scale is

$$pHconv_{Free \, to \, SWS} = \left(1 + \frac{S_{tot}}{K_S} + \frac{F_{tot}}{K_F} \right).$$

(4.11)

By combining eqs. (4.5), (4.7) and (4.9), the conversion between any two pH scales can be obtained. All the conversion factors can be calculated if the following five parameters are known: f_H, S_{tot}, F_{tot}, K_S, K_F (K_S and K_F on the free scale). The activity coefficient f_H depends on salinity and temperature. The concentrations S_{tot} and F_{tot} are estimated from salinity. The dissociation constants K_S and K_F depend on salinity, temperature and pressure. Together, this implies that the conversion between pH scales depends on salinity sal, temperature t and pressure p.

5 Equilibrium constants

An equilibrium constant is a property of a chemical reaction describing the equilibrium state. The equilibrium constants used in these calculations are defined by the equilibrium equations (3.1)-(3.3) and (3.24)-(3.31). The value of an equilibrium constant changes with physical conditions, and here the effects of salinity sal, temperature t and pressure p are considered. If $[H^+]$ is a part of the equilibrium equation, then the equilibrium constant will also have different values for different pH scales.

Formulas for converting an equilibrium constant between pH scales can be obtained by applying the conversion rules for $[H^+]$ to both sides of an equilibrium equation. As an example, consider eq. (3.28) for the dissociation constant K_B. Changing $[H^+]$ from one scale to another corresponds to changing K_B by the same factor. Since all the equilibrium equations (except (3.1)) depend on $[H^+]$ in the same way, this rule applies to all the equilibrium constants (except K_0).

Equilibrium constants and their dependence on conditions can be estimated from experiments. Such estimations can be found in literature. The estimations presented here are divided into two parts. The first part is the estimation over a range of salinities and temperatures for a base pressure $p_0 = 0$. The second part is the estimation of the change with pressure for a given temperature. The estimates of the various equilibrium constants can be for different pH scales.

The following sections describe how the different equilibrium constants are calculated.

5.1 Calculation of K_0

The solubility coefficient K_0 of carbon dioxide is defined by the equilibrium equation (3.1). This equation does not contain $[H^+]$, and hence K_0 does not depend on the pH scale. K_0 depends on salinity and temperature but is independent of pressure **Error! Reference source not found.**. The estimate of K_0 is in appendix A.3.3.

5.2 Calculation of K_S and K_F

The hydrogen sulphate and hydrogen fluoride dissociation constants K_S and K_F are needed for conversion between pH scales, and fortunately they do not need to be converted themselves; their estimates are always on the free scale. The values are first calculated for the given salinity sal, given temperature t and base pressure p_0, see appendix A.3.9-A.3.10. Then, the values are adjusted to the given pressure p, see appendix A.4.6-A.4.7. Note that the values of K_S and K_F for base pressure as well as given pressure are used in the calculation of other dissociation constants.

5.3 Calculation of K_1, K_2, K_{P1}, K_{P2}, K_{P3}, K_{Si}, K_B and K_W,

In general, the remaining equilibrium constants will need to be converted between pH scales which requires the values of f_H, S_{tot}, F_{tot}, K_S, K_F, see section 4.5 for pH scale conversion. To calculate the equilibrium constants for the given salinity sal, temperature t and pressure p, and with respect to pH scale chosen in options, the following steps are applied.

Base value

The dissociation constants are calculated for given salinity sal and temperature t and for base pressure $p_0 = 0$. Different estimates in literature are for different pH scales, and the values can be on any scale at this point. (Some sources report the dissociation constants in molal concentration for a pure water solution, and in these cases the values are adjusted to molal concentration for a seawater solution.) The base value estimates are listed in appendix A.3.

Convert to seawater scale

The dissociation constants are then converted to the seawater pH scale. Since the dissociation constants at this point are for salinity sal, temperature t and pressure p_0, the pH scale conversions must use the parameters f_H, S_{tot}, F_{tot}, K_S, K_F for these conditions. This implies using K_S and K_F for base pressure p_0.

Pressure effects

Next, the dissociation constants are adjusted to the given pressure p while remaining on the seawater scale. In addition to pressure p, the pressure corrections also depend on temperature t. The estimates of the pressure effects are listed in appendix A.4.

Convert to chosen scale

Finally, the dissociation constants are converted from seawater scale to the pH scale chosen in the user options. The values are now for salinity sal, temperature t and pressure p, and the pH scale conversion must use the parameters f_H, S_{tot}, F_{tot}, K_S, K_F for these conditions. This implies using K_S and K_F for given pressure p.

6 Settings

In MIKE ECO Lab, the settings for pH calculations are defined on a separate tab in the editor. These settings consist of the same four basis settings as the CO2SYS Program **Error! Reference source not found.**. These settings are:

- Set of constants
- K HSO4
- [B]T Value
- pH scale

The pH scale setting determines on which scale pH values are given; both for function input and output. The other three settings affect how the equation system is defined, such as the expression for alkalinity and the estimation of parameters.

In addition to the four basic settings there is an **Option selection** setting with four items:

- User defined
- Freshwater option
- Peng option
- GEOSECS option

The last three options define fixed combinations of the four basic settings, and the first option allows the user to choose between any combination of the four basic settings.

6.1 pH scale setting

This setting is equivalent to "pH Scale" in the CO2SYS Program **Error! Reference source not found.**. It determines the pH scale used for input and output values of pH. It is possible to choose between the four pH scales defined in section 4:

1. Total
2. Seawater (default)
3. Free
4. NBS

6.2 Set of constants setting

This setting is equivalent to "Set of Constants" in the CO2SYS Program **Error! Reference source not found.**. The setting has 14 options:

1. Roy
2. Goyet and Poisson
3. Hansson refit by Dickson and Millero
4. Mehrbach refit by Dickson and Millero (default)
5. Hansson and Mehrbach refit by Dickson and Millero
6. GEOSECS
7. Peng
8. Freshwater
9. Cai and Wang
10. Lueker
11. Prieto and Millero

12. Millero 2002
13. Millero 2006
14. Millero 2010

Options 1-5 and 9-14 only differ in the estimates for the base values (no pressure effects) of the dissociation constants K_1 and K_2. These options will be referred to collectively as standard options, and the calculations they have in common are likewise referred to as standard calculations. Options 6-8 represent special cases and differs from the standard options in several ways. For example, their expressions for alkalinity A_{tot} differs from the standard expression.

6.2.1   Set of constants: 6 GEOSECS

This option is meant to replicate the calculations of Ch. 3 *Carbonate Chemistry* by Takahashi et al. in *GEOSECS Pacific Expedition* by Broecker et al. (1982) /39/. The calculations are on the NBS scale. The GEOSECS option differs from the standard options in the following ways:

- Compared to the standard expression, the GEOSECS expression for alkalinity does not includes effects from phosphate, silicate or hydroxide, see section 3.2.2.
- The option has its own estimates of the dissociation constants K_1, K_2 and K_B, see appendix A.3.4, A.3.7 for the base value estimates and appendix A.4.1, A.4.4 for the pressure effects.
- The estimate of the total boron concentration B_{tot} differs from the standard estimate; it is about 1% lower according to the CO2SYS Program **Error! Reference source not found.**.
- The calculations do not distinguish between fugacity and partial pressure; that is, the fugacity coefficient for carbon dioxide is $\varphi_{CO_2} = 1$.

6.2.2   Set of constants: 7 Peng

This option is meant to replicate the calculations of Peng et al. (1987) /34/, which are similar to the calculations of Takahashi et al. (1982) /39/. The calculations are on the NBS scale. The Peng option differs from the standard options in the following ways:

- The expression for alkalinity differs from the standard expression by an additional amount equal to the total phosphorus P_{tot}.
- The estimates of the total boron concentration B_{tot} and the dissociation constants K_1, K_2 and K_B are the same as for the GEOSECS option.
- The Peng option uses its own base value estimates of the dissociation constants K_{P1}, K_{P2}, K_{P3}, K_{Si} and K_W, see appendix A.3.5, A.3.6, A.3.8, and uses the standard estimates of the pressure effects.
- The estimate of the activity coefficient f_H is different from the standard estimate. The CO2SYS Program **Error! Reference source not found.** reports that the values are about 1% higher than the standard estimations.
- As for the GEOSECS option, these calculations do not distinguish between fugacity and partial pressure; that is, the fugacity coefficient for carbon dioxide is $\varphi_{CO_2} = 1$.

6.2.3   Set of constants: 8 Freshwater

This option represents freshwater conditions corresponding to zero salinity. The option is not the same as using $sal = 0$ as input argument for one of the other options as these options use parameter estimates that may not be valid for low salinities. The freshwater option differs from the standard options in the following ways:

- The salinity is set to zero, $sal = 0$, regardless of its input value.
- The expression for alkalinity only includes effects from carbon, hydroxide and hydrogen, see eq. (3.23).
- The estimates of the dissociation constants K_1, K_2 and K_W are for freshwater conditions. See appendix A.3.4, A.3.8 for the base value estimates and appendix A.4.1, A.4.5 for the pressure effects.
- For freshwater, the free, total and seawater scales are identical. For $sal = 0$, the standard estimates give $S_{tot} = F_{tot} = 0$, and the total and seawater scales, defined by eqs. (4.5), (4.7), both become equal to the free scale. The only additional requirement is that K_S and K_F are non-zero.
- The activity coefficient is defined as $f_H = 1$ entailing that the NBS scale, defined by eq. (4.9), becomes equivalent to the other scales. Hence, there is no difference between pH scales for this option. (Note, this is a simplification; in reality, the activity coefficient is not one, and the NBS scale differs from the other pH scales.)

6.3   K HSO4 setting

This setting is equivalent to "KHSO$_4$" in the CO2SYS Program **Error! Reference source n ot found.**. There are two options:

1. Dickson (default)
2. Khoo et al.

The setting determines which estimate is used for the base value (no pressure effects) of the dissociation constant K_S of hydrogen sulphate, see appendix A.3.9 for the estimates.

6.4   [B]T value setting

This setting is equivalent to "[B]$_T$ Value" in the CO2SYS Program **Error! Reference s ource not found.**. There are two options:

1. Uppstrom (default)
2. Lee et al.

The setting determines which estimate is used for the total boron concentration B_{tot}, see appendix A.2.1 for the estimates. Note, this setting has no effect if **Set of constants** option 6, 7 or 8 is chosen.

6.5   Overview

Table 6.1 contains an overview of the settings and their impact on the calculations.

Table 6.1   Green cells indicate standard values. Red cells indicate non-standard values. Grey cells indicate that the value is not used.

	Set of constants: 1-5, 9-14 Standard	Set of constants: 6 GEOSECS	Set of constants: 7 Peng	Set of constants: 8 Freshwater (f)
sal	Input	Input	Input	$sal = 0$
P_{tot}	Input	Not used (c)	Input	Not used (c)
Si_{tot}	Input	Not used (c)	Input	Not used (c)
B_{tot}	Standard estimate (a)	GEOSECS estimate	GEOSECS estimate	Not used (c)
S_{tot}	Standard estimate	Standard estimate	Standard estimate	Standard estimate (d)
F_{tot}	Standard estimate	Standard estimate	Standard estimate	Standard estimate (d)
K_0	Standard estimate	Standard estimate	Standard estimate	Standard estimate
K_1, K_2	Each has different base value, no standard Standard pressure effect	GEOSECS base value GEOSECS pressure effect	GEOSECS base value GEOSECS pressure effect	Freshwater base value Freshwater pressure effect
K_{P1}, K_{P2}, K_{P3}	Standard base value Standard pressure effect	Not used (c)	Peng base value Standard pressure effect	Not used (c)
K_{Si}	Standard base value Standard pressure effect	Not used (c)	Peng base value Standard pressure effect	Not used (c)
K_B	Standard base value Standard pressure effect	GEOSECS base value GEOSECS pressure effect	GEOSECS base value GEOSECS pressure effect	Not used (c)
K_W	Standard base value Standard pressure effect	Not used (c)	Peng base value Standard pressure effect	Freshwater base value Freshwater pressure effect
K_S	Standard base value (b) Standard pressure effect	Standard base value (b) Standard pressure effect	Standard base value (b) Standard pressure effect	Standard base value (b) Standard pressure effect (e)
K_F	Standard base value Standard pressure effect	Standard base value Standard pressure effect	Standard base value Standard pressure effect	Standard base value (b)

				Standard pressure effect (e)
f_H: activity coefficient	Standard estimate	Standard estimate	Peng estimate	$f_H = 1$
φ_{CO_2}: fugacity coefficient	Standard estimate	$\varphi_{CO_2} = 1$	$\varphi_{CO_2} = 1$	Standard estimate
Definition of alkalinity A_{tot}	Standard expression	GEOSECS expression	Peng expression	Freshwater expression

a. Standard estimate depends on the **[B]T Value** option.
b. Standard base value depends on the **K HSO4** option.
c. Only used in alkalinity terms that do not enter the alkalinity expression.
d. The standard estimates give $S_{tot} = F_{tot} = 0$ for $sal = 0$.
e. The value must be non-zero to avoid division by zero in pH scale conversions.
f. The values of S_{tot}, F_{tot}, K_S and K_F are only used in the conversion between pH scales. The values ensure the free, total and seawater scales are the same.

7   Atmospheric CO_2 flux

The calculations behind the MIKE ECO Lab function FLUX_CO2 is based on Wanninkhof (1992) /3/ and the update Wanninkhof (2014) /4/. The transfer, or flux, of carbon dioxide across the air-water interface is (Wanninkhof 2014, /4/)

$$F_{CO_2} = k\, K_0\big(p_{CO_2}^{water} - p_{CO_2}^{air}\big), \tag{7.1}$$

where $p_{CO_2}^{water}$ is the partial pressure of CO_2 in equilibrium with surface water and $p_{CO_2}^{air}$ is the partial pressure of CO_2 in the air. Additionally, K_0 is the solubility and k is the gas transfer velocity. The calculations from Wanninkhof (2014) /4/ are valid for fluxes on a regional to global scale.

The gas transfer velocity k is calculated as (Wanninkhof 2014, /4/)

$$k = 0.251\, u_{10}^2 (Sc/660)^{-1/2}, \tag{7.2}$$

where u_{10} is the wind speed at 10 metres above the water surface and Sc is the Schmidt number. The value 660 is the Schmidt number for seawater at $20\,°\mathrm{C}$ and is used to normalize the Schmidt number. Since the gas transfer velocity k is traditionally in $\mathrm{cm\,hr^{-1}}$ while wind speed u_{10} is in $\mathrm{m\,s^{-1}}$, the coefficient 0.251 has the unit $\mathrm{cm\,hr^{-1}\,m^{-2}s^2}$. The coefficient 0.251 is estimated from averages of squared wind speeds, $\langle u_{10}^2 \rangle$. The value used for u_{10} should therefore be an average wind speed based on measurements of short intervals (Wanninkhof 2014, /4/). Eq. (7.2) is valid for wind speeds in the range $3\text{-}15\ \mathrm{m\,s^{-1}}$ and the overall uncertainty of k is 20% (Wanninkhof 2014, /4/).

Wanninkhof (2014) /4/ fits the Schmidt number to a fourth order polynomial in temperature t [°C]. For seawater with salinity $sal = 35\ \mathrm{psu}$, the Schmidt number is estimated as

$$Sc_{35} = 2116.8 - 136.25\, t + 4.7353\, t^2 - 0.092307\, t^3 + 0.0007555\, t^4 \tag{7.3}$$

and for freshwater with zero salinity, the Schmidt number is estimated as

$$Sc_0 = 1923.6 - 125.06\, t + 4.3773\, t^2 - 0.085681\, t^3 + 0.0007028\, t^4. \tag{7.4}$$

The estimates are valid for temperatures between $-2\,°\mathrm{C}$ and $40\,°\mathrm{C}$. For option 8 Freshwater in **Set of constants**, the Schmidt number $Sc = Sc_0$ is used, and for all other options the Schmidt number $Sc = Sc_{35}$ is used.

The solubility of carbon dioxide, K_0 [$\mathrm{mol\,L^{-1}\,atm^{-1}}$] is calculated as (Weiss (1974) /5/)

$$\begin{aligned}
K_0 = \exp\Big(&-58.0931 + 90.5069\Big(\frac{100}{T}\Big) + 22.294\ln\Big(\frac{T}{100}\Big) + 0.027766\, sal \\
&- 0.025888\, sal\Big(\frac{T}{100}\Big) + 0.0050578\, sal\Big(\frac{T}{100}\Big)^2\Big),
\end{aligned} \tag{7.5}$$

where T is the water temperature in Kelvin.

The MIKE ECO Lab function FLUX_CO2 takes the partial pressures in Pa and convert them to atm, see section 2.4. Then the flux F_{CO_2} in eq. (7.1) has the unit $\mathrm{cm\,mol\,hr^{-1}\,L^{-1}}$. Converting the flux to $\mathrm{gC\,m^{-2}\,d^{-1}}$ requires the conversion factor

$$12.0107\frac{\text{g-C}}{\text{mol}} \cdot 1000\frac{\text{L}}{\text{m}^3} \cdot 24\frac{\text{hr}}{\text{d}} \cdot 0.01\frac{\text{m}}{\text{cm}} = 2882.568 \left.\frac{\text{g-C}}{\text{m}^2\text{d}}\middle/\frac{\text{mol cm}}{\text{L hr}}\right. \tag{7.6}$$

Additionally, the function FLUX_CO2 returns the flux from water to air rather than from air to water as in eq. (7.1), and the sign of the flux is opposite of eq. (7.1). Therefore, the FLUX_CO2 function returns the value

$$Flux_{CO_2} = 2882.568\, k\, K_0\bigl(p_{CO_2}^{air} - p_{CO_2}^{water}\bigr) \tag{7.7}$$

8 References

/1/ Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.), 2007. *Guide to Best Practices for Ocean CO$_2$ Measurements.* PICES Special Publication 3, IOCCP Report No. 8. North Pacific Marine Science Organization.

/2/ Lewis E.R.; Wallace D.W.R. (1998): Program Developed for CO2 System Calculations. CDIAC. doi:10.15485/1464255

/3/ Wanninkhof, R. 1992. *Relationship between windspeed and gas exchange over the ocean.* J. Geophys. Res. (Oceans) 97(C5), pp. 7373–7382.

/4/ Wanninkhof, R. 2014. *Relationship between wind speed and gas exchange over the ocean revisited.* Limnology and Oceanography Methods. 12(6): 351-362.

/5/ Weiss, R.F. 1974. *Carbon dioxide in water and seawater: the solubility of a non-ideal gas.* Marine Chem. 2, pp. 203–215.

References taken directly from the CO2SYS Program **Error! Reference source not found.**:

/6/ Cai and Wang 1998, Limnol. Oceanogr. 43(4) (1998) 657-668.

/7/ Culberson, C. H. and Pytkowicz, R. M., *Effect of pressure on carbonic acid, boric acid, and the pH of seawater*, Limnology and Oceanography 13:403-417, 1968.

/8/ Culkin, F., in Chemical Oceanography, ed. Riley and Skirrow, 1965.

/9/ Dickson, A. G., J. Chemical Thermodynamics, 22:113-127, 1990.

/10/ Dickson, A. G. and Riley, J. P., Marine Chemistry 7:89-99, 1979.

/11/ Dickson and Millero, Deep-Sea Research, 34(10):1733-1743, 1987. (See also Corrigenda, Deep-Sea Research, 36:983, 1989.)

/12/ DOE handbook.

/13/ Edmond, John M. and Gieskes, J. M. T. M., *The calculation of the degree of seawater with respect to calcium carbonate under in situ conditions*, Geochemica et Cosmochemica Acta, 34:1261-1291, 1970.

/14/ Goyet and Poisson, Deep-Sea Research, 36(11):1635-1654, 1989.

/15/ Hansson, Deep-Sea Research, 20:461-478, 1973.

/16/ Hansson, Acta Chemica Scandanavia, 27:931-944, 1973.

/17/ Harned and Davis, J American Chemical Society, 65:2030-2037, 1943.

/18/ Harned and Owen, The Physical Chemistry of Electrolyte Solutions, 1958.

/19/ Harned and Scholes, J American Chemical Society, 43:1706-1709, 1941.

/20/ Kester, D. R., and Pytkowicz, R. M., Limnology and Oceanography 12:243-252, 1967.

/21/ Khoo, et al., Analytical Chemistry, 49(1):29-34, 1977.

/22/   Lee, Kim, Byrne, Millero, Feely, Yong-Ming Liu. 2010. Geochimica Et Cosmochimica Acta 74 (6).

/23/   Li et al., JGR 74:5507-5525, 1969.

/24/   Lyman, John, UCLA Thesis, 1957.

/25/   Lueker, Dickson, Keeling, 2000, Mar. Chem. 70 (2000) 105-119.

/26/   Mehrbach et al., Limn Oc, 18(6):897-907, 1973.

/27/   Millero, F. J., *The thermodynamics of the carbon dioxide system in seawater*, Geochemica et Cosmochemica Acta 43:1651-1661, 1979.

/28/   Millero, Frank J., *Influence of pressure on chemical processes in the sea*. Chapter 43 in Chemical Oceanography, eds. Riley, J. P. and Chester, R., Academic Press, 1983.

/29/   Millero, F. J., *Thermodynamics of the carbon dioxide system in the oceans*, Geochemica et Cosmochemica Acta 59:661-677, 1995.

/30/   Millero, 2010, Marine and Freshwater Research, v. 61, p. 139-142.

/31/   Millero, Graham, Huang, Bustos-Serrano, Pierrot. Mar.Chem. 100 (2006) 80-94.

/32/   Millero et al., 2002. Deep-Sea Res. I (49) 1705-1723.

/33/   Morris, A. W., and Riley, J. P., Deep-Sea Research 13:699-705, 1966

/34/   Peng, T. H., Takahashi, T., Broecker, W. S., & Olafsson, J. O. N. (1987). *Seasonal variability of carbon dioxide, nutrients and oxygen in the northern North Atlantic surface water: observations and a model.* Tellus B: Chemical and Physical Meteorology, 39(5), 439-458.

/35/   Prieto and Millero 2002. Geochim. et Cosmochim. Acta. 66(14) 2529-2540.

/36/   Riley, J. P., Deep-Sea Research 12:219-220, 1965.

/37/   Roy et al., Marine Chemistry, 44:249-267, 1993. (See also: Erratum, Marine Chemistry 45:337, 1994 and Erratum, Marine Chemistry 52:183, 1996)

/38/   Sillen, Martell, and Bjerrum, *Stability constants of metal-ion complexes*, The Chemical Society (London), Special Publ. 17:751, 1964.

/39/   Takahashi et al. (1982). Ch. 3 *Carbonate Chemistry.* In Broecker, W.S., Spencer, D.W., Craig H., 1982. *GEOSECS Pacific Expedition: Hydrographic data 1973-1974.* Vol. 3.

/40/   Uppstrom, L., Deep - Sea Research 21:161 - 162, 1974.

/41/   Weiss, R. F., Marine Chemistry 2:203-215, 1974.

/42/   Yao and Millero, Aquatic Geochemistry 1:53-88, 1995.

APPENDICES

APPENDIX A – Chemical and physical parameters

Literature values and estimations

A   Chemical and physical parameters

A.1   Molar mass

The molar mass for a simple chemical element is the same as the element's atomic weight. The values for the elements relevant here are

$$M_C = 12.011 \frac{g}{mol}$$

$$M_{Si} = 28.085 \frac{g}{mol}$$

$$M_P = 30.97761998 \frac{g}{mol}$$

A.2   Estimation of concentrations

This section presents the estimates of the total concentrations and for which settings they are used. It is possible to estimate the concentrations from salinity, when it is assumed the composition of seawater is fixed. The estimates are based on the code of the CO2SYS Program **Error! Reference source not found.**. In the following, sal denotes salinity in psu.

A.2.1   Total concentration of boron

The estimate of the total boron concentration depends on the settings for both **Set of constants** and **[B]T Value**.

Set of constants: 1-5, 9-14 Standard

[B]T Value: 1 Uppstrom
The total boron concentration B_{tot} is calculated in mol/kg-sw as

$$B_{tot} = 0.0004157 \cdot \frac{sal}{35} .$$

(A.1)

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Uppstrom (1974) /40/.

[B]T Value: 2 Lee et al.
The total boron concentration B_{tot} is calculated in mol/kg-sw as

$$B_{tot} = 0.0004326 \cdot \frac{sal}{35} .$$

(A.2)

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Lee et al. (2010) /22/.

Set of constants: 6, 7 GEOSECS, Peng

The total boron concentration B_{tot} is calculated in mol/kg-sw as

$$B_{tot} = 0.0004106 \cdot \frac{sal}{35} \ . \tag{A.3}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Culkin (1965) /8/.

Set of constants: 8 Freshwater

The total boron concentration B_{tot} is not used for this option.

A.2.2   Total concentration of sulphate

For all options, the total sulphate concentration S_{tot} is calculated in $\mathrm{mol/kg\text{-}sw}$ as

$$S_{tot} = \frac{0.14}{96.062} \cdot \frac{sal}{1.80655} \ . \tag{A.4}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Morris (1966) /33/.

A.2.3   Total concentration of fluorine

For all options, the total fluorine concentration F_{tot} is calculated in $\mathrm{mol/kg\text{-}sw}$ as

$$F_{tot} = \frac{0.000067}{18.998} \cdot \frac{sal}{1.80655} \ . \tag{A.5}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Riley (1965) /36/.

A.3   Estimation of constants from salinity and temperature

This section presents the estimates of physical and chemical constants that change with salinity and temperature. It also describes for which options the various estimates are used. Any pressure dependencies are addressed in section A.4. The estimates are based on the code of the CO2SYS Program **Error! Reference source not found.**. In the following, sal denotes salinity in psu. Conversion between temperature t in degrees Celsius and temperature T in Kelvin are calculated according to

$$\frac{T}{K} = \frac{t}{{}^\circ C} + 273.15. \tag{A.6}$$

Some intermediate calculations are employed repeatedly in the estimates. In correspondence with the CO2SYS Program **Error! Reference source not found.**, conversion from $\mathrm{mol/kg\text{-}H_2O}$ to $\mathrm{mol/kg\text{-}sw}$ is obtained by multiplying by

$$ratio_{WtoSW} = 1 - 0.001005 \ sal. \tag{A.7}$$

The ionic strength is calculated as

$$IonS = \frac{19.924 \ sal}{1000 - 1.005 \ sal}. \tag{A.8}$$

This expression is from the CO2SYS Program **Error! Reference source not found.** where they cite the DOE Handbook (ch. 5, p. 13/22, eq. 7.2.4) /12/.

A.3.1 Fugacity coefficient for carbon dioxide: φ_{CO_2}

The estimate of the fugacity coefficient for CO_2 depends on the **Set of constants** setting.

Set of constants: 1-5, 8-14 Standard, Freshwater

The fugacity coefficient is calculated as

$$\varphi_{CO_2} = \exp\left((B + 2\,\Delta)\frac{p_{atm}}{R\,T}\right) \tag{A.9}$$

where $p_{atm} = 1\text{ atm} = 1.01325\text{ bar}$ is the atmospheric pressure and

$$\Delta = 57.7 - 0.118\,T, \tag{A.10}$$

$$B = -1636.75 + 12.0408\,T - 0.0327957\,T^2 + 3.16528 \cdot 10^{-5}\,T^3. \tag{A.11}$$

Both Δ and B are in cm^3/mol. The estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Weiss (1974) /41/.

Set of constants: 6-7 GEOSECS, Peng

These options assume that there is no difference between fugacity and partial pressure, hence

$$\varphi_{CO_2} = 1. \tag{A.12}$$

A.3.2 Activity coefficient of hydrogen: f_H

The estimate of the hydrogen activity coefficient f_H depends on the **Set of constants** setting.

Set of constants: 1-6, 9-14 Standard, GEOSECS

The hydrogen activity coefficient f_H is calculated as

$$f_H = 1.2948 - 0.002036\,T + (0.0004607 - 0.000001475\,T)\,sal^2. \tag{A.13}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Takahashi et al. (1982, ch. 3 p. 80) /39/.

Set of constants: 7 Peng

The hydrogen activity coefficient f_H is calculated as

$$f_H = 1.29 - 0.00204\,T + (0.00046 - 0.00000148\,T)\,sal^2. \tag{A.14}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Peng et al. (1987) /34/ with the following comment:

"*They reference the GEOSECS report, but round the value given there off so that it is about .008 (1%) lower. It doesn't agree with the check value they give on p. 456.*"

Set of constants: 8 Freshwater

The hydrogen activity coefficient f_H is defined as

$$f_H = 1. \tag{A.15}$$

This is from the CO2SYS Program **Error! Reference source not found.** where they have the following comment:

"*this shouldn't occur in the program for this case*"

A.3.3 Solubility coefficient of carbon dioxide: K_0

The estimate of the solubility coefficient K_0 of carbon dioxide is the same for all options. It is calculated in $\mathrm{mol/(atm\ kg\text{-}sw)}$ as

$$lnK0 = -60.2409 + \frac{93.4517}{T/100} + 23.3585\ \ln\left(\frac{T}{100}\right)$$
$$+ sal\left(0.023517 - 0.023656\ \frac{T}{100} + 0.0047036\left(\frac{T}{100}\right)^2\right),$$

$$K_0 = \exp(lnK0). \tag{A.16}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Weiss (1974) /41/.

A.3.4 Dissociation constants of carbonic acid: K_1, K_2

The estimation of the dissociation constants K_1 and K_2 of carbonic acid depends on the **Set of constants** setting.

Set of constants: 1 Roy

The value of K_1 is calculated as

$$lnK1 = 2.83655 - \frac{2307.1266}{T} - 1.5529413\ \ln T$$
$$+ \left(-0.20760841 - \frac{4.0484}{T}\right)\sqrt{sal}\ + 0.08468345\ sal$$
$$- 0.00654208\ sal^{3/2},$$

$$K_1 = \exp(lnK1) \tag{A.17}$$

and the value of K_2 is calculated as

$$lnK2 = -9.226508 - \frac{3351.6106}{T} - 0.2005743\ln T$$
$$+ \left(-0.106901773 - \frac{23.9722}{T}\right)\sqrt{sal}\ + 0.1130822\ sal$$
$$- 0.00846934\ sal^{3/2},$$

$$K_2 = \exp(lnK2). \tag{A.18}$$

Both values are on the total scale and in $\mathrm{mol/kg\text{-}H_2O}$. They are converted to $\mathrm{mol/kg\text{-}sw}$ by multiplying by the factor in eq. (A.7). The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Roy et al. (1993, abstract and eq. 29, 30 p. 254) /37/ and include these comments:

"*!!! Typo: in the abstract on p. 249: in the eq. for lnK1* the last term should have S raised to the power 1.5.*"

They claim standard deviations (p. 254) of the fits as .0048 for lnK1 (.5% in K1) and .007 in lnK2 (.7% in K2). They also claim (p. 258) 2s precisions of .004 in pK1 and .006 in pK2. These are consistent, but Andrew Dickson (personal communication) obtained an rms deviation of about .004 in pK1 and .003 in pK2. This would be a 2s precision of about 2% in K1 and 1.5% in K2."

Set of constants: 2 Goyet and Poisson

The value of K_1 is calculated as

$$pK_1 = \frac{812.27}{T} + 3.356 - 0.00171\, sal \ln T + 0.000091\, sal^2,$$

$$K_1 = 10^{-pK_1} \tag{A.19}$$

and the value of K_2 is calculated as

$$pK_2 = \frac{1450.87}{T} + 4.604 - 0.00385\, sal \ln T + 0.000182\, sal^2,$$

$$K_2 = 10^{-pK_2}. \tag{A.20}$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Goyet and Poisson (1989, abstract and table 5 p. 1652) /14/ and include these comments:

"*The 2s precision in pK1 is .011, or 2.5% in K1.*
The 2s precision in pK2 is .02, or 4.5% in K2."

Set of constants: 3 Hansson refit by Dickson and Millero

The value of K_1 is calculated as

$$pK_1 = \frac{851.4}{T} + 3.237 - 0.0106\, sal + 0.000105\, sal^2,$$

$$K_1 = 10^{-pK_1} \tag{A.21}$$

and the value of K_2 is calculated as

$$pK_2 = -\frac{3885.4}{T} + 125.844 - 18.141 \ln T - 0.0192\, sal + 0.000132\, sal^2,$$

$$K_2 = 10^{-pK_2}. \tag{A.22}$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Dickson and Millero (1987, table 4 p. 1739) /11/ and note that the data are from Hansson (1973a,b) /15/, /16/. The CO2SYS Program **Error! Reference source not found.** also has the following comments:

"*Hansson gave his results on the Total scale (he called it the seawater scale) and in mol/kg-SW.*
!!! Typo in DM on p. 1739 in Table 4: the equation for pK2* for Hansson should have a .000132 *S^2 instead of a .000116 *S^2.
The 2s precision in pK1 is .013, or 3% in K1.
The 2s precision in pK2 is .017, or 4.1% in K2."

Set of constants: 4 Mehrbach refit by Dickson and Millero

The value of K_1 is calculated as

$$pK_1 = \frac{3670.7}{T} - 62.008 + 9.7944 \ln T - 0.0118 \, sal + 0.000116 \, sal^2,$$

$$K_1 = 10^{-pK_1} \tag{A.23}$$

and the value of K_2 is calculated as

$$pK_2 = \frac{1394.7}{T} + 4.777 - 0.0184 \, sal + 0.000118 \, sal^2,$$

$$K_2 = 10^{-pK_2}. \tag{A.24}$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Dickson and Millero (1987, table 4, p. 1739) /11/ and note that the data are from Mehrbach et al. (1973) /26/. The CO2SYS Program **Error! Reference source not found.** also has the following comments:

"Mehrbach et al gave results on the NBS scale.
The 2s precision in pK1 is .011, or 2.6% in K1.
The 2s precision in pK2 is .020, or 4.6% in K2"

Set of constants: 5 Hansson and Mehrbach refit by Dickson and Millero

The value of K_1 is calculated as

$$pK_1 = \frac{845}{T} + 3.248 - 0.0098 \, sal + 0.000087 sal^2,$$

$$K_1 = 10^{-pK_1} \tag{A.25}$$

and the value of K_2 is calculated as

$$pK_2 = \frac{1394.7}{T} + 4.777 - 0.0184 \, sal + 0.000118 \, sal^2,$$

$$K_2 = 10^{-pK_2}. \tag{A.26}$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Dickson and Millero (1987, table 5, p. 1740) /11/ and note that the data are from Hansson (1973a,b) /15/,/16/ and Mehrbach et al. (1973) /26/. The CO2SYS Program **Error! Reference source not found.** also comments as follows:

"!!! Typo in DM on p. 1740 in Table 5: the second equation should be pK2* =, not pK1* =.
The 2s precision in pK1 is .017, or 4% in K1.
The 2s precision in pK2 is .026, or 6% in K2."

Set of constants: 6, 7 GEOSECS, Peng

The value of K_1 is calculated as

$$logK_1 = 13.7201 - 0.031334\,T - \frac{3235.76}{T} - 0.000013\,sal \cdot T + 0.1032\,\sqrt{sal},$$

$$K_1 = 10^{logK_1} \tag{A.27}$$

and the value of K_2 is calculated as

$$sal_{pos} = \max(sal, 0.709716),$$

$$\begin{aligned}
logK_2 = &-5371.9645 - 1.671221\,T + 128375.28\,\frac{1}{T} + 2194.3055\log_{10}(T) \\
&- 0.22913\,sal_{pos} - 18.3802\log_{10}(sal_{pos}) + 0.00080944\,sal\,T \\
&+ 5617.11\frac{\log_{10}(sal_{pos})}{T} - 2.136\frac{sal_{pos}}{T},
\end{aligned}$$

$$K_2 = 10^{logK_2}. \tag{A.28}$$

Both values are on the NBS scale and are dimensionless. (They are dimensionless because $[\text{H}^+]_{NBS} = a_H$ is dimensionless.) The use of sal_{pos} instead of sal for K_2 is to ensure a strictly positive argument for the logarithm. The estimate of K_1 and the estimate of K_2, with sal instead of sal_{pos}, are from the CO2SYS Program **Error! Reference source not found.** where they cite Mehrbach et al. (1973) /26/ and include the following comments:

> "*The 2s precision in pK1 is .005, or 1.2% in K1.*
> *The 2s precision in pK2 is .008, or 2% in K2.*"

Set of constants: 8 Freshwater

The value of K_1 is calculated as

$$lnK_1 = 290.9097 - 14554.21\frac{1}{T} - 45.0575\ln T,$$

$$K_1 = \exp(lnK_1) \tag{A.29}$$

and the value of K_2 is calculated as

$$lnK_2 = 207.6548 - 11843.79\frac{1}{T} - 33.6485\ln T,$$

$$K_2 = \exp(lnK_2). \tag{A.30}$$

Both values are on the free scale and in $\text{mol/kg-H}_2\text{O}$. For this option, the free scale is equivalent to the total, and the seawater scale and $\text{mol/kg-H}_2\text{O}$ is equivalent to mol/kg-sw. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1979) /27/ and note that the data for K_1 is from Harned and Davis (1943) /17/ and the data for K_2 is from Harned and Davis (1941) /19/.

Set of constants: 9 Cai and Wang

The value of K_1 is calculated as

$$F_1 = 200.1\frac{1}{T} + 0.322,$$

$$pK_1 = 3404.71\frac{1}{T} + 0.032786\,T - 14.8435 - 0.071692\,F_1\,\sqrt{sal} + 0.0021487\,sal,$$

$$K_1 = 10^{-pK_1} \tag{A.31}$$

and the value of K_2 is calculated as

$$F_2 = -129.24\frac{1}{T} + 1.4381,$$

$$pK_2 = 2902.39\frac{1}{T} + 0.02379\,T - 6.498 - 0.3191\,F_2\,\sqrt{sal} + 0.0198\,sal,$$

$$K_2 = 10^{-pK_2}. \tag{A.32}$$

Both values are on the NBS scale and are dimensionless. (They are dimensionless because $[H^+]_{NBS} = a_H$ is dimensionless.) The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Cai and Wang (1998) /6/ and note that this is for estuarine use. The CO2SYS Program **Error! Reference source not found.** also includes the following comments:

> "*Data used in this work is from:*
> *K1: Merhback (1973) for S>15, for S<15: Mook and Keone (1975)*
> *K2: Merhback (1973) for S>20, for S<20: Edmond and Gieskes (1970)*
> *Sigma of residuals between fits and above data: å±0.015, +0.040 for K1 and K2, respectively.*
> *Sal 0-40, Temp 0.2-30*
> *[…]*
> *Their check values for F1 don't work out, not sure if this was correctly published...*"

For the conversion to the seawater scale, the CO2SYS Program **Error! Reference source not found.** has this remark:

> "*convert to SWS scale (uncertain at low Sal due to junction potential)*"

Set of constants: 10 Lueker

The value of K_1 is calculated as

$$pK_1 = 3633.86\frac{1}{T} - 61.2172 + 9.6777\ln T - 0.011555\,sal + 0.0001152\,sal^2,$$

$$K_1 = 10^{-pK_1} \tag{A.33}$$

and the value of K_2 is calculated as

$$pK_2 = 471.78\frac{1}{T} + 25.929 - 3.16967\ln T - 0.01781\,sal + 0.0001122\,sal^2,$$

$$K_2 = 10^{-pK_2}. \tag{A.34}$$

Both values are on the total scale and in $\mathrm{mol/kg\text{-}sw}$. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Lueker et al. (2000) /25/ and comment as follows:

"*This is Mehrbach's data refit after conversion to the total scale, for comparison with their equilibrator work.*"

Set of constants: 11 Prieto and Millero

The value of K_1 is calculated as

$$pK_1 = -43.6977 - 0.0129037\,sal + 0.0001364\,sal^2 + 2885.378\frac{1}{T} \\ + 7.045159\ln T,$$

$$K_1 = 10^{-pK_1} \qquad\qquad (A.35)$$

and the value of K_2 is calculated as

$$pK_2 = -452.094 + 13.142162\,sal - 0.0008101\,sal^2 + 21263.61\frac{1}{T} \\ + 68.483143\ln T + (-581.4428\,sal + 0.259601\,sal^2)\frac{1}{T} \\ - 1.967035\,sal\ln T,$$

$$K_2 = 10^{-pK_2}. \qquad\qquad (A.36)$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. These estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Prietor and Millero (2000) /35/ and comment as follows:

"*sigma for pK1 is reported to be 0.0056
sigma for pK2 is reported to be 0.010
This is from the abstract and pages 2536-2537*"

Set of constants: 12 Millero 2002

The value of K_1 is calculated as

$$pK_1 = 6.359 - 0.00664\,sal - 0.01322\,t + 0.00004989\,t^2,$$

$$K_1 = 10^{-pK_1} \qquad\qquad (A.37)$$

and the value of K_2 is calculated as

$$pK_2 = 9.867 - 0.01314\,sal - 0.01904\,t + 0.00002448\,t^2,$$

$$K_2 = 10^{-pK_2}. \qquad\qquad (A.38)$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. These estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Millero et al. (2002) /32/ and have the following comment:

"*Calculated from overdetermined WOCE-era field measurements
sigma for pK1 is reported to be 0.005. sigma for pK2 is reported to be 0.008.*"

This is from page 1715."

Set of constants: 13 Millero 2006

The value of K_1 is calculated as

$$pK_1^0 = -126.34048 + 6320.813\frac{1}{T} + 19.568224\ln T,$$

$$A_1 = 13.4191\sqrt{sal} + 0.0331\,sal - 0.0000533\,sal^2,$$

$$B_1 = -530.123\sqrt{sal} - 6.103\,sal,$$

$$C_1 = -2.0695\sqrt{sal},$$

$$pK_1 = A_1 + \frac{B_1}{T} + C_1\ln T + pK_1^0,$$

$$K_1 = 10^{-pK_1} \tag{A.39}$$

and the value of K_2 is calculated as

$$pK_2^0 = -90.18333 + 5143.692\frac{1}{T} + 14.613358\ln T,$$

$$A_2 = 21.0894\sqrt{sal} + 0.1248\,sal - 0.0003687\,sal^2,$$

$$B_2 = -772.483\sqrt{sal} - 20.051\,sal,$$

$$C_2 = -3.3336\sqrt{sal},$$

$$pK_2 = A_2 + \frac{B_2}{T} + C_2\ln T + pK_2^0,$$

$$K_2 = 10^{-pK_2}. \tag{A.40}$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Millero et al. (2006) /31/ and comment as follows:

"*S=1 to 50, T=0 to 50. From titrations in Gulf Stream seawater.*
[…] *pK1 sigma = 0.0054*
[…] *pK2 sigma = 0.011*"

Set of constants: 14 Millero 2010

The value of K_1 is calculated as

$$pK_1^0 = -126.34048 + 6320.813\frac{1}{T} + 19.568224\ln T,$$

$$A_1 = 13.4038\sqrt{sal} + 0.03206\,sal - 0.00005242\,sal^2,$$

$$B_1 = -530.659\sqrt{sal} - 5.821\,sal,$$

$$C_1 = -2.0664\sqrt{sal},$$

$$pK_1 = pK_1^0 + A_1 + \frac{B_1}{T} + C_1 \ln T,$$

$$K_1 = 10^{-pK_1} \tag{A.41}$$

and the value of K_2 is calculated as

$$pK_2^0 = -90.18333 + \frac{5143.692}{T} + 14.613358 \ln T,$$

$$A_2 = 21.3728 \sqrt{sal} + 0.1218 \, sal - 0.0003688 \, sal^2,$$

$$B_2 = -788.289 \sqrt{sal} - 19.189 \, sal,$$

$$C_2 = -3.374 \sqrt{sal},$$

$$pK_2 = A_2 + \frac{B_2}{T} + C_2 \ln T + pK_2^0,$$

$$K_2 = 10^{-pK_2}. \tag{A.42}$$

Both values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. The estimates of K_1 and K_2 are from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (2010) /30/ and note that this is for estuarine use. The CO2SYS Program **Error! Reference source not found.** also includes the following comment:

> "*Fits through compilation of real seawater titration results: Mehrbach et al. (1973), Mojica-Prieto & Millero (2002), Millero et al. (2006)*"

A.3.5 Dissociation constants of phosphoric acid: K_{P1}, K_{P2}, K_{P3}

The estimates of the dissociation constants K_{P1}, K_{P2} and K_{P3} of phosphoric acid depend on the setting **Set of constants**.

Set of constants: 1-5, 9-14 Standard

The value of K_{P1} is calculated as

$$lnK_{P1} = \frac{-4576.752}{T} + 115.54 - 18.453 \ln T + \left(\frac{-106.736}{T} + 0.69171 \right) \sqrt{sal}$$
$$+ \left(\frac{-0.65643}{T} - 0.01844 \right) sal,$$

$$K_{P1} = \exp(lnK_{P1}). \tag{A.43}$$

The value of K_{P2} is calculated as

$$lnK_{P2} = \frac{-8814.715}{T} + 172.1033 - 27.927 \ln(T) + \left(\frac{-160.34}{T} + 1.3566 \right) \sqrt{sal}$$
$$+ \left(\frac{0.37335}{T} - 0.05778 \right) sal,$$

$$K_{P2} = \exp(lnK_{P2}). \tag{A.44}$$

The value of K_{P3} is calculated as

$$lnK_{P3} = \frac{-3070.75}{T} - 18.126 + \left(\frac{17.27039}{T} + 2.81197\right)\sqrt{sal}$$
$$+ \left(\frac{-44.99486}{T} - 0.09984\right)sal,$$

$$K_{P3} = \exp(lnK_{P3}).$$ (A.45)

All three values are on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. These estimates are from the CO2SYS Program **Error! Reference source not found.** where they cite Yao and Millero (1995) /42/.

Set of constants: 7 Peng

The values of K_{P1}, K_{P2} and K_{P3} are calculated as

$$K_{P1} = 0.02,$$ (A.46)

$$K_{P2} = \exp\left(-9.039 - \frac{1450}{T}\right),$$ (A.47)

$$K_{P3} = \exp\left(4.466 - \frac{7276}{T}\right).$$ (A.48)

The value of K_{P1} is on the seawater scale and in $\mathrm{mol/kg\text{-}sw}$. The values of K_{P2} and K_{P3} are on the NBS scale and dimensionless. (They are dimensionless because $[\mathrm{H^+}]_{NBS} = a_H$ is dimensionless.) The value of K_{P1} is from the CO2SYS Program **Error! Reference source not found.** where they have the following comment:

> *"Peng et al. don't include the contribution from this term, but it is so small it doesn't contribute. It needs to be kept so that the routines work ok."*

The estimates of K_{P2} and K_{P3} are from the CO2SYS Program **Error! Reference source not found.** where they cite Kester and Pytkowicz (1967) /20/ and comment as follows:

> "*these are only for sals 33 to 36 and are on the NBS scale*"

Set of constants: 6, 8 GEOSECS, Freshwater

The values of K_{P1}, K_{P2} and K_{P3} are not used for these options.

A.3.6   Dissociation constant of silicic acid: K_{Si}

The estimate of the dissociation constant K_{Si} of silicic acid depends on the **Set of constants** setting.

Set of constants: 1-5, 9-14 Standard

The value of K_{Si} is calculated as

$$lnK_{Si} = \frac{-8904.2}{T} + 117.4 - 19.334\ln T + \left(\frac{-458.79}{T} + 3.5913\right)\sqrt{IonS}$$
$$+ \left(\frac{188.74}{T} - 1.5998\right)IonS + \left(\frac{-12.1652}{T} + 0.07871\right)(IonS)^2,$$

$$K_{Si} = \exp(lnK_{Si}).$$ (A.49)

The value is on the seawater scale and in $\mathrm{mol/kg\text{-}H_2O}$. The value is converted to $\mathrm{mol/kg\text{-}sw}$ by multiplying by the factor in eq. (A.7). This estimate of K_{Si} is from the CO2SYS Program **Error! Reference source not found.** where they cite Yao and Millero (1995) /42/.

Set of constants: 7 Peng

The value of K_{Si} is defined as

$$K_{Si} = 0.0000000004. \tag{A.50}$$

The value is on the NBS scale and is dimensionless. (It is dimensionless because $[\mathrm{H^+}]_{NBS} = a_H$ is dimensionless.) This estimate of K_{Si} is from the CO2SYS Program **Error! Reference source not found.** where they cite Sillen et al. (1964) /38/.

Set of constants: 6, 8 GEOSECS, Freshwater

The value of K_{Si} is not used for these options.

A.3.7 Dissociation constant of boric acid: K_B

The estimate of the dissociation constant K_B of boric acid depends on the **Set of constants** setting.

Set of constants: 1-5, 9-14 Standard

The value of K_B is calculated as

$$top = -8966.9 - 2890.53\sqrt{sal} - 77.942\,sal + 1.728\,\sqrt{sal}\,sal - 0.0996\,sal^2,$$

$$\begin{aligned} lnK_B = \frac{top}{T} &+ 148.0248 + 137.1942\,\sqrt{sal} + 1.62142\,sal \\ &+ \left(-24.4344 - 25.085\,\sqrt{sal} - 0.2474\,sal\right)\ln T + 0.053105\,\sqrt{sal}\,T, \end{aligned}$$

$$K_B = \exp(lnK_B). \tag{A.51}$$

The value is on the total scale and in $\mathrm{mol/kg\text{-}sw}$. This estimate of K_B is from the CO2SYS Program **Error! Reference source not found.** where they cite Dickson (1990) /9/.

Set of constants: 6, 7 GEOSECS, Peng

The value of K_B is calculated as

$$logK_B = -9.26 + 0.00886\,sal + 0.01\,t,$$

$$K_B = 10^{logK_B}. \tag{A.52}$$

The value is on the NBS scale and is dimensionless. (It is dimensionless because $[\mathrm{H^+}]_{NBS} = a_H$ is dimensionless.) This estimate of K_B is from the CO2SYS Program **Error! Reference source not found.** where they cite Lyman (1957) /24/ and Li et al. (1969) /23/.

Set of constants: 8 Freshwater

The value of K_B is not used for this option.

A.3.8   Dissociation constant of water: K_W

The estimate of the dissociation constants K_W of water depends on the **Set of constants** setting.

Set of constants: 1-5, 9-14 Standard

The value of K_W is calculated as

$$lnKW = 148.9802 - \frac{13847.26}{T} - 23.6521 \ln T$$
$$+ \left(-5.977 + \frac{118.67}{T} + 1.0495 \ln T \right) \sqrt{sal} - 0.01615\, sal,$$

$$K_W = \exp(lnKW).$$
(A.53)

The value is on the seawater scale and in $(\text{mol/kg-sw})^2$. This estimate of K_W is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1995) /29/ and comment as follows:

"his check value of 1.6 umol/kg-SW should be 6.2"

Set of constants: 6 GEOSECS

The value of K_W is not used for this option.

Set of constants: 7 Peng

The value of K_W is calculated as

$$lnKW = 148.9802 - \frac{13847.26}{T} - 23.6521 \ln T$$
$$+ \left(-79.2447 + \frac{3298.72}{T} + 12.0408 \ln T \right) \sqrt{sal}$$
$$- 0.019813\, sal,$$

$$K_W = \exp(lnKW).$$
(A.54)

The value is on the seawater scale and in $(\text{mol/kg-sw})^2$. This estimate of K_W is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1979) /27/.

Set of constants: 8 Freshwater

The value of K_W is calculated as

$$lnKW = 148.9802 - \frac{13847.26}{T} - 23.6521 \ln T,$$

$$K_W = \exp(lnKW).$$
(A.55)

The value is on the free scale, which is equivalent to the total and the seawater scale for this option. The value is in $(\text{mol/kg-H}_2\text{O})^2$ which is equivalent to $(\text{mol/kg-sw})^2$ for this option. Please note that this expression gives the same result as using $sal = 0$ in the standard estimate (A.53) or the Peng estimate (A.54). This estimate of K_W is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1979) /27/ and note that the data are from Harned and Owen (1958) /18/.

A.3.9 Dissociation constant of hydrogen sulphate: K_S

The estimate of the dissociation constant K_S of hydrogen sulphate depends on the **K HSO4** setting.

K HSO4: 1 Dickson

The value of K_S is calculated as

$$lnKS = \frac{-4276.1}{T} + 141.328 - 23.093 \ln(T)$$
$$+ \left(\frac{-13856}{T} + 324.57 - 47.986 \ln(T) \right) \sqrt{IonS} + \left(\frac{35474}{T} \right.$$
$$- 771.54 + 114.723 \ln(T) \right) IonS + \frac{-2698}{T} IonS^{3/2}$$
$$+ \frac{1776}{T} IonS^2,$$

$$K_S = \exp(lnKS). \tag{A.56}$$

The value is on the free scale and in $mol/kg\text{-}H_2O$. The value is converted to $mol/kg\text{-}sw$ by multiplying by the factor in eq. (A.7). This estimate of K_S is from the CO2SYS Program **Error! Reference source not found.** where they cite Dickson (1990, eqs. 22-23, p. 123 and table 4, p. 121) /9/ and comment as follows:

> "The goodness of fit is .021.
> It was given in mol/kg-H2O. I convert it to mol/kg-SW.
> TYPO!!!!!! on p. 121: the constant e9 should be e8."

K HSO4: 2 Khoo et al.

The value of K_S is calculated as

$$pKS = \frac{647.59}{T} - 6.3451 + 0.019085\,T - 0.5208\,\sqrt{IonS},$$

$$K_S = 10^{-pKS}. \tag{A.57}$$

The value is on the free scale and in $mol/kg\text{-}H_2O$. The value is converted to $mol/kg\text{-}sw$ by multiplying by the factor in eq. (A.7). This estimate of K_S is from the CO2SYS Program **Error! Reference source not found.** where they cite Khoo et al. (1977, eq. 20, p. 33) /21/ and comment as follows:

> "KS was found by titrations with a hydrogen electrode of artificial seawater containing sulfate (but without F) at 3 salinities from 20 to 45 and artificial seawater NOT containing sulfate (nor F) at 16 salinities from 15 to 45, both at temperatures from 5 to 40 deg C.
> KS is on the Free pH scale (inherently so).
> It was given in mol/kg-H2O. I convert it to mol/kg-SW.
> He finds log(beta) which = my pKS; his beta is an association constant.
> The rms error is .0021 in pKS, or about .5% in KS."

A.3.10 Dissociation constant of hydrogen fluoride: K_F

For all options, the value of the dissociation constant K_F of hydrogen fluoride is calculated as

$$lnKF = \frac{1590.2}{T} - 12.641 + 1.525\sqrt{IonS},$$

$$K_F = \exp(lnKF). \tag{A.58}$$

The value is on the free scale and in $\mathrm{mol/kg\text{-}H_2O}$. The value is converted to $\mathrm{mol/kg\text{-}sw}$ by multiplying by the factor in eq. (A.7). The estimate of K_F is from the CO2SYS Program **Error! Reference source not found.** where they cite Dickson and Riley (1979) /10/.

A.4 Pressure effects on constants

This section presents the estimates for pressure effects on the dissociation constants and for which options they are used. The pressure effects depend on temperature, but not on salinity. The estimates are based on the code of the CO2SYS Program **Error! Reference source not found.** where they have the following comment:

"*No salinity dependence is given for the pressure coefficients here. It is assumed that the salinity is at or very near Sal = 35. These are valid for the SWS pH scale, but the difference between this and the total only yields a difference of .004 pH units at 1000 bars, much less than the uncertainties in the values.*"

The pressure effects are applied by multiplying the dissociation constants by a correction factor. Let $K(p)$ denote a dissociation constant K for the hydrostatic pressure p, then the pressure effects have the form

$$K(p) = K(0)\, e^{\left(-\Delta V + \frac{1}{2}\kappa p\right)\frac{p}{RT}}, \tag{A.59}$$

where ΔV and κ are parameters that depend on temperature. The base values $K(0)$ of the dissociation constants without pressure effects were estimated in appendix A.3. For the gas constant R the following value is used:

$$R = 83.144621\frac{\mathrm{bar}\cdot\mathrm{cm^3}}{\mathrm{mol}\cdot\mathrm{K}}. \tag{A.60}$$

This value is from CO2SYS Program **Error! Reference source not found.** where they cite NIST Physical Reference Data (http://physics.nist.gov/cgi-bin/cuu/Value?r). Temperature t in degrees Celsius and temperature T in Kelvin are related according to eq. (A.6). In the following, the pressure effects are given as estimates of the parameters ΔV and κ; ΔV is in $\mathrm{cm^3/mol}$ and κ is in $\mathrm{cm^3/(mol\cdot bar)}$. Please note that a pressure correction is estimated with respect to a pH scale and is, in general, only valid for a dissociation constant on that scale. Unless otherwise noted, the pressure effects are for the seawater scale.

A.4.1 Dissociation constants of carbonic acid: K_1, K_2

The pressure effects on the dissociation constants K_1 and K_2 of carbonic acid depend on the **Set of constants** setting.

Set of constants: 1-5, 9-14 Standard

The pressure correction parameters for K_1 are calculated as

$$\Delta V = -25.5 + 0.1271\, t, \tag{A.61}$$

$$\kappa = \frac{-3.08 + 0.0877\,t}{1000} \tag{A.62}$$

and the pressure correction parameters for K_2 are calculated as

$$\Delta V = -15.82 - 0.0219\,t, \tag{A.63}$$

$$\kappa = \frac{1.13 + 0.1475\,t}{1000}\,. \tag{A.64}$$

These estimates are from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1995, table 9, eqs. 90-92, p. 675) /29/ and mention that the data are from Culberson and Pytkowicz (1968) /7/.

Set of constants: 6, 7 GEOSECS, Peng

The pressure correction parameters for K_1 are calculated as

$$\Delta V = -24.2 + 0.085\,t, \tag{A.65}$$

$$\kappa = 0 \tag{A.66}$$

and the pressure correction parameters for K_2 are calculated as

$$\Delta V = -16.4 + 0.04\,t, \tag{A.67}$$

$$\kappa = 0\,. \tag{A.68}$$

These estimates are from the CO2SYS Program **Error! Reference source not found.** where they cite Takahashi et al. (1982) /39/ and include the following comments:

"[Takashi et al.] *quotes Culberson and Pytkowicz, L and O 13:403-417, 1968: but the fits are the same as those in Edmond and Gieskes, GCA, 34:1261-1291, 1970 who in turn quote Li, personal communication*
[…] *The pressure dependence of K2 should have a 16.4, not 26.4. This matches the GEOSECS results and is in Edmond and Gieskes*"

Set of constants: 8 Freshwater

The pressure correction parameters for K_1 are calculated as

$$\Delta V = -30.54 + 0.1849\,\text{t} - 0.0023366\,t^2, \tag{A.69}$$

$$\kappa = \frac{-6.22 + 0.1368\,t - 0.001233\,t^2}{1000} \tag{A.70}$$

and pressure correction parameters for K_2 are calculated as

$$\Delta V = -29.81 + 0.115\,t - 0.001816\,t^2, \tag{A.71}$$

$$\kappa = \frac{-5.74 + 0.093\,t - 0.001896\,t^2}{1000}\,. \tag{A.72}$$

These estimates are from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1983) /28/.

A.4.2 Dissociation constants of phosphoric acid: K_{P1}, K_{P2}, K_{P3}

All the options that use the dissociation constants K_{P1}, K_{P2} and K_{P3} of phosphoric acid employ the same estimate for the pressure effects.

Set of constants: 1-5, 7, 9-14 Standard, Peng

The pressure correction parameters for K_{P1} are calculated as

$$\Delta V = -14.51 + 0.1211\, t - 0.000321\, t^2, \tag{A.73}$$

$$\kappa = \frac{-2.67 + 0.0427\, t}{1000}. \tag{A.74}$$

The pressure correction parameters for K_{P2} are calculated as

$$\Delta V = -23.12 + 0.1758\, t - 0.002647\, t^2, \tag{A.75}$$

$$\kappa = \frac{-5.15 + 0.09\, t}{1000}. \tag{A.76}$$

The pressure correction parameters for K_{P3} are calculated as

$$\Delta V = -26.57 + 0.202\, t - 0.003042\, t^2, \tag{A.77}$$

$$\kappa = \frac{-4.08 + 0.0714\, t}{1000}. \tag{A.78}$$

These estimates are from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1995, table 9, eqs. 90-92, p. 675) /29/.

Set of constants: 6, 8 GEOSECS, Freshwater

The values of K_{P1}, K_{P2} and K_{P3} are not used for these options.

A.4.3 Dissociation constant of silicic acid: K_{Si}

All the options that use the dissociation constant K_{Si} of silicic acid employ the same estimate for the pressure effects.

Set of constants: 1-5, 7, 9-14 Standard, Peng

The pressure correction parameters for K_{Si} are calculated as

$$\Delta V = -29.48 + 0.1622\, t - 0.002608\, t^2, \tag{A.79}$$

$$\kappa = -\frac{2.84}{1000}. \tag{A.80}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1995, table 9, eqs. 90-92, p. 675) /29/ with these comments:

> "*The only mention of this is Millero, 1995 where it is stated that the values have been estimated from the values of boric acid. HOWEVER, there is no listing of the values in the table. I used the values for boric acid from above.*"

Set of constants: 6, 8 GEOSECS, Freshwater

The value of K_{Si} is not used for these options.

A.4.4 Dissociation constant of boric acid: K_B

The pressure effects on the dissociation constant K_B of boric acid depend on the **Set of constants** setting.

Set of constants: 1-5, 9-14 Standard

The pressure correction parameters for K_B are calculated as

$$\Delta V = -29.48 + 0.1622\, t - 0.002608\, t^2, \tag{A.81}$$

$$\kappa = -\frac{2.84}{1000}. \tag{A.82}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1979, table 5, eqs. 7, 7a, 7b, pp. 1656-1657) /27/ and mention that the data are from Culberson and Pytkowicz (1968) /7/.

Set of constants: 6, 7 GEOSECS, Peng

The pressure correction parameters for K_B are calculated as

$$\Delta V = -27.5 + 0.095\, t, \tag{A.83}$$

$$\kappa = 0. \tag{A.84}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Takahashi et al. (1982) /39/ with the following comments:

"[Takashi et al.] *quotes Culberson and Pytkowicz, L and O 13:403-417, 1968: but the fits are the same as those in Edmond and Gieskes, GCA, 34:1261-1291, 1970 who in turn quote Li, personal communication*".

Set of constants: 8 Freshwater

The value of K_B is not used for this option.

A.4.5 Dissociation constant of water: K_W

The pressure effects on the dissociation constant K_W of water depend the **Set of constants** setting.

Set of constants: 1-5, 7, 9-14 Standard, Peng

The pressure correction parameters for K_W are calculated as

$$\Delta V = -20.02 + 0.1119\, t - 0.001409\, t^2, \tag{A.85}$$

$$\kappa = \frac{-5.13 + 0.0794\, t}{1000}. \tag{A.86}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1983) /28/.

Set of constants: 6 GEOSECS

The value of K_W is not used for this option.

Set of constants: 8 Freshwater

The pressure correction parameters for K_W are calculated as

$$\Delta V = -25.6 + 0.2324\,t - 0.0036246\,t^2, \tag{A.87}$$

$$\kappa = \frac{-7.33 + 0.1368\,t - 0.001233\,t^2}{1000}. \tag{A.88}$$

This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1983) /28/. The CO2SYS Program **Error! Reference source not found.** has these comments for the calculations:

> "*!!! NOTE the temperature dependence of KappaK1 and KappaKW
> for fresh water in Millero, 1983 are the same.*"

A.4.6 Dissociation constant of hydrogen sulphate: K_S

The pressure effects on the dissociation constant K_S of hydrogen sulphate are the same for all options. The pressure correction parameters are calculated as

$$\Delta V = -18.03 + 0.0466\,t + 0.000316\,t^2, \tag{A.89}$$

$$\kappa = \frac{-4.53 + 0.09\,t}{1000}. \tag{A.90}$$

The pressure correction is valid for the free scale. This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1995, table 9, eqs. 90-92, p. 675) /29/.

A.4.7 Dissociation constant of hydrogen fluoride: K_F

The pressure effects on the dissociation constant K_F of hydrogen fluoride are the same for all options. The pressure correction parameters are calculated as

$$\Delta V = -9.78 - 0.009\,t - 0.000942\,t^2, \tag{A.91}$$

$$\kappa = \frac{-3.91 + 0.054\,t}{1000}. \tag{A.92}$$

The pressure correction is valid for the free scale. This estimate is from the CO2SYS Program **Error! Reference source not found.** where they cite Millero (1995, table 9 and eqs. 90-92, p. 675) /29/.