
CO2 Partial Pressure and Fugacity

Before dealing with chemical equations in seawater, we should first focus on the compound in air that starts a series of reactions when dissolved, namely carbon dioxide. Its partial pressure is continuously monitored, by different stations around the world, the most famous one being the Mauna Loa Observatory (Hawaii).

The partial pressure of a gas in a mixture of gases is simply the total pressure multiplied by its mole fraction. However, the activity of CO2 is not exactly equal to its partial pressure. For accurate calculations, the fugacity of CO2, f_{CO_2} , may be used instead of its partial pressure. The fugacity of CO2 is numerically very similar to CO2 partial pressure in atm, and therefore corresponds to CO2 ppm in dry air by the Dalton law. The fugacity can be calculated from its partial pressure (Koerzinger,1999 Zeebe,2001), requiring two virial coefficients B and δ , which are defined as (Weiss,1974) :

$$B = (-1636.75 + 12.0408 \cdot T - 3.27957 \cdot 10^{-2} \cdot T^2 + 3.16528 \cdot 10^{-5} \cdot T^3) \cdot 10^{-6}$$
$$\delta = (57.7 - 0.118 \cdot T) \cdot 10^{-6} \quad T [K], \quad B [m^3 mol^{-1}]$$

$$f(CO_2) = p(CO_2) \cdot \exp\left(P_{tot} \frac{B + 2\delta}{RT}\right) \quad P_{tot} [Pa] \quad f(CO_2), p(CO_2) [\mu atm] \quad T [K] \quad R = 8.314 [JK^{-1}]$$

$f(CO_2)$ shall be corrected by accounting for water partial pressure (pH₂O) . Indeed it refers to dry air, so it must be slightly adjusted for vapor pressure of water at temperature T. This in turn depends on relative humidity (rH) and saturated water pressure, calculated according to the algorithm proposed by Weiss and Price,1980. This is calculated as a first step :

$$p(H_2O) = \exp\left[24.4543 - \frac{6745.09}{T} - 4.8489 \cdot \log\left(\frac{T}{100}\right) - 0.000544 \cdot S\right] \quad T [K], \quad S [(g - salt)/(kg - soln)] \quad p(H_2O) [atm], \quad \log = \log_e$$

Then $f(CO_2)$ is corrected introducing rH, although this value is usually left to 100 in the simulation (air is saturated over ocean surface).

$$f(CO_2)_{corr} = f(CO_2) \cdot \left[1 - p(H_2O) \cdot \frac{rH}{100}\right] \quad f(CO_2) [\mu atm] \quad 0 \leq rH \leq 100$$

Hydration of Carbon Dioxide (K_0) $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$

$$K_0 = \frac{[\text{H}_2\text{CO}_3^*]}{f(\text{CO}_2)}$$

$$K_0 = \exp\left\{\frac{9345.17}{T} - 60.2409 + 23.3585 * \log\left(\frac{T}{100}\right) + S * [0.023517 - 0.00023656 * T + 0.0047036 * \left(\frac{T}{100}\right)^2]\right\} \quad T[K] \quad S[g/kg-soln], \quad \log = \log_e$$

$f(\text{CO}_2)$ is the fugacity of CO_2 , which is numerically very similar to CO_2 partial pressure in μatm or ppmv (parts per million in volume), if total pressure is 1 atm. by the Dalton law.

H_2CO_3^* is the sum of the true acid form H_2CO_3 and the hydrated CO_2 , indicated by $\text{CO}_2(\text{aq})$. From now on asterisk is omitted, so that $[\text{H}_2\text{CO}_3]$ indicates the sum of acid form and hydrated CO_2 . The algorithm is taken from Zeebe,2001

Ionic Water Product due to $2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ reaction

$$K_w = [\text{H}^+][\text{OH}^-]$$

Water itself is a weak electrolyte whose dissociation must be carefully taken into account. In seawater the following expression is used to represent its dependence on temperature and salinity. As is the case for the following expressions, it should not be extrapolated to zero or near zero salinity, as it results from experiments with salinity from 25 to 45 (grams-of-salts/Kg-of-solution) (Zeebe,2001).

$$K_w = \exp\left\{148.96502 - \frac{13847.26}{T} - 23.6521 * \log(T) + \left[\frac{118.67}{T} - 5.977 + 1.0495 * \log(T)\right] * S^{0.5} - 0.01615 * S\right\}$$

$[\text{H}^+] = \text{Total scale}, \quad \log = \log_e, \quad \text{pH} = \text{pH}_{\text{SWS}}$

First Dissociation of Carbon Dioxide (K_1) $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$

$$K_1 = \frac{[HCO_3^-] \cdot [H^+]}{[H_2CO_3]}$$

$$K_1 = -10^{\left\{ \frac{6320.813}{T} + 19.568224 \cdot \log(T) - 126.34048 + 5.592953 \cdot S^{0.5} + 0.028845 \cdot S - (6.388 \cdot 10^{-5}) \cdot S^2 + \frac{(-225.7489 \cdot S^{0.5} - 4.761 \cdot S)}{T} - 0.8715109 \cdot S^{0.5} \cdot \log(T) \right\}}$$

(Waters,2014) $T[K]$ $S[g/kg-soln]$ $\log = \log_e$, $pH = Free Scale$

Second Dissociation Constant of Carbon Dioxide (K_2) $HCO_3^- \rightleftharpoons H^+ + HCO_3^{--}$

$$K_2 = \frac{[CO_3^{--}] \cdot [H^+]}{[HCO_3^-]}$$

$$K_2 = -10^{\left\{ \frac{5143.692}{T} + 14.613358 \cdot \log(T) - 90.18333 + 13.396949 \cdot S^{0.5} + 0.12193009 \cdot S - (3.8362 \cdot 10^{-4}) \cdot S^2 + \frac{(-472.8633 \cdot S^{0.5} - 19.03634 \cdot S)}{T} - 2.1563270 \cdot S^{0.5} \cdot \log(T) \right\}}$$

(Waters,2014) $T[K]$, $\log = \log_e$, $pH = Free Scale$

Solubility of calcite (K_{sp}) $CaCO_3 \rightleftharpoons Ca^{++} + CO_3^{--}$

$$K_{sp}(cal) = [Ca^{++}] \cdot [CO_3^{--}]$$

$$K_{sp}(cal) = 10^{\left\{ -171.9065 - 0.077993 \cdot T + \frac{2839.319}{T} + 71.595 \cdot \log_{10}(T) + (-0.77712 + 0.0028426 \cdot T + \frac{178.34}{T}) \cdot S^{0.5} - 0.07711 \cdot S + 0.0041249 \cdot S^{1.5} \right\}}$$

(Zeebe,2001) $T[K]$, $\log = \log_{10}$, $S[g/kg-soln]$

Solubility of Aragonite (K_{sp}) $CaCO_3 \rightleftharpoons Ca^{++} + CO_3^{--}$

$$K_{sp}(ara) = [Ca^{++}] \cdot [CO_3^{--}]$$

$$K_{sp}(ara) = 10^{[-171.945 - 0.077993 \cdot T + \frac{2903.293}{T} + 71.595 \cdot \log_{10}(T) + (-0.068393 + 0.0017276 \cdot T + \frac{88.135}{T}) \cdot S^{0.5} - 0.10018 \cdot S + 0.0059415 \cdot S^{1.5}]}$$

(Zeebe,2001) T [K], $\log = \log_{10}$, S [g/kg-soln]



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

$$K_B = \exp\left\{\frac{(-8966.9 - 2890.53 \cdot S^{0.5} - 77.942 \cdot S + 1.728 \cdot S^{1.5} - 0.0996 \cdot S^2)}{T} + 148.0248 + 137.1942 \cdot S^{0.5} + 1.62142 \cdot S - (24.4344 + 25.085 \cdot S^{0.5} + 0.2474 \cdot S) \cdot \log(T) + 0.053105 \cdot S^{0.5} \cdot T\right\}$$

(Zeebe,2001) T [K], $pH = Free Scale$, $\log = \log_e$



$$K_S = \frac{[H^+] \cdot [SO_4^{2-}]}{[HSO_4^-]}$$

$$K_S = \exp\left\{\frac{-4276.1}{T} + 141.328 - 23.039 \cdot \log(T) + \left(\frac{-13856}{T} + 324.57 - 47.986 \cdot \log(T)\right) \cdot I^{0.5} + \left(\frac{35474}{T} - 771.54 + 114.723 \cdot \log(T)\right) \cdot I - \frac{2698}{T} \cdot I^{1.5} + \frac{1766}{T} \cdot I^2 + \log(1 - 0.001005 \cdot S)\right\}$$

$$I(\text{ionic strenght}) = \frac{19.924 \cdot S}{1000 - 1.005 \cdot S}$$

(Zeebe,2001) T [K], $pH = Free Scale$, $\log = \log_e$



$$K_F = \frac{[H^+] \cdot [F^-]}{[HF]}$$

$$K_F = \exp\left\{\frac{1590.2}{T} - 12.641 + 1.525 \cdot I^{0.5} + \log(1 - 0.001005 \cdot S)\right\}$$

(Zeebe, 2001) T [K], $pH = \text{Free Scale} (*)$, $I = \text{ionic strength}$, $\log = \log_e$

(*) Differently from Zeebe, 2001 K_F value has NOT been converted to pH Total Scale, so pH Free Scale is used.

The three Dissociations of Phosphoric Acid H_3PO_4

For the three dissociation reactions of phosphoric acid in seawater and the following of silicic acid in seawater, the formulae for empiric constants are reported, but these are not used at the present for the calculation in the 'SeaWaterCalc' code. The concentration of the two acids is very low in seawater and locally variable. They could easily be implemented by inserting them in the code.

$$K_{1P} = \frac{[H^+] \cdot [H_2PO_4^-]}{[H_3PO_4]} \quad H_3PO_4 \Leftrightarrow H^+ + H_2PO_4^-$$

$$K_{1P} = \frac{[H^+] \cdot [HPO_4^{2-}]}{[H_2PO_4^-]} \quad H_2PO_4^- \Leftrightarrow H^+ + HPO_4^{2-}$$

$$K_{1P} = \frac{[H^+] \cdot [PO_4^{3-}]}{[HPO_4^{2-}]} \quad HPO_4^{2-} \Leftrightarrow H^+ + PO_4^{3-}$$

$$K_{1P} = \exp\left\{\frac{-4576.752}{T} + 115.525 - 18.453 \cdot \log(T) + \left(\frac{-106.736}{T} + 0.69171\right) \cdot S^{0.5} + \left(\frac{-0.65643}{T} - 0.01844\right) \cdot S\right\}$$

$$K_{2P} = \exp\left\{\frac{-8814.715}{T} + 172.0883 - 27.927 \cdot \log(T) + \left(\frac{-160.34}{T} + 1.3566\right) \cdot S^{0.5} + \left(\frac{0.37335}{T} - 0.05778\right) \cdot S\right\}$$

$$K_{3P} = \exp\left\{\frac{-3070.75}{T} - 18.141 + \left(\frac{17.27039}{T} + 2.81197\right) \cdot S^{0.5} + \left(\frac{-44.99486}{T} - 0.09984\right) \cdot S\right\}$$

(Zeebe, 2001) T [K], $pH = \text{Total Scale}$, $\log = \log_e$, S [g/kg - soln]

Dissociation of Silicic Acid $\text{Si(OH)}_4 \rightleftharpoons \text{H}^+ + \text{H}_3\text{SiO}_4^-$

$$K_{\text{Si}} = \frac{[\text{H}^+][\text{H}_3\text{SiO}_4^-]}{[\text{H}_4\text{SiO}_4]}$$

$$K_{\text{Si}} = \exp\left\{\frac{-8904.2}{T} + 117.385 - 19.334 \cdot \log(T) + \left(3.5913 - \frac{458.79}{T}\right) \cdot I^{0.5} + \left(\frac{188.74}{T} - 1.5998\right) \cdot I + \left(0.07871 - \frac{12.1652}{T}\right) \cdot I^2 + \log(1 - 0.001005 S)\right\}$$

(Zeebe, 2001) T [K], $[\text{H}^+] = \text{Total Scale}$, I (ionic strength) = $\frac{19.924 \cdot S}{(1000 - 1.005 \cdot S)}$, $\log = \log_e$