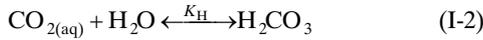
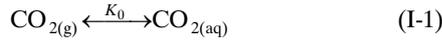


# Appendix I

## Carbonate system thermodynamics

The inorganic aqueous carbonate system in the ocean comprises four dissolved species,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , characterized by the following series of reactions



where  $K_0$  is the solubility coefficient of  $\text{CO}_2$ ,  $K_{\text{H}}$  is the dissociation constant of  $\text{H}_2\text{O}$ , and  $K_1$  and  $K_2$  are the first and second dissociation constants of carbonic acid, respectively, all referenced to seawater. Given the total dissolved inorganic  $\text{CO}_2$  ( $\Sigma\text{CO}_2$ ) and carbonate alkalinity ( $A_{\text{C}}$ ) concentration in seawater, this system can be defined [Millero and Sohn, 1992] by solving for three of the dissolved carbonate species

$$[\text{CO}_2] = \Sigma\text{CO}_2 - A_{\text{C}} +$$

$$\frac{A_{\text{C}} \cdot K - \Sigma\text{CO}_2 \cdot K - 4 \cdot A_{\text{C}} + Z}{2 \cdot (K - 4)} \quad (\text{I-5})$$

$$[\text{HCO}_3^-] = \frac{\Sigma\text{CO}_2 \cdot K - Z}{K - 4} \quad (\text{I-6})$$

$$[\text{CO}_3^{2-}] = \frac{A_{\text{C}} \cdot K - \Sigma\text{CO}_2 \cdot K - 4 \cdot A_{\text{C}} + Z}{2 \cdot (K - 4)} \quad (\text{I-7})$$

where

$$K = \frac{K_1}{K_2} \quad (\text{I-8})$$

and

$$Z = \left( (4 \cdot A_{\text{C}} + \Sigma\text{CO}_2 \cdot K - A_{\text{C}} \cdot K)^2 + 4 \cdot (K - 4) \cdot A_{\text{C}}^2 \right)^{0.5} \quad (\text{I-9})$$

The total alkalinity ( $A_{\text{T}}$ ) of seawater is defined as the “concentration of all the bases that can accept  $\text{H}^+$  when a titration is made with  $\text{HCl}$  to the carbonic acid endpoint” [Millero and Sohn, 1992]. However, in order to improve overall model computational efficiency, the exact definition of Dickson [1981] is simplified by omitting the relatively

minor contributions made by S, F, and N species. In addition, since the contribution from phosphoric acid to total alkalinity is relatively small and exhibits very little temperature or pressure dependence, this is approximated by a simple linear dependence on ambient  $\text{PO}_4^{3-}$  concentration (producing an additional error in  $A_{\text{T}}$  of  $\leq 0.01\%$ ).  $A_{\text{T}}$  is therefore written

$$A_{\text{T}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{H}_4\text{BO}_4^-] + [\text{H}_3\text{SiO}_4^-] + [\text{OH}^-] + 1.1[\text{PO}_4^{3-}] \quad (\text{I-10})$$

Carbonate alkalinity ( $A_{\text{C}}$ ) is defined as

$$A_{\text{C}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (\text{I-11})$$

and thus can be approximated by

$$A_{\text{C}} = A_{\text{T}} - \left( [\text{H}_4\text{BO}_4^-] + [\text{H}_3\text{SiO}_4^-] + [\text{OH}^-] + 1.1[\text{PO}_4^{3-}] \right) \quad (\text{I-12})$$

The concentrations of  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ,  $\text{H}_4\text{BO}_4^-$ , and  $\text{H}_3\text{SiO}_4^-$  are calculated via their respective dissociation constants,  $K_1$ ,  $K_2$ ,  $K_{\text{H}}$ ,  $K_{\text{B}}$ , and  $K_{\text{Si}}$ , defined by

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{O}][\text{CO}_2]} \quad (\text{I-13})$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (\text{I-14})$$

$$K_{\text{B}} = \frac{[\text{H}^+][\text{H}_4\text{BO}_4^-]}{[\text{H}_2\text{O}][\text{H}_3\text{BO}_3]} \quad (\text{I-15})$$

$$K_{\text{H}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (\text{I-16})$$

$$K_{\text{Si}} = \frac{[\text{H}^+][\text{H}_3\text{SiO}_4^-]}{[\text{H}_4\text{SiO}_4]} \quad (\text{I-17})$$

where  $[\text{H}_2\text{O}] \equiv 1$ . Dissociation constants are typically written as empirically-determined multi-variate regressions of temperature and salinity (or total ionic strength), detailed in Table I-1. All calculations assume the same seawater  $p\text{H}$  scale ( $p\text{H}_{\text{SWS}}$ ) [Millero, 1995]. It is therefore necessary to make a correction to  $K_{\text{B}}$  to account for its being determined

on the total pH ( $pH_{\text{tot}}$ ) scale. Rather than make an explicit conversion from a  $pH_{\text{tot}}$  to  $pH_{\text{SWS}}$  basis, which requires consideration of the dissociation of HF and  $H_2SO_4$  [Millero, 1995], since there is little dependence on salinity a simple linear dependence on temperature is made. A correction must also be made to  $K_{\text{Si}}$  since it was not determined in seawater. The concentration of silicic acid and phosphoric acids are taken directly from the ocean tracer field, while that of boric acid in seawater is simply estimated from salinity [Millero, 1982].

The fugacity of  $CO_2$  in seawater ( $fCO_2$ ) rather than the partial pressure ( $pCO_2$ ) is calculated as the  $CO_2$ -seawater system exhibits considerable non-ideality, with the value of  $fCO_2$  in air about 0.3% lower than that of  $pCO_2$  at pressures of order of 1 atm.  $fCO_2$  is given by Weiss [1974]

$$fCO_2 = \frac{[CO_2]}{Q_{CO_2}} \quad (\text{I-18})$$

The thermodynamics of the solid-aqueous system are defined by the solubility products for the two solid phases of calcium carbonate ( $CaCO_3$ ), calcite ( $K_{\text{cal}}$ ) and aragonite ( $K_{\text{arg}}$ ), and calculated using empirical functions of temperature and salinity [Mucci, 1983] (given in Table I-1). From these, the saturation state of  $CaCO_3$  in seawater can be obtained, which is defined in terms of a solubility ratio ( $\Omega$ ) for each phase

$$\Omega_{\text{cal}} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{\text{cal}}} \quad (\text{I-19})$$

$$\Omega_{\text{arg}} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{\text{arg}}} \quad (\text{I-20})$$

### Determination of pH

It remains to determine the hydrogen ion concentration ( $[H^+]$ ) and thus the pH of the system. Since there is no analytical solution, this is estimated by means of an iterative numerical approximation. The sequence of stages in this is as follows

1. An initial guess made of  $[H^+]$ ; at model spin-up this is taken to be  $7 \times 10^{-9}$ , otherwise the equilibrium value from the previous time step is assumed.
2.  $CO_2$  alkalinity is estimated from the current value of  $[H^+]$ , from which the concentrations of  $HCO_3^-$ ,  $CO_3^{2-}$ , and  $CO_{2(aq)}$  are calculated.
3.  $[HCO_3^-]$ ,  $[CO_3^{2-}]$ , and  $[CO_2]$  calculated in (2) are used in conjunction with the two dissociation constants of carbonic acid ( $K_1$ ,  $K_2$ ) to produce two different estimates for  $[H^+]$

$$[H^+]_1 = K_1 \cdot \frac{[CO_2]}{[HCO_3^-]} \quad (\text{I-21})$$

$$[H^+]_2 = K_2 \cdot \frac{[HCO_3^-]}{[CO_3^{2-}]} \quad (\text{I-22})$$

4. A new estimate of  $[H^+]$  is then made by combining the two estimates made above

**Table I-1** Empirical Descriptions of Aqueous Carbonate System Dissociation Constants

Constant	Thermodynamic approximation	Reference
$K_1$	$\ln(K_1) = 2.18867 - 2275.036 / T - 1.468591 \cdot \ln(T) + (-0.138681 - 9.33291 / T) \cdot S^{0.5} + 0.0726483 \cdot S - 0.00574938 \cdot S^{1.5}$	Millero [1995]
$K_2$	$\ln(K_2) = -0.84226 - 3741.1288 / T - 1.437139 \cdot \ln(T) + (-0.128417 - 24.41239 / T) \cdot S^{0.5} + 0.1195308 \cdot S - 0.0912840 \cdot S^{1.5}$	Millero [1995]
$K_B$	$\ln(K_B) = 148.0248 + 137.1942 \cdot S^{0.5} + 1.62142 \cdot S + (-8966.90 - 2890.53 \cdot S^{0.5} - 77.942 \cdot S + 1.728 \cdot S^{1.5} - 0.0996 \cdot S^2) / T + (-24.4344 - 25.085 \cdot S^{0.5} - 0.2474 \cdot S) \cdot \ln(T) + 0.053105 \cdot S^{0.5} \cdot T$	Dickson [1990]
$K_H$	$\ln(K_H) = 148.9802 - 13847.26 / T - 23.6521 \cdot \ln(T) + (-5.977 + 118.67 / T + 1.0495 \cdot \ln(T)) \cdot S^{0.5} - 0.01615 \cdot S$	Millero [1992]
$K_{\text{Si}}$	$\ln(K_{\text{Si}}) = 117.40 - 8904.2 / T - 19.334 \ln(T) + (3.5913 - 458.79 / T) \cdot I^{0.5} + (-1.5998 + 188.74 / T) \cdot I + (0.07871 - 12.1652 / T) \cdot I^2$ <sup>1</sup>	Millero [1995]
$K_{\text{cal}}$	$\log_{10}(K_{\text{cal}}) = -171.9065 - 0.077993 \cdot T + 2839.319 / T + 71.595 \cdot \log_{10}(T) + (-0.77712 + 0.0028426 \cdot T + 178.34 / T) \cdot S^{0.5} - 0.07711 \cdot S + 0.0041249 \cdot S^{1.5}$	Mucci [1983]
$K_{\text{arg}}$	$\log_{10}(K_{\text{cal}}) = -171.9450 - 0.077993 \cdot T + 2903.293 / T + 71.595 \cdot \log_{10}(T) + (-0.068393 + 0.0017276 \cdot T + 88.135 / T) \cdot S^{0.5} - 0.10018 \cdot S + 0.0059415 \cdot S^{1.5}$	Mucci [1983]

<sup>1</sup>  $I$  is the ionic strength, defined [Millero, 1982];  $I = 19.92 \cdot S / (10000 - 1005 \cdot S)$

$$[\text{H}^+] = \left( [\text{H}^+]_1 \cdot [\text{H}^+]_2 \right)^{0.5} \quad (\text{I-23})$$

5. If the difference between new and old estimates of  $[\text{H}^+]$  is greater than 0.1% (equivalent to an error in  $f\text{CO}_2$  of 0.6 ppmv under typical oceanic conditions), steps #2 through #5 are repeated until an approximate convergence is obtained.

#### Pressure-dependence of system thermodynamics

Pressure correction of dissociation constants is carried out assuming a conversion between depth and pressure of 1 dbar  $\text{m}^{-1}$ . The error in this is no more than  $\sim 3\%$ , even at the deep ocean depths (10000 m). Corrections are applied to all of  $K_1$ ,  $K_2$ ,  $K_w$ ,  $K_B$ , and  $K_{\text{Si}}$ . However, the influence on the carbonate system as a whole of pressure effects on the dissociation constants of HF and  $\text{H}_2\text{SO}_4$  (used in converting between different pH scales) are insignificant, and as such are omitted. The general form of the pressure correction factor is [Millero, 1979]

$$\ln \left( \frac{K(P)}{K(0)} \right) = - \left( \frac{\Delta V}{RT} \right) \cdot P + \left( \frac{0.5 \cdot \Delta \kappa}{RT} \right) \cdot P^2 \quad (\text{I-24})$$

where  $P$  is the applied pressure in bars,  $T$  is the temperature ( $^{\circ}\text{C}$ ),  $\Delta V$  and  $\Delta \kappa$  are the molar volume and compressibility change for the dissociation reactions, respectively, and  $R$  is the gas constant ( $83.145 \text{ bar cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ). For each dissociation reaction the values of  $\Delta V$  and  $\Delta \kappa$  in seawater are approximated as function only of temperature (assuming a salinity of 35‰) by

$$\Delta V = a_0 + a_1 \cdot T + a_2 \cdot T^2 \quad (\text{I-25})$$

$$10^3 \cdot \Delta \kappa = b_0 + b_1 \cdot T \quad (\text{I-26})$$

with the coefficients  $a_0 \dots b_1$  given in Table I-2. There is no available relationship describing the effect of pressure on the dissociation of silicic acid. The same pressure effect as for boric acid is therefore assumed.

**Table I-2** Coefficients for Describing Dissociation Constants as a Function of Pressure

Acid	$a_0$	$a_1$	$a_2$	$b_0$	$b_1$	Reference
$\text{H}_2\text{CO}_3$	-2.55E+01	+1.27E-01	+0.00E+00	-3.08E+00	+8.77E-02	Millero [1995]
$\text{HCO}_3^-$	-1.58E+01	-2.19E-02	+0.00E+00	+1.13E+00	-1.47E-01	Millero [1995]
$\text{H}_3\text{BO}_3$	-2.86E+01	+1.21E-01	-3.21E-04	-3.00E+00	+4.27E-02	Millero [1982]
$\text{H}_2\text{O}$	-2.00E+01	+1.12E-01	-1.41E-03	-5.13E+00	+7.49E-02	Millero [1982]
$\text{CaCO}_3$ (calcite)	-4.88E+01	+5.30E-01	+0.00E+00	-1.18E+01	+3.69E-01	Ingle [1975], Millero [1979]
$\text{CaCO}_3$ (aragonite)	-4.60E+01	+5.30E-01	+0.00E+00	-1.18E+01	+3.69E-01	Millero [1979]

