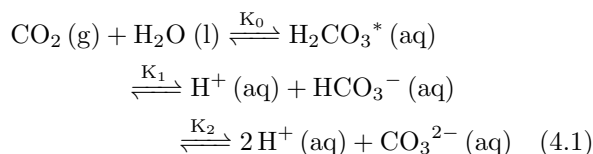


## Chapter 4

# pCO<sub>2</sub> & Marine Carbonate Derivation

The atmospheric concentration of carbon dioxide (pCO<sub>2</sub>) is a primary factor influencing global climate today and through deep time. The oceanic inorganic carbon reservoir is over 50 times that of the atmosphere, so atmosphere-ocean exchange drives pCO<sub>2</sub> over millennial timescales. The goal of this section is to derive a quantitative model which relates pCO<sub>2</sub> to the measurable ocean carbonate system.

When CO<sub>2</sub> dissolves, it reacts with water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>)<sup>1</sup>, bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>). These reactions are reversible, so the following equilibrium is established:



K<sub>0,1,2</sub> are measurable concentration ratios of reactants by products at equilibrium:

$$K_0 = [\text{H}_2\text{CO}_3^*]/\text{pCO}_2 \quad (4.2)$$

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3^*] \quad (4.3)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (4.4)$$

Dissolved Inorganic Carbon (DIC) and Alkalinity (Alk) are also measurable:

$$\begin{aligned} \text{DIC} &= \underset{0.5\%}{[\text{H}_2\text{CO}_3^*]} + \underset{88.6\%}{[\text{HCO}_3^-]} + \underset{10.9\%}{[\text{CO}_3^{2-}]} \\ &\approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \end{aligned} \quad (4.5)$$

<sup>1</sup>It is difficult to distinguish between dissolved carbon dioxide and carbonic acid, so they are grouped as a single species

Alk is the charge-balanced<sup>2</sup> excess of bases in solution, primarily carbonic conjugate bases:

$$\begin{aligned} \text{Alk} &= \underset{76.8\%}{[\text{HCO}_3^-]} + \underset{18.7\%}{2[\text{CO}_3^{2-}]} + \\ &\quad \underset{4.2\%}{[\text{B(OH)}_4^-]} + \underset{0.2\%}{(\Sigma[\text{B}] - \Sigma[\text{A}])} \\ &\approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \end{aligned} \quad (4.6)$$

Rearranging equilibrium constant expressions gives:

$$[\text{H}^+] = K_2 \cdot [\text{HCO}_3^-]/[\text{CO}_3^{2-}] \quad (4.4)$$

$$[\text{H}_2\text{CO}_3^*] = [\text{H}^+][\text{HCO}_3^-]/K_1 \quad (4.3)$$

$$\text{pCO}_2 = [\text{H}_2\text{CO}_3^*]/K_0 \quad (4.2)$$

Sequential substitution and simplification gives:

$$\text{pCO}_2 = \frac{K_2}{K_0 \cdot K_1} \cdot \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]} \quad (4.7)$$

Subtracting (4.6) from (4.5) and substituting the result back into (4.5) gives:

$$[\text{CO}_3^{2-}] \approx \text{Alk} - \text{DIC}$$

$$[\text{HCO}_3^{2-}] \approx 2\text{DIC} - \text{Alk}$$

Finally, substituting back into (4.7) gives:

$$\boxed{\text{pCO}_2 \approx \frac{K_2}{K_0 \cdot K_1} \cdot \frac{(2\text{DIC} - \text{Alk})^2}{\text{Alk} - \text{DIC}}}$$

<sup>2</sup>Concentrations of species which exchange more than one proton are scaled accordingly.