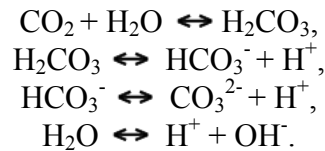


pC/pH Diagrams for Open Systems

The pC/pH diagrams for open systems are similar to those described for the closed systems. The primary difference is that in an open system a component of the system exists as a gas and the system is open to the atmosphere. Or, in other words, the system can exchange matter and energy with the atmosphere. The most important environmental example of such a system is carbon dioxide (CO₂), carbonic acid (H₂CO₃), bicarbonate ion (HCO₃⁻), and carbonate ion (CO₃²⁻) in lakes, rivers, and oceans.

The reactions occurring in this system are:



The equilibrium relationships for this system are:

$$\begin{aligned}K_w &= [\text{H}^+][\text{OH}^-] = 10^{-14}, \\ K_{\text{CO}_2} &= \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}} = 10^{-1.47}, \\ K_1 &= \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{-6.35}, \\ K_2 &= \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.33},\end{aligned}$$

where P_{CO_2} is the partial pressure of CO₂ in the atmosphere.

The open system pC/pH diagrams contain lines describing the concentration of hydroxide (OH⁻) and hydronium ion (H⁺) identical to those for closed systems. However, because open systems can exchange matter with the atmosphere the total inorganic carbon concentration is not constant as it is for a closed system, but varies as a function of pH. The total inorganic carbon concentration is the sum of all inorganic carbon species as it was for closed systems. In this case:

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

The concentration of H₂CO₃, HCO₃⁻, and CO₃²⁻, as a function of pH and P_{CO_2} , can be calculated from the equilibrium relationships given previously. The equations for these lines are:

$$[\text{H}_2\text{CO}_3] = (\text{K}_{\text{CO}_2})(\text{P}_{\text{CO}_2}) = (\text{P}_{\text{CO}_2})10^{-1.47}$$

$$-\log[\text{H}_2\text{CO}_3] = -\log(\text{P}_{\text{CO}_2}) + 1.47,$$

$$[\text{HCO}_3^-] = \frac{(\text{K}_1)(\text{P}_{\text{CO}_2})(10^{-1.47})}{\text{H}^+} = \frac{(10^{-6.35})(\text{P}_{\text{CO}_2})(10^{-1.47})}{\text{H}^+}$$

$$-\log[\text{HCO}_3^-] = -\log(\text{P}_{\text{CO}_2}) + 7.82 - \text{pH}, \text{ and}$$

$$[\text{CO}_3^{2-}] = \frac{(\text{K}_2)(10^{-6.35})(\text{P}_{\text{CO}_2})(10^{-1.47})}{(\text{H}^+)} = \frac{(10^{-10.33})(10^{-6.35})(\text{P}_{\text{CO}_2})(10^{-1.47})}{(\text{H}^+)}$$

$$-\log[\text{CO}_3^{2-}] = -\log(\text{P}_{\text{CO}_2}) + 18.15 - 2\text{pH}.$$

As mentioned previously and demonstrated by the above equations the concentrations of H_2CO_3 , HCO_3^- , and CO_3^{2-} vary as a function of both pH and P_{CO_2} . This means that as P_{CO_2} has varied naturally over the years during ice ages and warming, the concentration of H_2CO_3 , HCO_3^- , and CO_3^{2-} in surface waters has changed. It also means that P_{CO_2} changes caused by global warming will alter the surface water concentrations of these species.

References:

Stumm, W. and J.J.Morgan, *Aquatic Chemistry*, John Wiley & Sons, New York, 1996.