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 (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}) in lakes, rivers, and oceans.

The reactions occurring in this system are:

$$CO_2 + H_2O \leftrightarrow H_2CO_3,$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+,$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+,$$
$$H_2O \leftrightarrow H^+ + OH^-.$$

The equilibrium relationships for this system are:

$$K_w = [H^+][OH^-] = 10^{-14},$$

$$K_{CO2} = \frac{[H_2CO_3]}{P_{CO_2}} = 10^{-1.47},$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.35},$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10\text{-}^{10.33},$$

where P_{CO2} is the partial pressure of CO_2 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:

$$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}].$$

The concentration of H_2CO_3, HCO_3^-, and CO_3^{2-}, as a function of pH and P_{CO2}, can be calculated from the equilibrium relationships given previously. The equations for these lines are:

$[H_2CO_3] = (K_{CO2})(P_{CO2}) = (P_{CO2})10^{-1.47}$
$-\log[H_2CO_3] = -\log(P_{CO2}) + 1.47$,

$$[HCO_3^-] = \frac{(K_1)(P_{CO_2})(10^{-1.47})}{H^+} = \frac{(10^{-6.35})(P_{CO_2})(10^{-1.47})}{H^+}$$

$-\log[HCO_3^-] = -\log(P_{CO2}) + 7.82 - pH$, and

$$[CO_3^{2-}] = \frac{(K_2)(10^{-6.35})(P_{CO_2})(10^{-1.47})}{(H^+)^2} = \frac{(10^{-10.33})(10^{-6.35})(P_{CO_2})(10^{-1.47})}{(H^+)^2}$$

$-\log[CO_3^{2-}] = -\log(P_{CO2}) + 18.15 - 2pH$.

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_{CO2}. This means that as P_{CO2} 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_{CO2} 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.