The Carbonate System

Importance

Dissolution and precipitation of carbonate rocks and soils depends on the presence of carbonate species in solution

- Carbonate species are necessary for all biological systems
- Aquatic photosynthesis is affected by the presence of dissolved carbonate species
- Carbonates play important role in neutralization of strong bases and acids.
- The chemistry of many important reactions is affected by the presence of carbonate species.
- Carbon dioxide from the atmosphere is dissolved or volatilized from water.

Components

The carbonate system (also called the carbonic acid system) is a diprotic acid system. There are three soluble components:

- Carbonic Acid, H_2CO_3*, Can donate two protons (a weak acid)
- Bicarbonate, HCO_3^-, is amphoteric (can donate or accept one proton, acid or base)
- Carbonate, CO_3^{2-}, can accept two protons (a base)

Chemical equilibrium models for the study of the carbonic acid system

Open system. Assumes that the water is in equilibrium with the partial pressure of CO_2 in the atmosphere. This model is used when there is ample time for atmospheric carbon dioxide to saturate a solution. For example, this chemical model can be used to study the chemistry of shallow lakes, cooling towers and geological formations.

Closed system. The acid-base reactions are much faster than gas dissolution equilibrium reactions. Natural systems tend to change relatively rapidly thus no equilibrium with the surrounding atmosphere is attained. The closed system is therefore is commonly used in most environmental engineering and environmental science applications. Equilibrium with the atmosphere is ignored in this case.

Chemical Reactions in an open carbonate system

- Dissolution/volatilization of carbon dioxide ($CO_{2,g}$) creates carbonic acid ($H_2CO_3^{*)}$ in water
- Carbonic acid donates one proton to create bicarbonate, HCO_3^-
- Bicarbonate donates the last proton to form carbonate, CO_3^{2-}
- The dissolution/volatilization of carbonic acid is a very slow reaction as compared to the acid base reactions involved in proton transfer
- Chemical reactions and corresponding equilibrium constants for the carbonate system are presented below

Chemical Reactions in the Carbonate System

Reaction	Explanation	Equilibrium constant (25°C)
$CO_{2,g} + H_2O \Longleftrightarrow H_2CO_3^*$	Dissolution of CO_2	$pK_H = 1.5$ (at 25°C)
$H_2CO_3^* \Longleftrightarrow HCO_3^- + H^+$	First deprotonation stage	$pK_1 = 6.3$ (at 25°C)
$HCO_3^- \Longleftrightarrow CO_3^{2-} + H^+$	Second deprotonation stage	$PK_2 = 10.3$ (at 25°C)

Note: The first chemical reaction is ignored in the closed carbonate system

The Closed Carbonate System

The Law of Mass Action yields the following equations for the first and second deprotonation reactions:

$$K_1 = \frac{(HCO_3^-)(H^+)}{(H_2CO_3^*)} = 10^{-6.3} \qquad (1)$$

$$K_2 = \frac{(CO_3^{2-})(H^+)}{(HCO_3^-)} = 10^{-10.3} \qquad (2)$$

In a closed system carbon dioxide is not lost or gained to the atmosphere. That is the concentration of total carbonates species in solution, C_T, is constant irrelevantly of the pH of the solution. Therefore:

$$C_T = H_2CO_3^* + HCO_3^- + CO_3^{2-} \qquad (3)$$

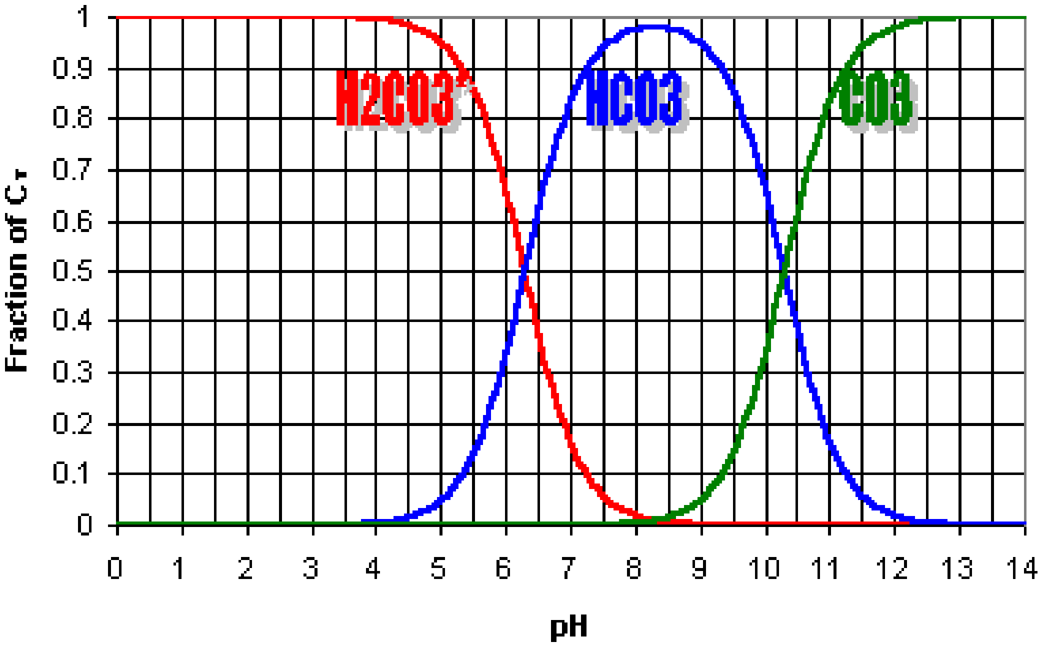
Equations 1-3 represent a system of three simultaneous equations with three unknowns ($H_2CO_3^*$, HCO_3^-, and CO_3^{2-}) for a given C_T concentration. Solving simultaneously equations 1 through 3 yields:

$$\frac{(H_2CO_3^*)}{C_T} = \frac{1}{1+\frac{K_1}{(H^+)}+\frac{K_1K_2}{(H^+)^2}} \qquad (4)$$

$$\frac{(HCO_3^-)}{C_T} = \frac{1}{\frac{(H+)}{K_1}+1+\frac{K_2}{(H^+)}} \qquad (5)$$

$$\frac{(CO_3^{2-})}{C_T} = \frac{1}{\frac{(H^+)^2}{K_1K_2}+\frac{(H^+)}{K_2}+1} \qquad (6)$$

Equations 4, 5 and 6 are functions of the proton concentration, H^+ only. It is customary to use pH instead of H^+ in most applications. Therefore it is possible to obtain values for the three unknowns using for any pH or H+ concentration (where $pH = \log_{10}(H^+)$). The following figure is a graphical summary of the relative concentrations of the three carbonate species in the pH range of 0 to 14.



This figure can be used in lieu of the equations above to obtain the relative concentrations of the three species for any pH condition. For example at a pH = 7.0 the relative concentrations of $H_2CO_3^*$, HCO_3^-, and CO_3^{2-} are 17%, 83% and less than 1.0% respectively.