9.3: Water Chemistry

Some of the chemical and biochemical phenomena that occur in water are illustrated in Figure 9.4.[2] Physically, the body of water shown is stratified during summer months with a warmer, less dense epilimnion floating over a colder, more dense hypolimnion, with little mixing between the two. The epilimnion is in contact with the atmosphere and has a significant content of dissolved oxygen. Therefore, oxidized inorganic species predominate in the epilimnion. The hypolimnion is anoxic because microorganisms consume all the dissolved O_2 in it and it is not in contact with the atmosphere. Reduced inorganic species predominate in the hypolimnion. A major factor in the chemistry of this system is the biochemical photosynthetic production of organic matter represented $\{CH_2O\}$. Organic matter is a biochemical reducing agent and when it sinks into the hypolimnion it is oxidized by microorganism-mediated processes that, for example, reduce NO_3^- and SO_4^{2-} to NH_4^+ and H_2S, respectively. Two important microbially-mediated oxidation-reduction reactions of $\{CH_2O\}$ are reaction with dissolved O_2,

$$(CH_2O) + O_2 \rightarrow CO_2 + H_2O \tag{9.3.1}$$

which depletes dissolved oxygen in water making the hypolimnion anoxic and methane fermentation,

$$2(CH_2O) \rightarrow CH_4 + CO_2 \tag{9.3.2}$$

which produces combustible methane gas. The ability of $\{CH_2O\}$ to react with dissolved O_2 is a measure of the potential of water to become depleted in the oxygen needed by fish and other aquatic organisms and is expressed as **biochemical oxygen demand**, **BOD**, an important water quality parameter.

The photosynthetic biochemical production of biomass results in some important chemical reactions. As illustrated in Figure 9.4, algae use dissolved HCO_3^- ion as a carbon source and in so doing produce carbonate ion, CO_3^{2-}. Two additional reactions of carbonate ion are shown in Figure 9.4. One is its hydrolysis reaction with H_2O molecules back to HCO_3^- with production of OH^- ion. This makes the water basic, an important aquatic acid-base reaction. A second reaction of carbonate is that with dissolved Ca^{2+} to produce solid $CaCO_3$, an important precipitation reaction in water that has been responsible for formation of large deposits of limestone.

All major oxidation-reduction reactions in natural water are carried out by microorganisms acting as catalysts and extracting energy released by the reactions. An example shown in Figure 9.4 is the biochemical reduction of SO_4^{2-} to H_2S. in which sulfate acts as an oxidizing agent to oxidize biomass ($\{CH_2O\}$) in the absence of molecular O_2. Taking place in the hypolimnion and sediments, this reaction is responsible for the foul odor of hydrogen sulfide in some bodies of water and swamps.

Another important phenomenon in natural water and wastewater is the formation of metal chelates in which metal ions are bound in two or more places by organic substances. Humic substances produced by the partial biodegradation of biomass are complex large organic molecules with numerous aromatic ring structures containing oxygen in functional groups including carboxyl (-CO2H) and phenolic hydroxyl (-OH). These groups can lose H+to produce negatively charged groups capable of bonding with metal ions as shown below for the chelation of Fe^{2+} ion:

$$\tag{9.3.3}$$
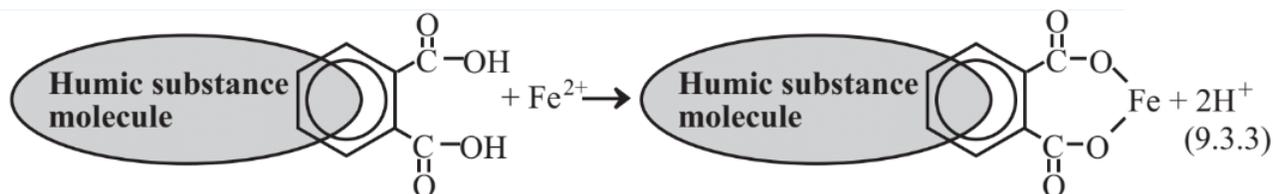
The most important humic substances in water are the lower-molecular-mass fulvic acids. These species tend to chelate Fe^{2+} ion producing a yellow material called *gelbstoffe* (German for "yellow stuff.)" Metal ions bound with fulvic acid are hard to remove from water and, since iron is a very undesirable water impurity, drastic measures such as destruction of the fulvic acid with chlorine may be required to remove the chelated iron.

Phase Interactions in Aquatic Chemistry

Figure 9.4 illustrates the process of exchange of dissolved solutes in water with sediments. Interactions between water and solid, gas, and other liquid phases are very important in aquatic chemistry. Aquatic biochemical processes involve exchange of materials between water solution and cells of microorganisms. For example, when photosynthesis occurs in water (Figure 9.4), dissolved HCO_3^- ion is transferred into a cell of floating photosynthetic phytoplankton for conversion to biomass. As a product of this

reaction gaseous O_2 is released from the cell, some of it dissolving in water and some floating to the top as O_2 bubbles. As noted above, the CO_3^{2-}ion generated as a byproduct of photosynthesis reacts with dissolved Ca^{2+} ion to produce solid $CaCO_3$. The reverse process occurs when bacterially-produced dissolved carbon dioxide reacts with solid calcium carbonate.

$$CO_2(aq) + H_2O + CaCO_3(s) \rightarrow Ca^{2+}(aq) + 2\,HCO_3^-(aq) \tag{9.3.3}$$
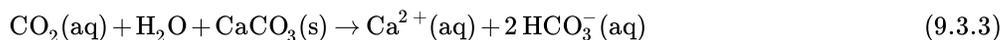
to put calcium ion and bicarbonate ion into solution. Both of these species are important in water. The Ca^{2+} ion is responsible for **water hardness**, named for a tendency to form precipitates with soap anions that are useless for cleaning, and HCO_3^- is **water alkalinity**, the ability to neutralize acids.

A particular kind of phase that interacts with water consists of colloidal particles, which are very small particles of the order of a micrometer in size that are suspended in water. There are three kinds of colloidal particles as shown in Figure 9.5. Many significant materials exist as colloidal particles in water including bacterial and algal cells, clay minerals, soap, and a variety of pollutants. The behavior of colloids is intermediate between that of true solutions and bulk materials such as those in sediments. This behavior is strongly influenced by the very high surface-to-volume ratio of colloids. Aggregation of colloidal particles is an important and often challenging aspect of water treatment, for example in the settling and separation of microorganisms involved in the biological treatment of wastewater.

**Association (micelle)   Hydrophilic   Hydrophobic**
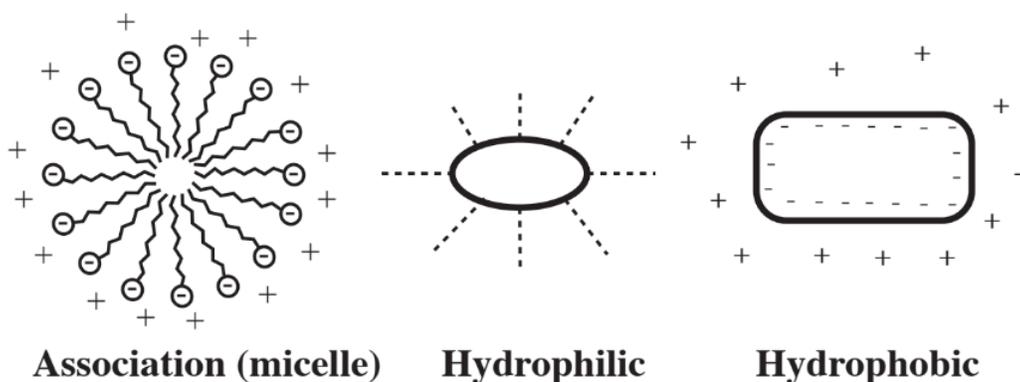
Figure 9.5. Representation of three kinds of colloidal particles in water. Association colloids are composed of micelles in which long hydrocarbon chains on fatty acid anions cluster in the center of the colloid and the anionic functional groups on the ends of the hydrocarbon chains are located around the periphery of the micelle in contact with water. Soap forms association colloids in water. Hydrophilic colloids are materials such as proteins or bacterial cells that are stabilized by their bonding to water. Hydrophobic colloids are repelled by water, but are stabilized by their electrical charges which prevent them from aggregating together.

Acid-Base Phenomena in Water

Natural water almost always contains acids capable of releasing H^+ ion and may contain solutes that can accept H^+ ion and thus act as bases. The most common acidic substance in water is dissolved CO_2, which may enter water from the atmosphere or in higher concentrations as a product of the microbial decay of organic matter. Dissolved carbon dioxide produces H^+ ion by the following reaction with water:

$$CO_2(aq) + H_2O \leftrightarrows H^+ + HCO_3^- \tag{9.3.4}$$

The double arrows denote that the reaction is reversible. Since carbon dioxide is a weak acid, the equilibrium of the reaction lies to the left as expressed by the following acid dissociation constant in which pK_{a1}= -logK_{a1}:

$$\backslash K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35 \tag{9.3.5}$$

The HCO_3^- ion can also lose H^+:

$$HCO_3^- \leftrightarrows H^+ + CO_3^{2-} \tag{9.3.6}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK_{a2} = 10.33 \tag{9.3.7}$$

Otherwise pure water in equilibrium with air contains some dissolved CO_2 from the atmosphere, which is 390 parts per million CO_2 by volume. Solubility calculations can be used to show that the dissolved carbon dioxide concentration water, $[CO_2(aq)]$, in equilibrium with air is 1.276×10^{-5} M (moles/liter). When each CO_2 reacts with H_2O, one H^+ and one HCO_3^- arereproduced. Substitution into the equilibrium constant expression Equation 9.3.6 leads to $[H^+] = 2.38 \times 10^{-6}$ M, pH = 5.62, slightly more acidic than neutral pH 7. Therefore, rainwater is naturally slightly acidic. Natural water with a pH less than 5.62 likely contains pollutant strong acid, most commonly H_2SO_4 from acid rain.

Most water that has been in contact with the geosphere contains alkalinity, the ability to react with H^+ ion and neutralize acidity. Generally alkalinity is due to the presence of HCO_3^- ion which undergoes the following reaction with H^+ ion:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \qquad (9.3.8)$$

Alkalinity is normally introduced into water by the reaction of dissolved CO_2 with $CaCO_3$ mineral as shown in Reaction 9.3.4. Because of the presence of alkalinity, most natural waters such as those used to supply municipal water systems are slightly basic with a pH around 8 rather than being slightly acidic like rainwater.