3 FUNDAMENTALS OF AQUATIC CHEMISTRY

3.1. WATER QUALITY AND QUANTITY

Throughout history, the quality and quantity of water available to humans have been vital factors in determining their well-being. Whole civilizations have disappeared because of water shortages resulting from changes in climate. Even in temperate climates, fluctuations in precipitation cause problems. Devastating droughts in Africa during the 1980s resulted in catastrophic crop failures and starvation. In 1997 an unprecedented flood struck huge sections of North Dakota inundating most of the City of Grand Forks, and in 1998 floods produced by torrential rains from Hurricane Mitch killed thousands in Central America. In 1999 heat killed a number of people in the central and eastern United States and a drought devastated crops and water supplies. In September 1999 Hurricane Floyd produced a 500-year flood in eastern North Carolina.

Waterborne diseases such as cholera and typhoid killed millions of people in the past and still cause great misery in less developed countries. Ambitious programs of dam and dike construction have reduced flood damage, but they have had a number of undesirable side effects in some areas, such as inundation of farmland by reservoirs and failure of unsafe dams. Globally, problems with quantity and quality of water supply remain and in some respects are becoming more serious. These problems include increased water use due to population growth, contamination of drinking water by improperly discarded hazardous wastes (see Chapter 19), and destruction of wildlife by water pollution.

Aquatic chemistry, the subject of this chapter, must consider water in rivers, lakes, estuaries, oceans, and underground, as well as the phenomena that determine the distribution and circulation of chemical species in natural waters. Its study requires some understanding of the sources, transport, characteristics, and composition of water. The chemical reactions that occur in water and the chemical species found in it are strongly influenced by the environment in which the water is found. The chemistry of water exposed to the atmosphere is quite different from that of water at the

bottom of a lake. Microorganisms play an essential role in determining the chemical composition of water. Thus, in discussing water chemistry, it is necessary to consider the many general factors that influence this chemistry.

The study of water is known as **hydrology** and is divided into a number of subcategories. **Limnology** is the branch of the science dealing with the characteristics of fresh water including biological properties, as well as chemical and physical properties. **Oceanography** is the science of the ocean and its physical and chemical characteristics. The chemistry and biology of the Earth's vast oceans are unique because of the ocean's high salt content, great depth, and other factors.

Sources and Uses of Water: The Hydrologic Cycle

The world's water supply is found in the five parts of the **hydrologic cycle** (Figure 3.1). About 97% of Earth's water is found in the oceans. Another fraction is present as water vapor in the atmosphere (clouds). Some water is contained in the solid state as ice and snow in snowpacks, glaciers, and the polar ice caps. Surface water is found in lakes, streams, and reservoirs. Groundwater is located in aquifers underground.
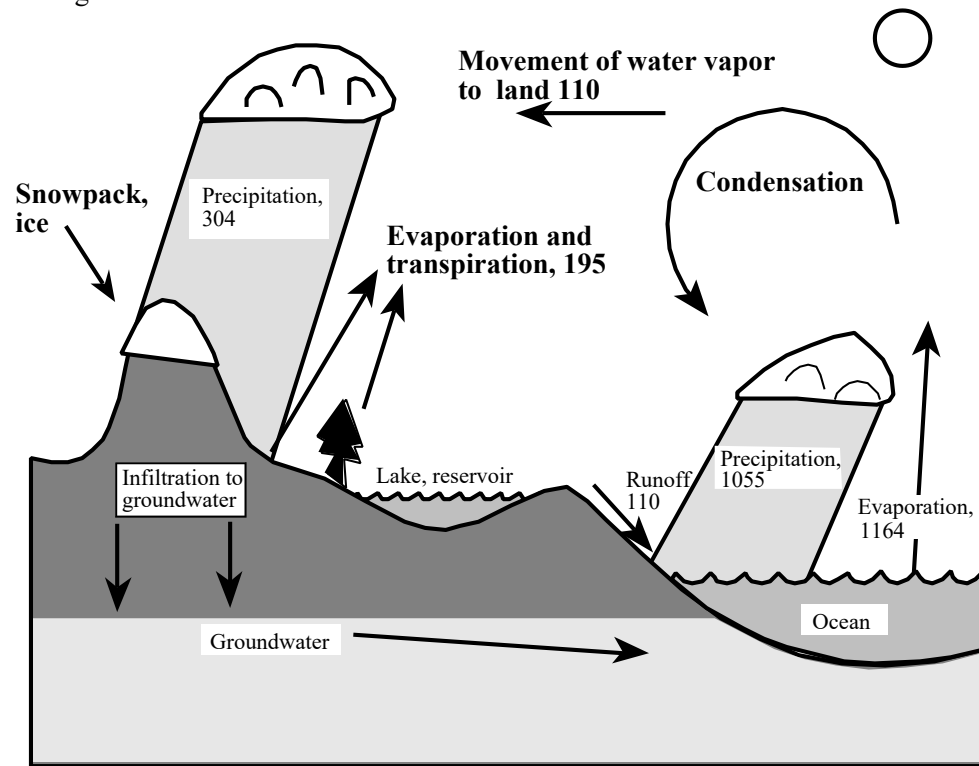

Figure 3.1. The hydrologic cycle, quantities of water in trillions of liters per day.

There is a strong connection between the *hydrosphere,* where water is found, and the *lithosphere*, which is that part of the geosphere accessible to water. Human activities affect both. For example, disturbance of land by conversion of grasslands or forests to agricultural land or intensification of agricultural production may reduce

vegetation cover, decreasing **transpiration** (loss of water vapor by plants) and affecting the microclimate. The result is increased rain runoff, erosion, and accumulation of silt in bodies of water. The nutrient cycles may be accelerated, leading to nutrient enrichment of surface waters. This, in turn, can profoundly affect the chemical and biological characteristics of bodies of water.

The water that humans use is primarily fresh surface water and groundwater, the sources of which may differ from each other significantly. In arid regions, a small fraction of the water supply comes from the ocean, a source that is likely to become more important as the world's supply of fresh water dwindles relative to demand. Saline or brackish groundwaters may also be utilized in some areas.

In the continental United States, an average of approximately 1.48×10^{13} liters of water fall as precipitation each day, which translates to 76 cm per year. Of that amount, approximately 1.02×10^{13} liters per day, or 53 cm per year, are lost by evaporation and transpiration. Thus, the water theoretically available for use is approximately 4.6×10^{12} liters per day, or only 23 centimeters per year. At present, the U.S. uses 1.6×10^{12} liters per day, or 8 centimeters of the average annual precipitation. This amounts to an almost tenfold increase from a usage of 1.66×10^{11} liters per day at the turn of the century. Even more striking is the per capita increase from about 40 liters per day in 1900 to around 600 liters per day now. Much of this increase is accounted for by high agricultural and industrial use, which each account for approximately 46% of total consumption. Municipal use consumes the remaining 8%.

Since about 1980, however, water use in the U.S. has shown an encouraging trend with total consumption down by about 9% during a time in which population grew 16%, according to figures compiled by the U.S. Geological Survey.[1] This trend, which is illustrated in Figure 3.2, has been attributed to the success of efforts to conserve water, especially in the industrial (including power generation) and agricultural sectors. Conservation and recycling have accounted for much of the decreased use in the industrial sector. Irrigation water has been used much more efficiently by replacing spray irrigators, which lose large quantities of water to the action of wind and to evaporation, with irrigation systems that apply water directly to soil. Trickle irrigation systems that apply just the amount of water needed directly to plant roots are especially efficient.

A major problem with water supply is its nonuniform distribution with location and time. As shown in Figure 3.3, precipitation falls unevenly in the continental U.S. This causes difficulties because people in areas with low precipitation often consume more water than people in regions with more rainfall. Rapid population growth in the more arid southwestern states of the U.S. during the last four decades has further aggravated the problem. Water shortages are becoming more acute in this region which contains six of the nation's eleven largest cities (Los Angeles, Houston, Dallas, San Diego, Phoenix, and San Antonio). Other problem areas include Florida, where overdevelopment of coastal areas threatens Lake Okeechobee; the Northeast, plagued by deteriorating water systems; and the High Plains, ranging from the Texas panhandle to Nebraska, where irrigation demands on the Oglala aquifer are dropping the water table steadily with no hope of recharge. These problems are minor, however, in comparison to those in some parts of Africa where water shortages are contributing to real famine conditions.
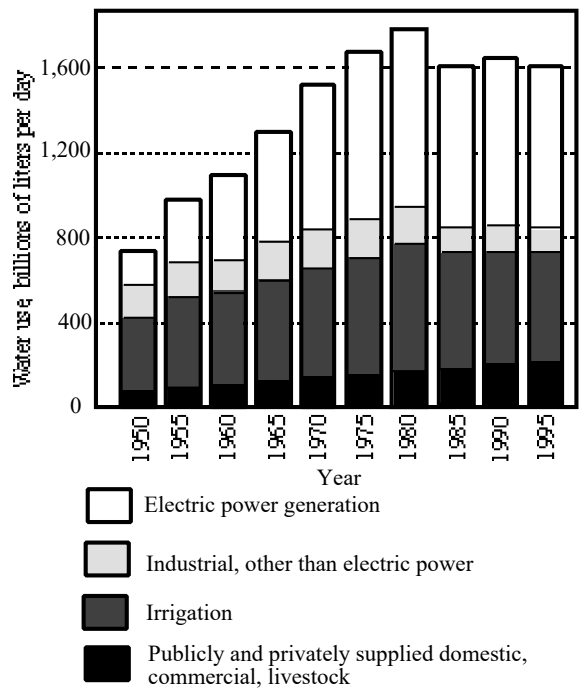
Figure 3.2. Trends in Water Use in The United States (Data from U.S. Geological Survey).
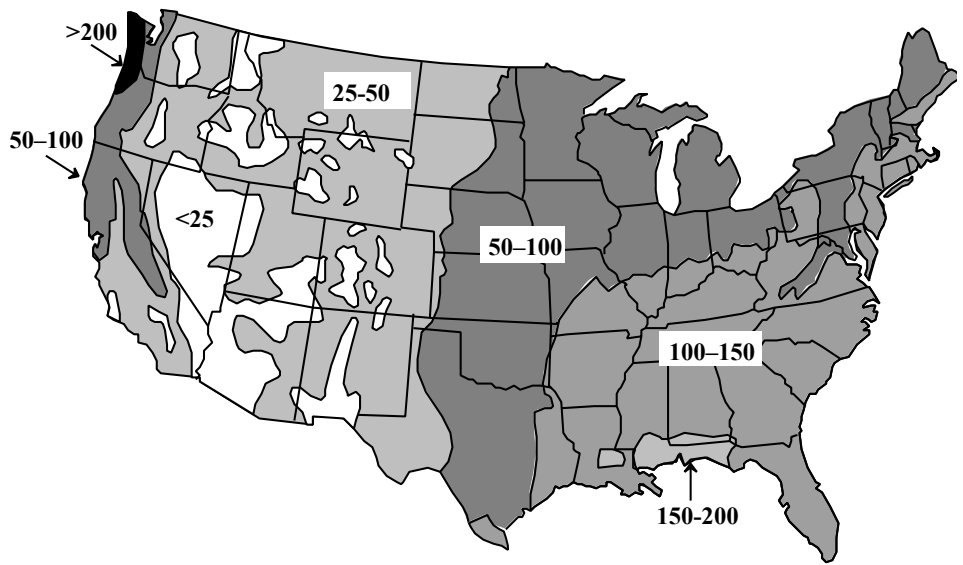

Figure 3.3. Distribution of precipitation in the continental U.S., showing average annual rainfall in centimeters.

## 3.2. THE PROPERTIES OF WATER, A UNIQUE SUBSTANCE

Water has a number of unique properties that are essential to life. Some of the special characteristics of water include its polar character, tendency to form hydrogen bonds, and ability to hydrate metal ions. These properties are listed in Table 3.1.

Table 3.1. Important Properties of Water

Property	Effects and Significance
Excellent solvent	Transport of nutrients and waste products, making biological processes possible in an aqueous medium
Highest dielectric constant of any common liquid	High solubility of ionic substances and their ionization in solution
Higher surface tension than any other liquid	Controlling factor in physiology; governs drop and surface phenomena
Transparent to visible and longer-wavelength fraction of ultraviolet light	Colorless, allowing light required for photosynthesis to reach considerable depths in bodies of water
Maximum density as a liquid at 4°C	Ice floats; vertical circulation restricted in stratified bodies of water
Higher heat of evaporation than any other material	Determines transfer of heat and water molecules between the atmosphere and bodies of water
Higher latent heat of fusion than any other liquid except ammonia	Temperature stabilized at the freezing point of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

The Water Molecule

Water's properties can best be understood by considering the structure and bonding of the water molecule:
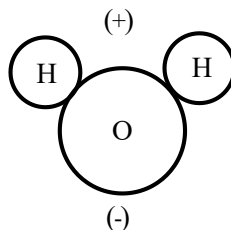
The water molecule is made up of two hydrogen atoms bonded to an oxygen atom.

The three atoms are not in a straight line; instead, as shown above, they form an angle of 105°. Because of water's bent structure and the fact that the oxygen atom attracts the negative electrons more strongly than do the hydrogen atoms, the water molecule behaves like a *dipole* having opposite electrical charges at either end. The water dipole may be attracted to either positively or negatively charged ions. For example, when NaCl dissolves in water as positive Na^+ ions and negative Cl^- ions, the positive sodium ions are surrounded by water molecules with their negative ends pointed at the ions, and the chloride ions are surrounded by water molecules with their positive ends pointing at the negative ions, as shown in Figure 3.4. This kind of attraction for ions is the reason why water dissolves many ionic compounds and salts that do not dissolve in other liquids.
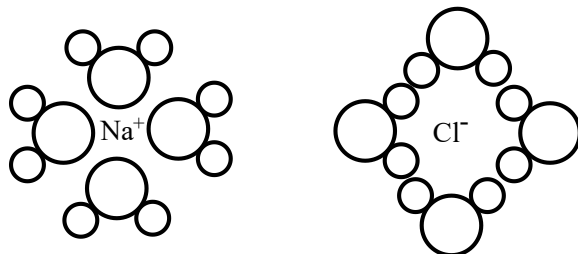

Figure 3.4. Polar water molecules surrounding Na^+ ion (left) and Cl^- ion (right).

A second important characteristic of the water molecule is its ability to form **hydrogen bonds**. Hydrogen bonds are a special type of bond that can form between the hydrogen in one water molecule and the oxygen in another water molecule. This bonding takes place because the oxygen has a partial negative charge and the hydrogen a partial positive charge. Hydrogen bonds, shown in Figure 3.5 as dashed lines, hold the water molecules together in large groups.
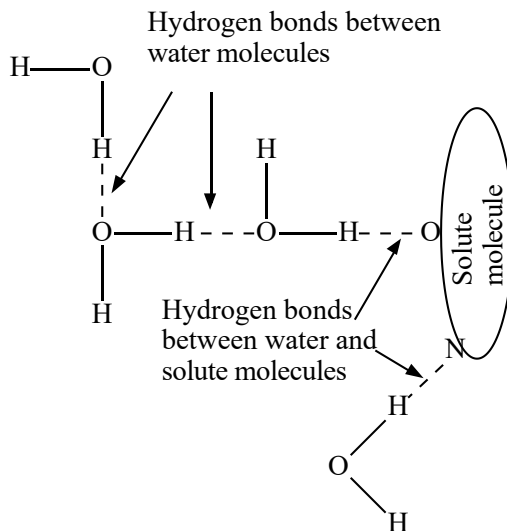

Figure 3.5. Hydrogen bonding between water molecules and between water molecules and a solute molecule in solution.

Hydrogen bonds also help to hold some solute molecules or ions in solution. This happens when hydrogen bonds form between the water molecules and hydrogen, nitrogen, or oxygen atoms on the solute molecule (see Figure 3.5). Hydrogen bonding also aids in retaining extremely small particles called *colloidal particles* in suspension in water (see Section 5.4).

Water is an excellent solvent for many materials; thus it is the basic transport medium for nutrients and waste products in life processes. The extremely high dielectric constant of water relative to other liquids has a profound effect upon its solvent properties in that most ionic materials are dissociated in water. With the exception of liquid ammonia, water has the highest heat capacity of any liquid or solid, l cal $\times$ g^{-1} $\times$ deg^{-1}. Because of this high heat capacity, a relatively large amount of heat is required to change appreciably the temperature of a mass of water; hence, a body of water can have a stabilizing effect upon the temperature of nearby geographic regions. In addition, this property prevents sudden large changes of temperature in large bodies of water and thereby protects aquatic organisms from the shock of abrupt temperature variations. The extremely high heat of vaporization of water, 585 cal/g at 20°C, likewise stabilizes the temperature of bodies of water and the surrounding geographic regions. It also influences the transfer of heat and water vapor between bodies of water and the atmosphere. Water has its maximum density at 4°C, a temperature above its freezing point. The fortunate consequence of this fact is that ice floats, so that few large bodies of water ever freeze solid. Furthermore, the pattern of vertical circulation of water in lakes, a determining factor in their chemistry and biology, is governed largely by the unique temperature-density relationship of water.

3.3. THE CHARACTERISTICS OF BODIES OF WATER

The physical condition of a body of water strongly influences the chemical and biological processes that occur in water. **Surface water** occurs primarily in streams, lakes, and reservoirs. **Wetlands** are flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants. **Estuaries** are arms of the ocean into which streams flow. The mixing of fresh and salt water gives estuaries unique chemical and biological properties. Estuaries are the breeding grounds of much marine life, which makes their preservation very important.

Water's unique temperature-density relationship results in the formation of distinct layers within nonflowing bodies of water, as shown in Figure 3.6. During the summer a surface layer (**epilimnion**) is heated by solar radiation and, because of its lower density, floats upon the bottom layer, or **hypolimnion**. This phenomenon is called **thermal stratification.** When an appreciable temperature difference exists between the two layers, they do not mix but behave independently and have very different chemical and biological properties. The epilimnion, which is exposed to light, may have a heavy growth of algae. As a result of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic. In the hypolimnion, bacterial action on biodegradable organic material may cause the water to become anaerobic (lacking dissolved oxygen). As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion.
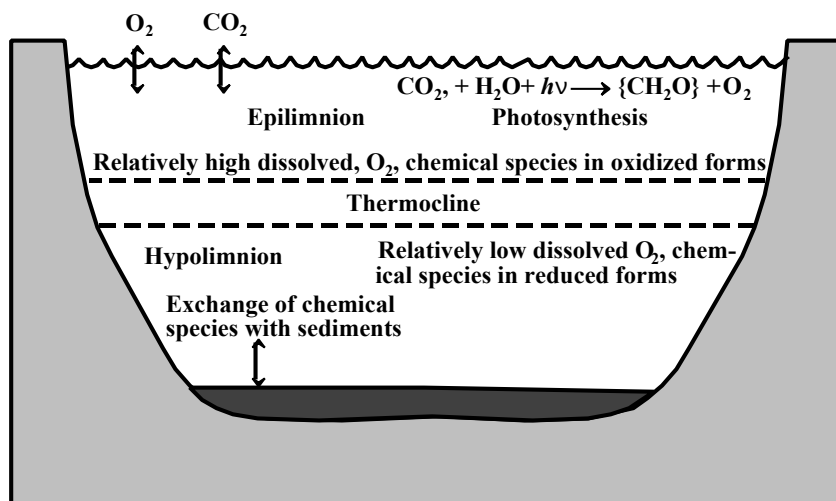
Figure 3.6. Stratification of a lake.

The shear-plane, or layer between epilimnion and hypolimnion, is called the **thermocline**. During the autumn, when the epilimnion cools, a point is reached at which the temperatures of the epilimnion and hypolimnion are equal. This disappearance of thermal stratification causes the entire body of water to behave as a hydrological unit, and the resultant mixing is known as **overturn**. An overturn also generally occurs in the spring. During the overturn, the chemical and physical characteristics of the body of water become much more uniform, and a number of chemical, physical, and biological changes may result. Biological activity may increase from the mixing of nutrients. Changes in water composition during overturn may cause disruption in water-treatment processes.

3.4. AQUATIC LIFE

The living organisms (**biota**) in an aquatic ecosystem may be classified as either autotrophic or heterotrophic. **Autotrophic** organisms utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. Algae are the most important autotrophic aquatic organisms because they are **producers** that utilize solar energy to generate biomass from CO_2 and other simple inorganic species.

Heterotrophic organisms utilize the organic substances produced by autotrophic organisms as energy sources and as the raw materials for the synthesis of their own biomass. **Decomposers** (or **reducers**) are a subclass of the heterotrophic organisms and consist of chiefly bacteria and fungi, which ultimately break down material of biological origin to the simple compounds originally fixed by the autotrophic organisms.

The ability of a body of water to produce living material is known as its **productivity.** Productivity results from a combination of physical and chemical factors. High productivity requires an adequate supply of carbon (CO_2), nitrogen (nitrate),

phosphorus (orthophosphate), and trace elements such as iron. Water of low productivity generally is desirable for water supply or for swimming. Relatively high productivity is required for the support of fish and to serve as the basis of the food chain in an aquatic ecosystem. Excessive productivity results in decay of the biomass produced, consumption of dissolved oxygen, and odor production, a condition called **eutrophication**.

Life forms higher than algae and bacteria—fish, for example—comprise a comparatively small fraction of the biomass in most aquatic systems. The influence of these higher life forms upon aquatic chemistry is minimal. However, aquatic life is strongly influenced by the physical and chemical properties of the body of water in which it lives. *Temperature, transparency,* and *turbulence* are the three main physical properties affecting aquatic life. Very low water temperatures result in very slow biological processes, whereas very high temperatures are fatal to most organisms. The transparency of water is particularly important in determining the growth of algae. Turbulence is an important factor in mixing processes and transport of nutrients and waste products in water. Some small organisms (**plankton**) depend upon water currents for their own mobility.

Dissolved oxygen (**DO**) frequently is the key substance in determining the extent and kinds of life in a body of water. Oxygen deficiency is fatal to many aquatic animals such as fish. The presence of oxygen can be equally fatal to many kinds of anaerobic bacteria. **Biochemical oxygen demand, BOD,** discussed as a water pollutant in Section 7.9, refers to the amount of oxygen utilized when the organic matter in a given volume of water is degraded biologically.

Carbon dioxide is produced by respiratory processes in water and sediments and can also enter water from the atmosphere. Carbon dioxide is required for the photosynthetic production of biomass by algae and in some cases is a limiting factor. High levels of carbon dioxide produced by the degradation of organic matter in water can cause excessive algal growth and productivity.

The salinity of water also determines the kinds of life forms present. Irrigation waters may pick up harmful levels of salt. Marine life obviously requires or tolerates salt water, whereas many freshwater organisms are intolerant of salt.

3.5. INTRODUCTION TO AQUATIC CHEMISTRY

To understand water pollution, it is first necessary to have an appreciation of chemical phenomena that occur in water. The remaining sections of this chapter discuss aquatic acid-base and complexation phenomena. Oxidation-reduction reactions and equilibria are discussed in Chapter 4, and details of solubility calculations and interactions between liquid water and other phases are given in Chapter 5. The main categories of aquatic chemical phenomena are illustrated in Figure 3.7.

Aquatic environmental chemical phenomena involve processes familiar to chemists, including acid-base, solubility, oxidation-reduction, and complexation reactions. Although most aquatic chemical phenomena are discussed here from the thermodynamic (equilibrium) viewpoint, it is important to keep in mind that kinetics—rates of reactions—are very important in aquatic chemistry. Biological processes play a key

role in aquatic chemistry. For example, algae undergoing photosynthesis can raise the pH of water by removing aqueous CO_2, thereby converting an HCO_3^- ion to a CO_3^{2-} ion; this ion in turn reacts with Ca^{2+} in water to precipitate $CaCO_3$.
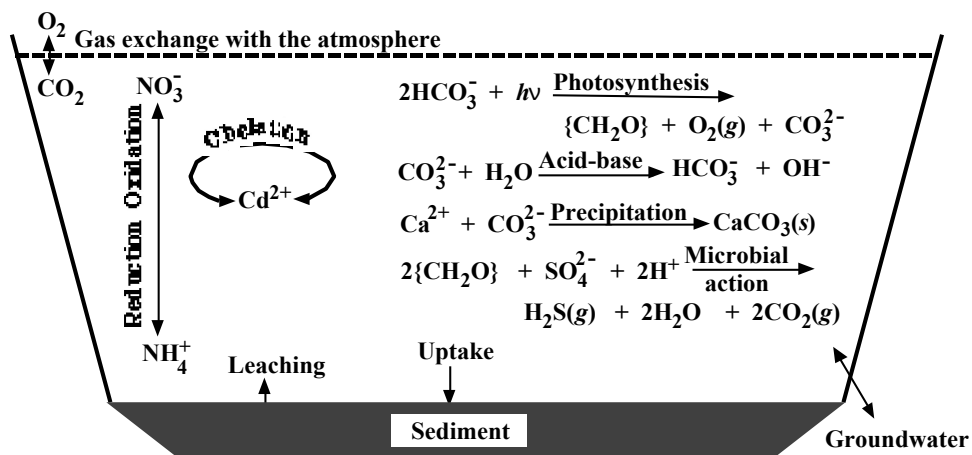

Figure 3.7. Major aquatic chemical processes.

Compared to the carefully controlled conditions of the laboratory, it is much more difficult to describe chemical phenomena in natural water systems. Such systems are very complex and a description of their chemistry must take many variables into consideration. In addition to water, these systems contain mineral phases, gas phases, and organisms. As open, dynamic systems, they have variable inputs and outputs of energy and mass. Therefore, except under unusual circumstances, a true equilibrium condition is not obtained, although an approximately steady-state aquatic system frequently exists. Most metals found in natural waters do not exist as simple hydrated cations in the water, and oxyanions often are found as polynuclear species, rather than as simple monomers. The nature of chemical species in water containing bacteria or algae is strongly influenced by the action of these organisms. Thus, an exact description of the chemistry of a natural water system based upon acid-base, solubility, and complexation equilibrium constants, redox potential, pH, and other chemical parameters is not possible. Therefore, the systems must be described by simplified **models**, often based around equilibrium chemical concepts. Though not exact, nor entirely realistic, such models can yield useful generalizations and insights pertaining to the nature of aquatic chemical processes, and provide guidelines for the description and measurement of natural water systems. Though greatly simplified, such models are very helpful in visualizing the conditions that determine chemical species and their reactions in natural waters and wastewaters.

3.6. GASES IN WATER

Dissolved gases—O_2 for fish and CO_2 for photosynthetic algae—are crucial to the welfare of living species in water. Some gases in water can also cause problems, such as the death of fish from bubbles of nitrogen formed in the blood caused by exposure

to water supersaturated with N_2. Volcanic carbon dioxide evolved from the waters of Lake Nyos in the African country of Cameroon asphyxiated 1,700 people in 1986.

The solubilities of gases in water are calculated with **Henry's Law**, which states that *the solubility of a gas in a liquid is proportional to the partial pressure of that gas in contact with the liquid.* These calculations are discussed in some detail in Chapter 5.

Oxygen in Water

Without an appreciable level of dissolved oxygen, many kinds of aquatic organisms cannot exist in water. Dissolved oxygen is consumed by the degradation of organic matter in water. Many fish kills are caused not from the direct toxicity of pollutants but from a deficiency of oxygen because of its consumption in the bio-degradation of pollutants.

Most elemental oxygen comes from the atmosphere, which is 20.95% oxygen by volume of dry air. Therefore, the ability of a body of water to reoxygenate itself by contact with the atmosphere is an important characteristic. Oxygen is produced by the photosynthetic action of algae, but this process is really not an efficient means of oxygenating water because some of the oxygen formed by photosynthesis during the daylight hours is lost at night when the algae consume oxygen as part of their metabolic processes. When the algae die, the degradation of their biomass also consumes oxygen.

The solubility of oxygen in water depends upon water temperature, the partial pressure of oxygen in the atmosphere, and the salt content of the water. It is important to distinguish between oxygen *solubility*, which is the maximum dissolved oxygen concentration at equilibrium, and dissolved oxygen *concentration*, which is generally not the equilibrium concentration and is limited by the rate at which oxygen dissolves. The calculation of oxygen solubility as a function of partial pressure is discussed in Section 5.3, where it is shown that the concentration of oxygen in water at 25°C in equilibrium with air at atmospheric pressure is only 8.32 mg/L. Thus, water in equilibrium with air cannot contain a high level of dissolved oxygen compared to many other solute species. If oxygen-consuming processes are occurring in the water, the dissolved oxygen level may rapidly approach zero unless some efficient mechanism for the reaeration of water is operative, such as turbulent flow in a shallow stream or air pumped into the aeration tank of an activated sludge secondary waste treatment facility (see Chapter 8). The problem becomes largely one of kinetics, in which there is a limit to the rate at which oxygen is transferred across the air-water interface. This rate depends upon turbulence, air bubble size, temperature, and other factors.

If organic matter of biological origin is represented by the formula $\{CH_2O\}$, the consumption of oxygen in water by the degradation of organic matter may be expressed by the following biochemical reaction:

$$\{CH_2O\} \ + \ O_2 \ \rightarrow \ CO_2 + H_2O \tag{3.6.1}$$

The weight of organic material required to consume the 8.3 mg of O_2 in a liter of water in equilibrium with the atmosphere at 25°C is given by a simple stoichiometric

calculation based on Equation 3.6.1, which yields a value of 7.8 mg of {CH$_2$O}. Thus, the microorganism-mediated degradation of only 7 or 8 mg of organic material can completely consume the oxygen in one liter of water initially saturated with air at 25°C. The depletion of oxygen to levels below those that will sustain aerobic organisms requires the degradation of even less organic matter at higher temperatures (where the solubility of oxygen is less) or in water not initially saturated with atmospheric oxygen. Furthermore, there are no common aquatic chemical reactions that replenish dissolved oxygen; except for oxygen provided by photosynthesis, it must come from the atmosphere.

The temperature effect on the solubility of gases in water is especially important in the case of oxygen. The solubility of oxygen in water decreases from 14.74 mg/L at 0°C to 7.03 mg/L at 35°C. At higher temperatures, the decreased solubility of oxygen, combined with the increased respiration rate of aquatic organisms, frequently causes a condition in which a higher demand for oxygen accompanied by lower solubility of the gas in water results in severe oxygen depletion.

3.7. WATER ACIDITY AND CARBON DIOXIDE IN WATER

Acid-base phenomena in water involve loss and acceptance of H$^+$ ion. Many species act as **acids** in water by releasing H$^+$ ion, others act as **bases** by accepting H$^+$, and the water molecule itself does both. An important species in the acid-base chemistry of water is bicarbonate ion, HCO$_3^-$, which may act as either an acid or a base:

$$HCO_3^- \; \square \; \rightarrow \; CO_3^{2-} \; + \; H^+ \qquad\qquad (3.7.1)$$

$$HCO_3^- \; + \; H^+ \; \square \; \rightarrow \; CO_2(aq) \; + \; H_2O \qquad\qquad (3.7.2)$$

Acidity as applied to natural water and wastewater is the capacity of the water to neutralize OH$^-$; it is analogous to alkalinity, the capacity to neutralize H$^+$, which is discussed in the next section. Although virtually all water has some alkalinity acidic water is not frequently encountered, except in cases of severe pollution. Acidity generally results from the presence of weak acids, particularly CO$_2$, but sometimes includes others such as H$_2$PO$_4^-$, H$_2$S, proteins, and fatty acids. Acidic metal ions, particularly Fe^{3+}, may also contribute to acidity.

From the pollution standpoint, strong acids are the most important contributors to acidity. The term *free mineral acid* is applied to strong acids such as H$_2$SO$_4$ and HCl in water. Acid mine water is a common water pollutant that contains an appreciable concentration of free mineral acid. Whereas total acidity is determined by titration with base to the phenolphthalein endpoint (pH 8.2), free mineral acid is determined by titration with base to the methyl orange endpoint (pH 4.3).

The acidic character of some hydrated metal ions may contribute to acidity:

$$Al(H_2O)_6^{3+} \; \square \; \rightarrow \; Al(H_2O)_5OH^{2+} \; + \; H^+ \qquad\qquad (3.7.3)$$
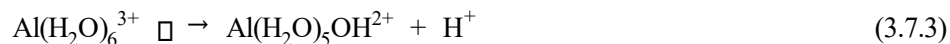
Some industrial wastes, such as spent steel pickling liquor, contain acidic metal ions and often some excess strong acid. The acidity of such wastes must be measured in calculating the amount of lime or other chemicals required to neutralize the acid.

Carbon Dioxide in Water

The most important weak acid in water is carbon dioxide, CO_2. Because of the presence of carbon dioxide in air and its production from microbial decay of organic matter, dissolved CO_2 is present in virtually all natural waters and wastewaters. Rainfall from even an absolutely unpolluted atmosphere is slightly acidic due to the presence of dissolved CO_2. Carbon dioxide, and its ionization products, bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}) have an extremely important influence upon the chemistry of water. Many minerals are deposited as salts of the carbonate ion. Algae in water utilize dissolved CO_2 in the synthesis of biomass. The equilibrium of dissolved CO_2 with gaseous carbon dioxide in the atmosphere,

$$CO_2(water) \rightleftharpoons CO_2(atmosphere) \qquad (3.7.4)$$

and equilibrium of CO_3^{2-} ion between aquatic solution and solid carbonate minerals,

$$MCO_3(\text{slightly soluble carbonate salt}) \rightleftharpoons M^{2+} + CO_3^{2-} \qquad (3.7.5)$$
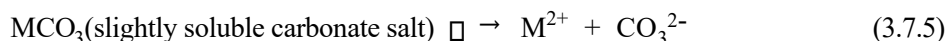
have a strong buffering effect upon the pH of water.

Carbon dioxide is only about 0.037% by volume of normal dry air. As a consequence of the low level of atmospheric CO_2, water totally lacking in alkalinity (capacity to neutralize H^+, see Section 3.8) in equilibrium with the atmosphere contains only a very low level of carbon dioxide. However, the formation of HCO_3^- and CO_3^{2-} greatly increases the solubility of carbon dioxide. High concentrations of free carbon dioxide in water may adversely affect respiration and gas exchange of aquatic animals. It may even cause death and should not exceed levels of 25 mg/L in water.

A large share of the carbon dioxide found in water is a product of the breakdown of organic matter by bacteria. Even algae, which utilize CO_2 in photosynthesis, produce it through their metabolic processes in the absence of light. As water seeps through layers of decaying organic matter while infiltrating the ground, it may dissolve a great deal of CO_2 produced by the respiration of organisms in the soil. Later, as water goes through limestone formations, it dissolves calcium carbonate because of the presence of the dissolved CO_2:

$$CaCO_3(s) + CO_2(aq) + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (3.7.6)$$

This process is the one by which limestone caves are formed. The implications of the above reaction for aquatic chemistry are discussed in greater detail in Section 3.9.

The concentration of gaseous CO_2 in the atmosphere varies with location and season; it is increasing by about one part per million (ppm) by volume per year. For purposes of calculation here, the concentration of atmospheric CO_2 will be taken as 350 ppm (0.0350%) in dry air. At 25°C, water in equilibrium with unpolluted air containing 350 ppm carbon dioxide has a $CO_2(aq)$ concentration of 1.146×10^{-5} M (see Henry's law calculation of gas solubility in Section 5.3), and this value will be used for subsequent calculations.

Although CO_2 in water is often represented as H_2CO_3, the equilibrium constant for the reaction

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \tag{3.7.7}$$

is only around 2×10^{-3} at 25°C, so just a small fraction of the dissolved carbon dioxide is actually present as H_2CO_3. In this text, nonionized carbon dioxide in water will be designated simply as CO_2, which in subsequent discussions will stand for the total of dissolved molecular CO_2 and undissociated H_2CO_3.

The CO_2-HCO_3^--CO_3^{2-} system in water may be described by the equations,

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \tag{3.7.8}$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35 \tag{3.7.9}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{3.7.10}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK_{a2} = 10.33 \tag{3.7.11}$$

where $pK_a = -\log K_a$. The predominant species formed by CO_2 dissolved in water depends upon pH. This is best shown by a **distribution of species diagram** with pH as a master variable as illustrated in Figure 3.8. Such a diagram shows the major
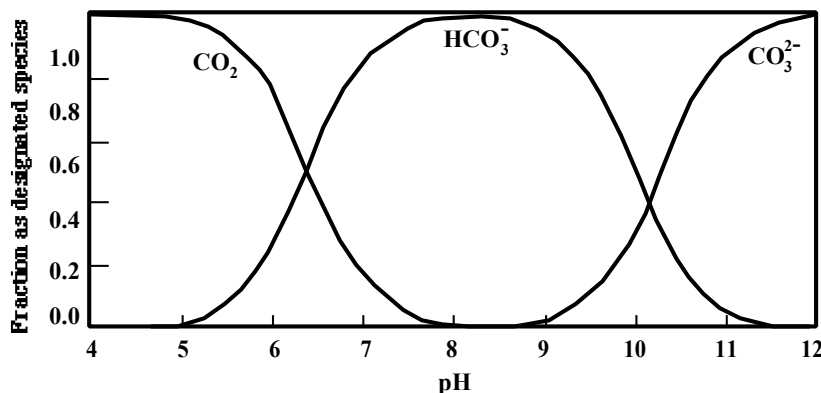

Figure 3.8. Distribution of species diagram for the CO_2–HCO_3^-–CO_3^{2-} system in water.

species present in solution as a function of pH. For CO_2 in aqueous solution, the diagram is a series of plots of the fractions present as CO_2, HCO_3^-, and CO_3^{2-} as a function of pH. These fractions, designated as α_x, are given by the following expressions:

$$\alpha_{CO_2} = \frac{[CO_2]}{[CO_2] + [HCO_3^-] + [CO_3^{2-}]} \tag{3.7.12}$$

$$\alpha_{HCO_3^-} = \frac{[HCO_3^-]}{[CO_2] + [HCO_3^-] + [CO_3^{2-}]} \tag{3.7.13}$$

$$\alpha_{CO_3^{2-}} = \frac{[CO_3^{2-}]}{[CO_2] + [HCO_3^-] + [CO_3^{2-}]} \tag{3.7.14}$$

Substitution of the expressions for K_{a1} and K_{a2} into the α expressions gives the fractions of species as a function of acid dissociation constants and hydrogen ion concentration:

$$\alpha_{CO_2} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{3.7.15}$$

$$\alpha_{HCO_3^-} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{3.7.16}$$

$$\alpha_{CO_3^{2-}} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{3.7.17}$$

Calculations from these expressions show the following:

- For pH significantly below pK_{a1}, α_{CO_2} is essentially 1
- When pH = pK_{a1}, $\alpha_{CO_2} = \alpha_{HCO_3^-}$
- When pH = $\frac{1}{2}(pK_{a1} + pK_{a2})$, $\alpha_{HCO_3^-}$ is at its maximum value of 0.98
- When pH = pK_{a2}, $\alpha_{HCO_3^-} = \alpha_{CO_3^{2-}}$
- For pH significantly above pK_{a2}, $\alpha_{CO_3^{2-}}$ is essentially 1.

The distribution of species diagram in Figure 3.8 shows that hydrogen carbonate (bicarbonate) ion (HCO_3^-) is the predominant species in the pH range found in most waters, with CO_2 predominating in more acidic waters.

As mentioned above, the value of $[CO_2(aq)]$ in water at 25°C in equilibrium with air that is 350 ppm CO_2 is 1.146×10^{-5} M. The carbon dioxide dissociates partially in water to produce equal concentrations of H^+ and HCO_3^-:

$$CO_2 + H_2O \; \square \; \rightarrow \; HCO_3^- + H^+ \qquad\qquad (3.7.18)$$

The concentrations of H^+ and HCO_3^- are calculated from K_{a1}:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{[H^+]^2}{1.146 \times 10^{-5}} = 4.45 \times 10^{-7} \qquad\qquad (3.7.19)$$

$$[H^+] = [HCO_3^-] = (1.146 \times 10^{-5} \times 4.45 \times 10^{-7})^{1/2} = 2.25 \times 10^{-6}$$

$$pH = 5.65$$

This calculation explains why pure water that has equilibrated with the unpolluted atmosphere is slightly acidic with a pH somewhat less than 7.

3.8. ALKALINITY

The capacity of water to accept H^+ ions (protons) is called **alkalinity**. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Frequently, the alkalinity of water must be known to calculate the quantities of chemicals to be added in treating the water. Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids. These characteristics may be detrimental for water to be used in boilers, food processing, and municipal water systems. Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of a water to support algal growth and other aquatic life, so it can be used as a measure of water fertility. Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \qquad\qquad (3.8.1)$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \qquad\qquad (3.8.2)$$

$$OH^- + H^+ \rightarrow H_2O \qquad\qquad (3.8.3)$$

Other, usually minor, contributors to alkalinity are ammonia and the conjugate bases of phosphoric, silicic, boric, and organic acids.

At pH values below 7, $[H^+]$ in water detracts significantly from alkalinity, and its concentration must be subtracted in computing the total alkalinity. Therefore, the following equation is the complete equation for alkalinity in a medium where the only contributors to it are HCO_3^-, CO_3^{2-}, and OH^-:

$$[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH]^- - [H^+] \qquad\qquad (3.8.4)$$

Alkalinity generally is expressed as *phenolphthalein alkalinity*, corresponding to titration with acid to the pH at which HCO_3^- is the predominant carbonate species (pH 8.3), or *total alkalinity*, corresponding to titration with acid to the methyl

orange endpoint (pH 4.3), where both bicarbonate and carbonate species have been converted to CO_2.

It is important to distinguish between high *basicity*, manifested by an elevated pH, and high *alkalinity*, the capacity to accept H^+. Whereas pH is an *intensity* factor, alkalinity is a *capacity* factor. This may be illustrated by comparing a solution of 1.00×10^{-3} M NaOH with a solution of 0.100 M HCO_3^-. The sodium hydroxide solution is quite basic, with a pH of 11, but a liter of it will neutralize only 1.00×10^{-3} mole of acid. The pH of the sodium bicarbonate solution is 8.34, much lower than that of the NaOH. However, a liter of the sodium bicarbonate solution will neutralize 0.100 mole of acid; therefore, its alkalinity is 100 times that of the more basic NaOH solution.

In engineering terms, alkalinity frequently is expressed in units of mg/L of $CaCO_3$, based upon the following acid-neutralizing reaction:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \tag{3.8.5}$$
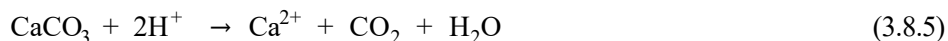
The equivalent weight of calcium carbonate is one-half its formula weight. Expressing alkalinity in terms of mg/L of $CaCO_3$ can, however, lead to confusion, and the preferable notation for the chemist is equivalents/L, the number of moles of H^+ neutralized by the alkalinity in a liter of solution.

Contributors to Alkalinity at Different pH Values

Natural water typically has an alkalinity, designated here as "[alk]," of 1.00×10^{-3} equivalents per liter (eq/L), meaning that the alkaline solutes in 1 liter of the water will neutralize 1.00×10^{-3} moles of acid. The contributions made by different species to alkalinity depend upon pH. This is shown here by calculation of the relative contributions to alkalinity of HCO_3^-, CO_3^{2-}, and OH^- at pH 7.00 and pH 10.00. First, for water at pH 7.00, $[OH^-]$ is too low to make any significant contribution to the alkalinity. Furthermore, as shown by Figure 3.8, at pH 7.00 $[HCO_3^-] \gg [CO_3^{2-}]$. Therefore, the alkalinity is due to HCO_3^- and $[HCO_3^-] = 1.00 \times 10^{-3}$ M. Substitution into the expression for K_{a1} shows that at pH 7.00 and $[HCO_3^-] = 1.00 \times 10^{-3}$ M, the value of $[CO_2(aq)]$ is 2.25×10^{-4} M, somewhat higher than the value that arises from water in equilibrium with atmospheric air, but readily reached due to the presence of carbon dioxide from bacterial decay in water and sediments.

Consider next the case of water with the same alkalinity, 1.00×10^{-3} eq/L that has a pH of 10.00. At this higher pH both OH^- and CO_3^{2-} are present at significant concentrations compared to HCO_3^- and the following may be calculated:

$$[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] = 1.00 \times 10^{-3} \tag{3.8.6}$$

The concentration of CO_3^{2-} is multiplied by 2 because each CO_3^{2-} ion can neutralize 2 H^+ ions. The other two equations that must be solved to get the concentrations of HCO_3, CO_3^{2-}, and OH^- are

$$[OH^-] = \frac{K_W}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-10}} = 1.00 \times 10^{-4} \qquad (3.8.7)$$

and

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]} \qquad (3.8.8)$$

Solving these three equations gives $[HCO_3^-] = 4.64 \times 10^{-4}$ M and $[CO_3^{2-}] = 2.18 \times 10^{-4}$ M, so the contributions to the alkalinity of this solution are the following:

$$
\begin{array}{rl}
& 4.64 \times 10^{-4} \text{ eq/L from } HCO_3^- \\
2 \times 2.18 \times 10^{-4} = & 4.36 \times 10^{-4} \text{ eq/L from } CO_3^{2-} \\
& \underline{1.00 \times 10^{-4} \text{ eq/L from } OH^-} \\
\text{alk} = & 1.00 \times 10^{-3} \text{ eq/L}
\end{array}
$$

Dissolved Inorganic Carbon and Alkalinity

The values given above can be used to show that at the same alkalinity value the concentration of total dissolved inorganic carbon, [C],
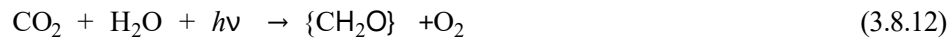
$$[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \qquad (3.8.9)$$

varies with pH. At pH 7.00,

$$[C]_{pH\ 7} = 2.25 \times 10^{-4} + 1.00 \times 10^{-3} + 0 = 1.22 \times 10^{-3} \qquad (3.8.10)$$
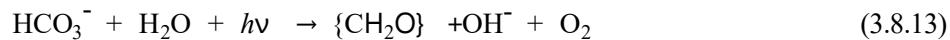
whereas at pH 10.00,

$$[C]_{pH\ 10} = 0 + 4.64 \times 10^{-4} + 2.18 \times 10^{-4} = 6.82 \times 10^{-4} \qquad (3.8.11)$$

The calculation above shows that the dissolved inorganic carbon concentration at pH 10.00 is only about half that at pH 7.00. This is because at pH 10 major contributions to alkalinity are made by CO_3^{2-} ion, each of which has twice the alkalinity of each HCO_3^- ion, and by OH^-, which does not contain any carbon. The lower inorganic carbon concentration at pH 10 shows that the aquatic system can donate dissolved inorganic carbon for use in photosynthesis with a change in pH but none in alkalinity. This pH-dependent difference in dissolved inorganic carbon concentration represents a significant potential source of carbon for algae growing in water which fix carbon by the overall reactions

$$CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2 \qquad (3.8.12)$$

and

$$HCO_3^- + H_2O + h\nu \rightarrow \{CH_2O\} + OH^- + O_2 \qquad (3.8.13)$$

As dissolved inorganic carbon is used up to synthesize biomass, $\{CH_2O\}$, the water becomes more basic. The amount of inorganic carbon that can be consumed

before the water becomes too basic to allow algal reproduction is proportional to the alkalinity. In going from pH 7.00 to pH 10.00, the amount of inorganic carbon consumed from 1.00 L of water having an alkalinity of 1.00×10^{-3} eq/L is

$$[C]_{pH\ 7} \times 1\ L - [C]_{pH\ 10} \times 1\ L =$$

$$1.22 \times 10^{-3}\ mol - 6.82 \times 10^{-4}\ mol\ =\ 5.4 \times 10^{-4}\ mol \qquad (3.8.14)$$

This translates to an increase of 5.4×10^{-4} mol/L of biomass. Since the formula mass of $\{CH_2O\}$ is 30, the weight of biomass produced amounts to 16 mg/L. Assuming no input of additional CO_2, at higher alkalinity more biomass is produced for the same change in pH, whereas at lower alkalinity less is produced. Because of this effect, biologists use alkalinity as a measure of water fertility.

Influence of Alkalinity on CO_2 Solubility

The increased solubility of carbon dioxide in water with an elevated alkalinity can be illustrated by comparing its solubility in pure water (alkalinity 0) to its solubility in water initially containing 1.00×10^{-3} M NaOH (alkalinity 1.00×10^{-3} eq/L). The number of moles of CO_2 that will dissolve in a liter of pure water from the atmosphere containing 350 ppm carbon dioxide is

$$Solubility\ =\ [CO_2(aq)] + [HCO_3^-] \qquad (3.8.15)$$

Substituting values calculated in Section 3.7 gives

$$Solubility\ =\ 1.146 \times 10^{-5} + 2.25 \times 10^{-6} = 1.371 \times 10^{-5}\ M$$

The solubility of CO_2 in water, initially 1.00×10^{-3} M in NaOH, is about 100-fold higher because of uptake of CO_2 by the reaction
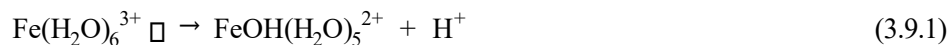
$$CO_2(ag)\ +\ OH^-\ \square\ \rightarrow\ HCO_3^- \qquad (3.8.16)$$

so that

$$Solubility\ =\ [CO_2(aq)] + [HCO_3^-]$$
$$=\ 1.146 \times 10^{-5} + 1.00 \times 10^{-3}\ =\ 1.01 \times 10^{-3}\ M \qquad (3.8.17)$$

3.9. CALCIUM AND OTHER METALS IN WATER

Metal ions in water, commonly denoted M^{n+}, exist in numerous forms. A bare metal ion, Ca^{2+} for example, cannot exist as a separate entity in water. In order to secure the highest stability of their outer electron shells, metal ions in water are bonded, or *coordinated*, to other species. These may be water molecules or other stronger bases (electron-donor partners) that might be present. Therefore, metal ions in water solution are present in forms such as the **hydrated** metal cation $M(H_2O)_x^{n+}$. Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including acid-base,

$$Fe(H_2O)_6^{3+} \square \rightarrow FeOH(H_2O)_5^{2+} + H^+ \tag{3.9.1}$$

precipitation,

$$Fe(H_2O)_6^{3+} \square \rightarrow Fe(OH)_3(s) + 3H_2O + 3H^+ \tag{3.9.2}$$

and oxidation-reduction reactions:

$$Fe(H_2O)_6^{2+} \square \rightarrow Fe(OH)_3(s) + 3H_2O + e^- + 3H^+ \tag{3.9.3}$$

These all provide means through which metal ions in water are transformed to more stable forms. Because of reactions such as these and the formation of dimeric species, such as $Fe_2(OH)_2^{4+}$, the concentration of simple hydrated $Fe(H_2O)_6^{3+}$ ion in water is vanishingly small; the same holds true for many other hydrated metal ions dissolved in water.

Hydrated Metal Ions as Acids

Hydrated metal ions, particularly those with a charge of +3 or more, tend to lose H^+ ion from the water molecules bound to them in aqueous solution, and fit the definition of Brönsted acids, according to which acids are H^+ donors and bases are H^+ acceptors. The acidity of a metal ion increases with charge and decreases with increasing radius. As shown by the reaction,

$$Fe(H_2O)_6^{3+} \square \rightarrow Fe(H_2O)_5OH^{2+} + H^+ \tag{3.9.4}$$

hydrated iron(III) ion is an acid, a relatively strong one with a K_{a1} of 8.9×10^{-4}, so that solutions of iron(III) tend to have low pH values. Hydrated trivalent metal ions, such as iron(III), generally are minus at least one hydrogen ion at neutral pH values or above. For tetravalent metal ions, the completely protonated forms, $M(H_2O)_x^{4+}$, are rare even at very low pH values. Commonly, O^{2-} is coordinated to tetravalent metal ions; an example is the vanadium(IV) species, VO^{2+}. Generally, divalent metal ions do not lose a hydrogen ion at pH values below 6, whereas monovalent metal ions such as Na^+ do not act as acids at all, and exist in water solution as simple hydrated ions.

The tendency of hydrated metal ions to behave as acids may have a profound effect upon the aquatic environment. A good example is *acid mine water* (see Chapter 7), which derives part of its acidic character from the acidic nature of hydrated iron(III):

$$Fe(H_2O)_6^{3+} \square \rightarrow Fe(OH)_3(s) + 3H^+ + 3H_2O \tag{3.9.5}$$
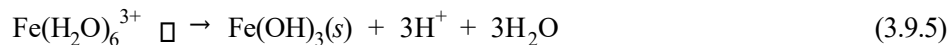
Hydroxide, OH⁻, bonded to a metal ion, may function as a bridging group to join two or more metals together as shown by the following dehydration-dimerization process:

$$2Fe(H_2O)_5OH^{2+} \rightarrow (H_2O)_4Fe \underset{O}{\overset{O}{\diagdown \diagup}} Fe(H_2O)_4^{4+} + 2H_2O \tag{3.9.6}$$
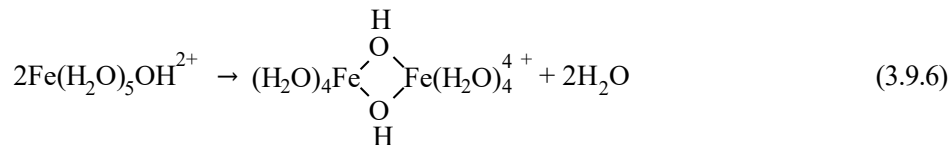
Among the metals other than iron(III) forming polymeric species with OH⁻ as a bridging group are Al(III), Be(II), Bi(III), Ce(IV), Co(III), Cu(II), Ga(III), Mo(V), Pb(II), Sc(II), Sn(IV), and U(VI). Additional hydrogen ions may be lost from water molecules bonded to the dimers, furnishing OH⁻ groups for further bonding and leading to the formation of polymeric hydrolytic species. If the process continues, colloidal hydroxy polymers are formed and, finally, precipitates are produced. This process is thought to be the general one by which hydrated iron(III) oxide, $Fe_2O_3 \cdot x(H_2O)$, (also called ferric hydroxide, $Fe(OH)_3$), is precipitated from solutions containing iron(III).
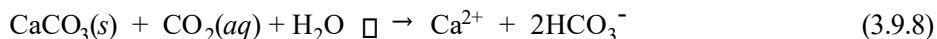
Calcium in Water

Of the cations found in most fresh-water systems, calcium generally has the highest concentration. The chemistry of calcium, although complicated enough, is simpler than that of the transition metal ions found in water. Calcium is a key element in many geochemical processes, and minerals constitute the primary sources of calcium ion in waters. Among the primary contributing minerals are gypsum, $CaSO_4 \cdot 2H_2O$; anhydrite, $CaSO_4$; dolomite, $CaMg(CO_3)_2$; and calcite and aragonite, which are different mineral forms of $CaCO_3$.

Calcium ion, along with magnesium and sometimes iron(II) ion, accounts for **water hardness**. The most common manifestation of water hardness is the curdy precipitate formed by soap in hard water. *Temporary hardness* is due to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O \tag{3.9.7}$$
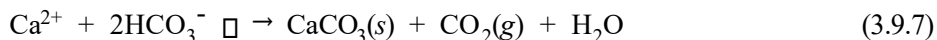
Increased temperature may force this reaction to the right by evolving CO_2 gas, and a white precipitate of calcium carbonate may form in boiling water having temporary hardness.

Water containing a high level of carbon dioxide readily dissolves calcium from its carbonate minerals:

$$CaCO_3(s) + CO_2(aq) + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{3.9.8}$$

When this reaction is reversed and CO_2 is lost from the water, calcium carbonate deposits are formed. The concentration of CO_2 in water determines the extent of dissolution of calcium carbonate. The carbon dioxide that water may gain by equilibration with the atmosphere is not sufficient to account for the levels of calcium

dissolved in natural waters, especially groundwaters. Rather, the respiration of micro-organisms degrading organic matter in water, sediments, and soil,

$$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O \tag{3.9.9}$$

accounts for the very high levels of CO_2 and HCO_3^- observed in water and is very important in aquatic chemical processes and geochemical transformations.

Dissolved Carbon Dioxide and Calcium Carbonate Minerals

The equilibrium between dissolved carbon dioxide and calcium carbonate minerals is important in determining several natural water chemistry parameters such as alkalinity, pH, and dissolved calcium concentration (Figure 3.9). For fresh water, the typical figures quoted for the concentrations of both HCO_3^- and Ca^{2+} are
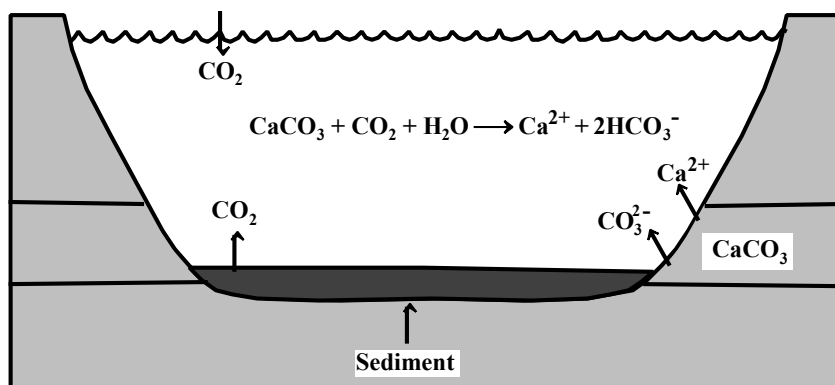

Figure 3.9. Carbon dioxide-calcium carbonate equilibria.

1.00×10^{-3} M. It may be shown that these are reasonable values when the water is in equilibrium with limestone, $CaCO_3$, and with atmospheric CO_2. The concentration of CO_2 in water in equilibrium with air has already been calculated as 1.146×10^{-5} M. The other constants needed to calculate $[HCO_3^-]$ and $[Ca^{2+}]$ are the acid dissociation constant for CO_2:
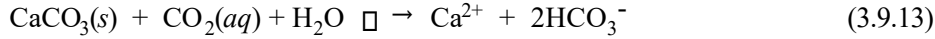
$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \tag{3.9.10}$$

the acid dissociation constant of HCO_3^-:

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \tag{3.9.11}$$

and the solubility product of calcium carbonate (calcite):

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.47 \times 10^{-9} \tag{3.9.12}$$

The reaction between calcium carbonate and dissolved CO_2 is

$$CaCO_3(s) + CO_2(aq) + H_2O \;\square\; \rightarrow \; Ca^{2+} + 2HCO_3^- \tag{3.9.13}$$

for which the equilibrium expression is the following:

$$K' = \frac{[Ca^{2+}][HCO_3^-]^2}{[CO_2]} = \frac{K_{sp}K_{a1}}{K_{a2}} = 4.24 \times 10^{-5} \tag{3.9.14}$$

The stoichiometry of Reaction 3.9.13 gives a bicarbonate ion concentration that is twice that of calcium. Substitution of the value of CO_2 concentration into the expression for K' yields values of 4.99×10^{-4} M for $[Ca^{2+}]$ and 9.98×10^{-4} for $[HCO_3^-]$. Substitution into the expression for K_{sp} yields 8.96×10^{-6} M for $[CO_3^{2-}]$. When known concentrations are substituted into the product $K_{a1}K_{a2}$,

$$K_{a1}K_{a2} = \frac{[H^+]^2[CO_3^{2-}]}{[CO_2]} = 2.09 \times 10^{-17} \tag{3.9.15}$$

a value of 5.17×10^{-9} M is obtained for $[H^+]$ (pH 8.29). The alkalinity is essentially equal to $[HCO_3^-]$, which is much higher than $[CO_3^{2-}]$ or $[OH^-]$.

To summarize, for water in equilibrium with solid calcium carbonate and atmospheric CO_2, the following concentrations are calculated:

$$[CO_2] = 1.146 \times 10^{-5} \text{ M} \qquad [Ca^{2+}] = 4.99 \times 10^{-4} \text{ M}$$

$$[HCO_3^-] = 9.98 \times 10^{-4} \text{ M} \qquad [H^+] = 5.17 \times 10^{-9} \text{ M}$$

$$[CO_3^{2-}] = 8.96 \times 10^{-6} \text{ M} \qquad pH = 8.29$$

Factors such as nonequilibrium conditions, high CO_2 concentrations in bottom regions, and increased pH due to algal uptake of CO_2 cause deviations from these values. Nevertheless, they are close to the values found in a large number of natural water bodies.

3.10. COMPLEXATION AND CHELATION

The properties of metals dissolved in water depend largely upon the nature of metal species dissolved in the water. Therefore, **speciation** of metals plays a crucial role in their environmental chemistry in natural waters and wastewaters. In addition to the hydrated metal ions, for example, $Fe(H_2O)_6^{3+}$ and hydroxy species such as $FeOH(H_2O)_5^{2+}$ discussed in the preceding section, metals may exist in water reversibly bound to inorganic anions or to organic compounds as **metal complexes**. For example, a cyanide ion can bond to dissolved iron(II):

$$Fe(H_2O)_6^{2+} + CN^- \;\square\; \rightarrow \; FeCN(H_2O)_5^+ + H_2O \tag{3.10.1}$$
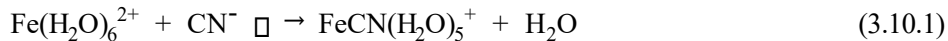
Additional cyanide ions may bond to the iron to form $Fe(CN)_2$, $Fe(CN)_3^-$, $Fe(CN)_4^{2-}$, $Fe(CN)_5^{3-}$, and $Fe(CN)_6^{4-}$, where the water molecules still bound to the iron(II) are omitted for simplicity. This phenomenon is called **complexation**; the species that binds with the metal ion, CN^- in the example above, is called a **ligand**, and the product in which the ligand is bound with the metal ion is a **complex**, **complex ion**, or **coordination compound**. A special case of complexation in which a ligand bonds in two or more places to a metal ion is called **chelation**. In addition to being present as metal complexes, metals may occur in water as **organometallic** compounds containing carbon-to-metal bonds. The solubilities, transport properties, and biological effects of such species are often vastly different from those of the metal ions themselves. Subsequent sections of this chapter consider metal species with an emphasis upon metal complexation, especially chelation, in which particularly strong metal complexes are formed.

In the example above, the cyanide ion is a **unidentate ligand**, which means that it possesses only one site that bonds to a metal ion. Complexes of unidentate ligands are of relatively little importance in solution in natural waters. Of considerably more importance are complexes with **chelating agents.** A chelating agent has more than one atom that may be bonded to a central metal ion at one time to form a ring structure. Thus, pyrophosphate ion, $P_2O_7^{4-}$, bonds to two sites on a calcium ion to form a chelate:

$$O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O \quad 2-$$

$$Ca$$
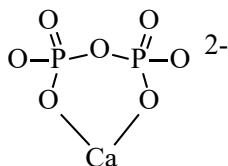
In general, since a chelating agent may bond to a metal ion in more than one place simultaneously (Figure 3.10), chelates are more stable than complexes involv-
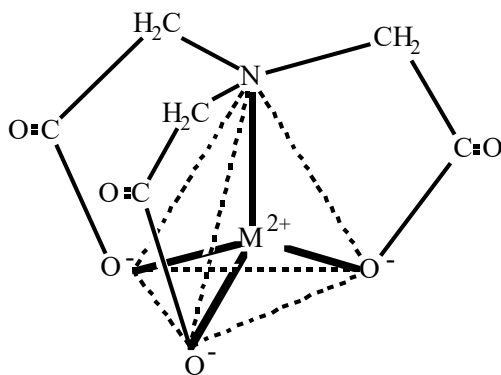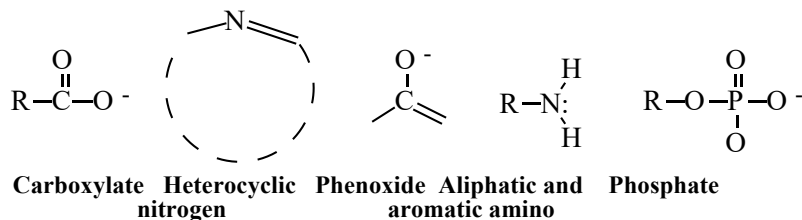

Figure 3.10. Nitrilotriacetate chelate of a divalent metal ion in a tetrahedral configuration.

ing unidentate ligands. Stability tends to increase with the number of chelating sites available on the ligand. Structures of metal chelates take a number of different forms, all characterized by rings in various configurations. The structure of a tetrahedrally coordinated chelate of nitrilotriacetate ion is shown in Figure 3.10.

The ligands found in natural waters and wastewaters contain a variety of functional groups which can donate the electrons required to bond the ligand to a

metal ion.[2] Among the most common of these groups are:

$$R-\underset{\underset{O}{\|}}{C}-O^-$$

Carboxylate

$$\underset{\underset{\diagup\;\;\;\;\;\;\diagdown}{\diagdown\;\;\;\;\;\diagup}}{\overset{N}{\diagup\;\;\;\;\;\;\diagdown}}$$

Heterocyclic
nitrogen

$$\underset{\underset{}{C}}{\overset{O^-}{\diagup}}$$

Phenoxide

$$R-\underset{\underset{H}{|}}{\overset{H}{|}}{N}:$$

Aliphatic and
aromatic amino

$$R-O-\underset{\underset{O}{|}}{\overset{O}{\|}}{P}-O^-$$

Phosphate

These ligands complex most metal ions found in unpolluted waters and biological systems (Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, VO^{2+}). They also bind to contaminant metal ions such as Co^{2+}, Ni^{2+}, Sr^{2+}, Cd^{2+}, and Ba^{2+}.

Complexation may have a number of effects, including reactions of both ligands and metals. Among the ligand reactions are oxidation-reduction, decarboxylation, and hydrolysis. Complexation may cause changes in oxidation state of the metal and may result in a metal becoming solubilized from an insoluble compound. The formation of insoluble complex compounds removes metal ions from solution.

Complex compounds of metals such as iron (in hemoglobin) and magnesium (in chlorophyll) are vital to life processes. Naturally occurring chelating agents, such as humic substances and amino acids, are found in water and soil. The high concentration of chloride ion in seawater results in the formation of some chloro complexes. Synthetic chelating agents such as sodium tripolyphosphate, sodium ethylenediaminetetraacetate (EDTA), sodium nitrilotriacetate (NTA), and sodium citrate are produced in large quantities for use in metal-plating baths, industrial water treatment, detergent formulations, and food preparation. Small quantities of these compounds enter aquatic systems through waste discharges.

Occurrence and Importance of Chelating Agents in Water

Chelating agents are common potential water pollutants. These substances can occur in sewage effluent and industrial wastewater such as metal plating wastewater. Chelates formed by the strong chelating agent ethylenediaminetetraacetate (EDTA, structure illustrated at the beginning of Section 3.13) have been shown to greatly increase the migration rates of radioactive ^{60}Co from pits and trenches used by the Oak Ridge National Laboratory in Oak Ridge, Tennessee, for disposal of intermediate-level radioactive waste[3]. EDTA was used as a cleaning and solubilizing agent for the decontamination of hot cells, equipment, and reactor components. Analysis of water from sample wells in the disposal pits showed EDTA concentrations of 3.4×10^{-7} M. The presence of EDTA 12-15 years after its burial attests to its low rate of biodegradation. In addition to cobalt, EDTA strongly chelates radioactive plutonium and radioisotopes of Am^{3+}, Cm^{3+}, and Th^{4+}. Such chelates with negative charges are much less strongly sorbed by mineral matter and are vastly more mobile than the unchelated metal ions.

Contrary to the above findings, only very low concentrations of chelatable radioactive plutonium were observed in groundwater near the Idaho Chemical Processing Plant's low-level waste disposal well.[4] No plutonium was observed in wells at any significant distance from the disposal well. The waste processing procedure