Manahan, Stanley E. "FUNDAMENTALS OF AQUATIC CHEMISTRY"
Environmental Chemistry
Boca Raton: CRC Press LLC, 2000

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.

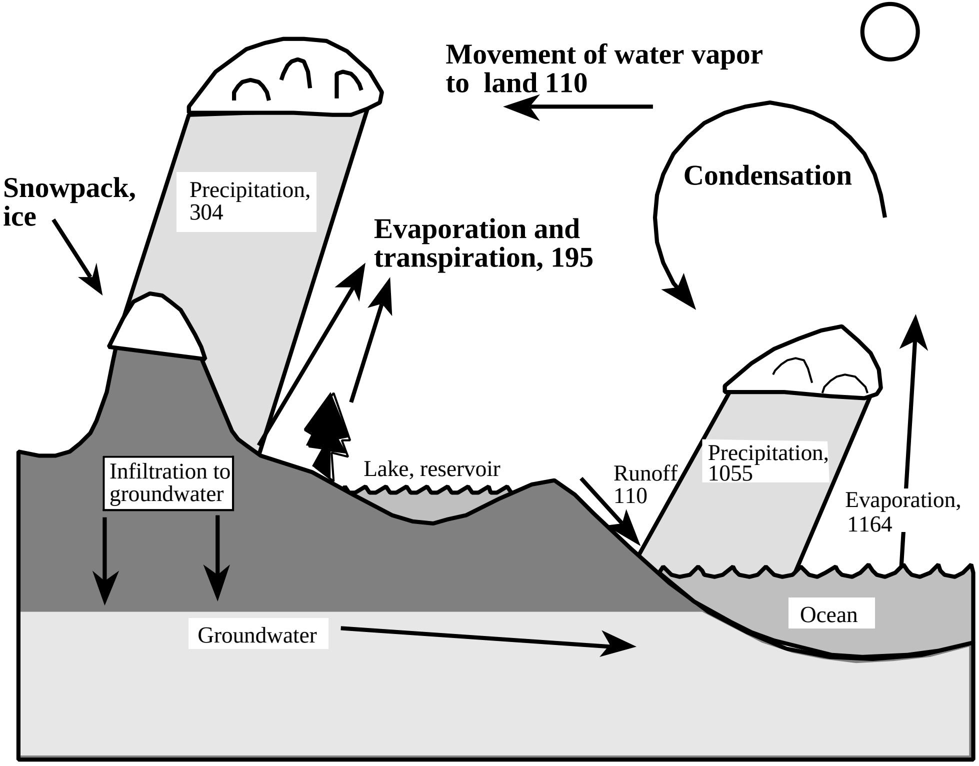


Figure 3.1. The hydrologic cycle, quantities of water in trillions of liters per day.

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.

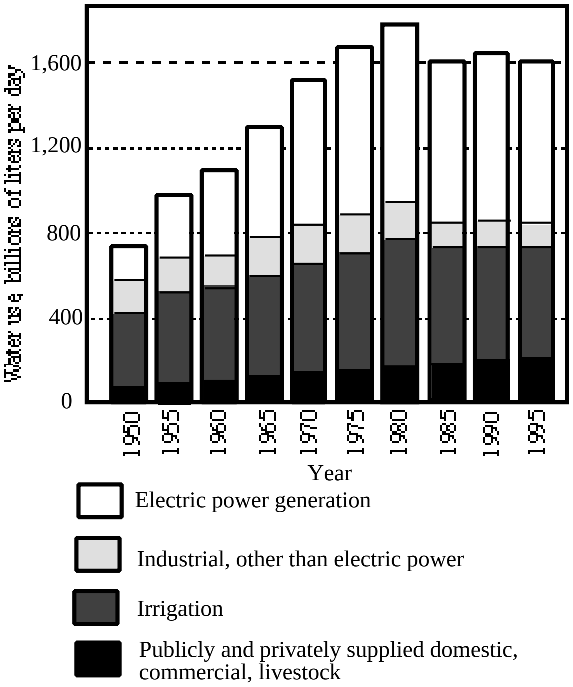


Figure 3.2. Trends in Water Use in The United States (Data from U.S. Geological Survey).

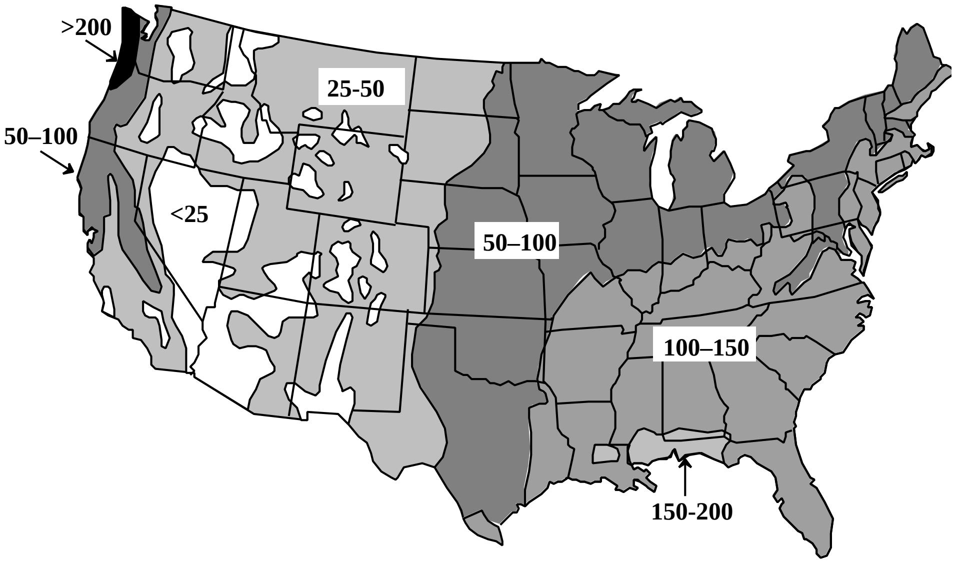


Figure 3.3. Distribution of precipitation in the continental U.S., showing average annual rainfall in centimeters.

3.2. THE PROPERTIES OF WATER, A UNIQUE SUBSTANCE

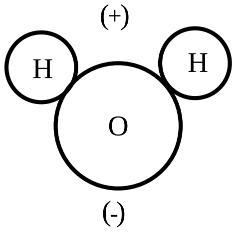
Water has a number of unique properties that are essential to life. Some of the special characteristics of water include its polar character, tendency to form hydrogen bonds, and ability to hydrate metal ions. These properties are listed in Table 3.1.

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.

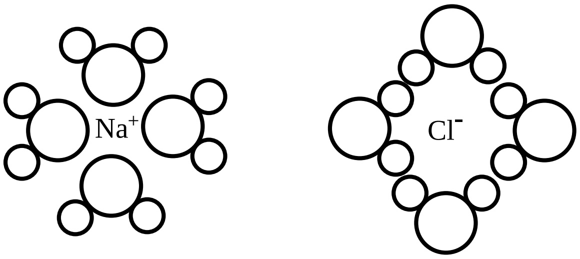


Figure 3.4. Polar water molecules surrounding Na^+ ion (left) and Cl^- ion (right).

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.

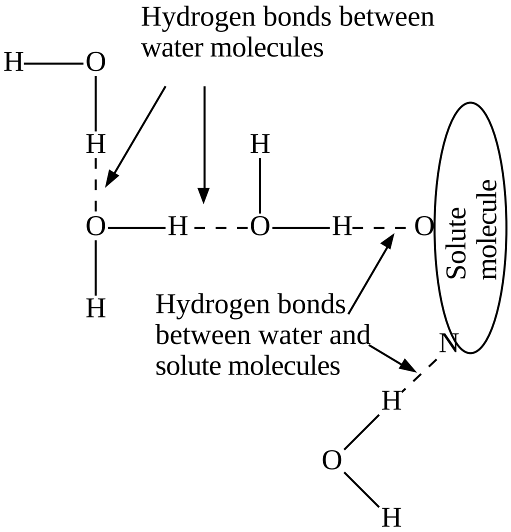


Figure 3.5. Hydrogen bonding between water molecules and between water molecules and a solute molecule in solution.

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.

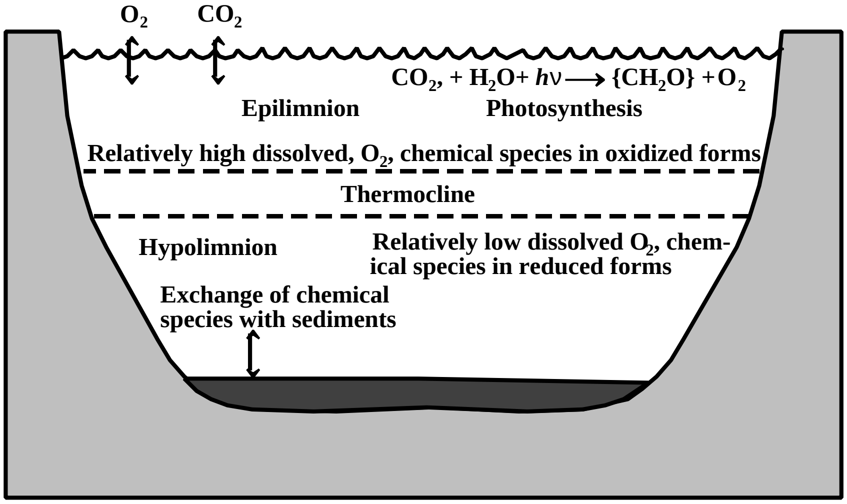


Figure 3.6. Stratification of a lake.

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 $CaCO_3$.

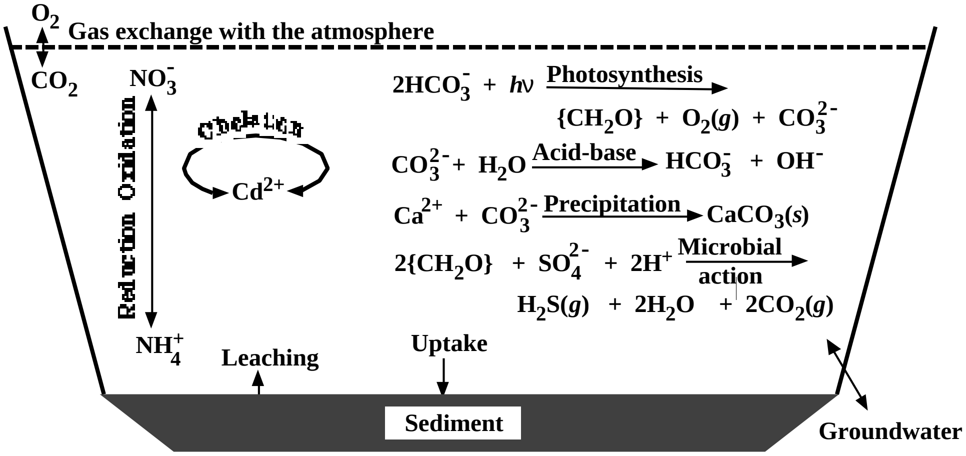


Figure 3.7. Major aquatic chemical processes.

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 biodegradation 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 $\{CH_2O\}$. 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:

$$HCO_3^- \leftrightarrows CO_3^{2-} + H^+ \tag{3.7.1}$$

$$HCO_3^- + H^+ \leftrightarrows CO_2(aq) + H_2O \tag{3.7.2}$$

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 $H_2PO_4^-$, H_2S, 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_2SO_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:

$$Al(H_2O)_6^{3+} \leftrightarrows Al(H_2O)_5OH^{2+} + H^+ \tag{3.7.3}$$

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,

$$CO_2(\text{water}) \leftrightarrows CO_2(\text{atmosphere}) \tag{3.7.4}$$

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

$$MCO_3(\text{slightly soluble carbonate salt}) \leftrightarrows M^{2+} + CO_3^{2-} \tag{3.7.5}$$

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:

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

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

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

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,

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

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

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

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

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 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:

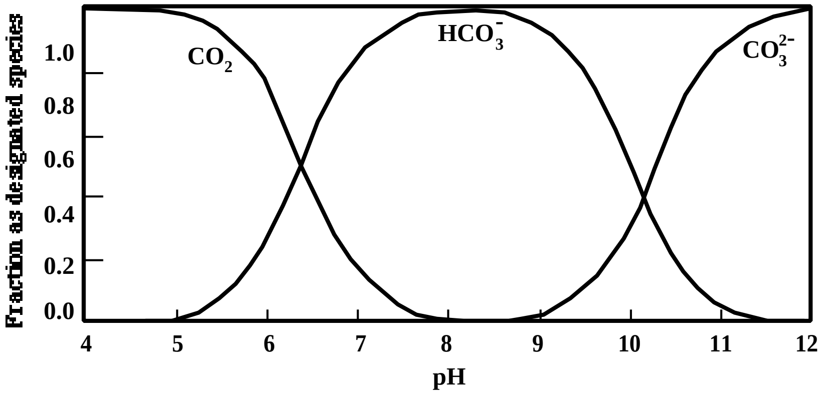


Figure 3.8. Distribution of species diagram for the CO_2–HCO_3^-–CO_3^{2-} system in water.

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

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

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

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:

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

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

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

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^-:

$$CO_2 + H_2O \leftrightarrows HCO_3^- + H^+ \qquad (3.7.18)$$

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

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

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

$$pH = 5.65$$

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:

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

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

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

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^-:

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

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

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

and

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

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],

$$[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (3.8.9)$$

varies with pH. At pH 7.00,

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

whereas at pH 10.00,

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

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

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

and

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

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

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

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

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

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

Substituting values calculated in Section 3.7 gives

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

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

$$CO_2(ag) + OH^- \leftarrow\rightarrow HCO_3^- \qquad (3.8.16)$$

so that

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

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,

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

precipitation,

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

and oxidation-reduction reactions:

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

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,

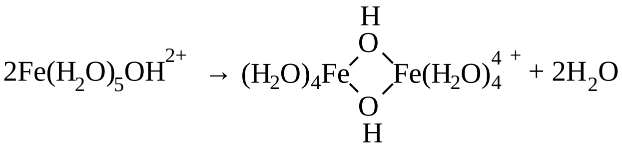
$$Fe(H_2O)_6^{3+} \leftarrow\rightarrow Fe(H_2O)_5OH^{2+} + H^+ \qquad (3.9.4)$$

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):

$$Fe(H_2O)_6^{3+} \leftarrow\rightarrow Fe(OH)_3(s) + 3H^+ + 3H_2O \qquad (3.9.5)$$

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:



$$2Fe(H_2O)_5OH^{2+} \rightarrow (H_2O)_4Fe\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\diamond}}Fe(H_2O)_4^{4+} + 2H_2O \tag{3.9.6}$$

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, $Fe_2O_3{\bullet}x(H_2O)$, (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, $CaSO_4{\bullet}2H_2O$; 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:

$$Ca^{2+} + 2HCO_3^- \leftarrow\rightarrow CaCO_3(s) + CO_2(g) + H_2O \tag{3.9.7}$$

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:

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

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 microorganisms 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

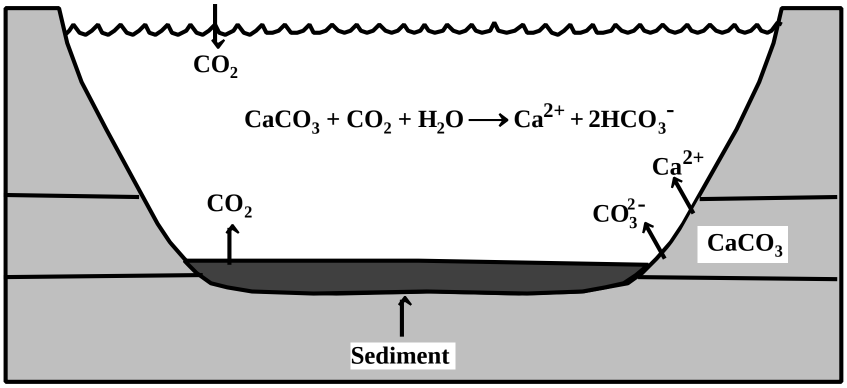


Figure 3.9. Carbon dioxide-calcium carbonate equilibria.

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

$$CaCO_3(s) + CO_2(aq) + H_2O \leftarrow\rightarrow Ca^{2+} + 2HCO_3^- \quad (3.9.13)$$

for which the equilibrium expression is the following:

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

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 $K_{a1}K_{a2}$,

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

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:

$[CO_2] = 1.146 \times 10^{-5}$ M
$[Ca^{2+}] = 4.99 \times 10^{-4}$ M
$[HCO_3^-] = 9.98 \times 10^{-4}$ M
$[H^+] = 5.17 \times 10^{-9}$ M
$[CO_3^{2-}] = 8.96 \times 10^{-6}$ M
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.

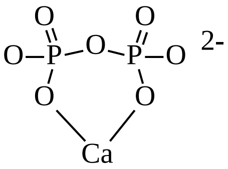
3.10. COMPLEXATION AND CHELATION

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):

$$Fe(H_2O)_6^{2+} + CN^- \leftarrow\rightarrow FeCN(H_2O)_5^+ + H_2O \quad (3.10.1)$$

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:



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 involving 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.

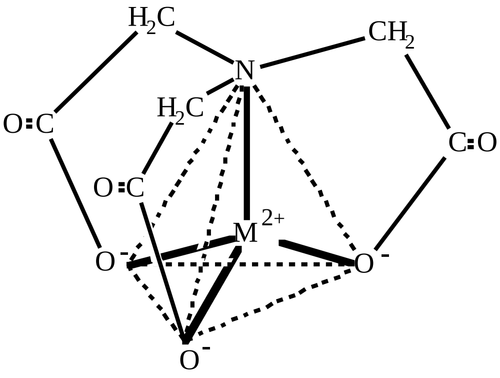
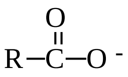


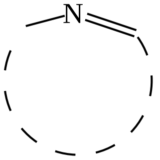
Figure 3.10. Nitrilotriacetate chelate of a divalent metal ion in a tetrahedral configuration.

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:

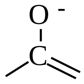


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$$

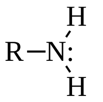
Carboxylate



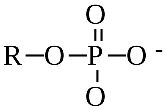
Heterocyclic nitrogen



Phenoxide



Aliphatic and aromatic amino



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

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 used was designed to destroy any chelating agents in the waste prior to disposal, and no chelating agents were found in the water pumped from the test wells.

The fate of radionuclide metal chelates that have been discarded in soil is obviously important. If some mechanism exists to destroy the chelating agents, the radioactive metals will be much less mobile. Although EDTA is only poorly biodegradable, nitrilotriacetate, NTA, is degraded by the action of *Chlatobacter heintzii* bacteria. In addition to uncomplexed NTA, these bacteria have been shown to degrade NTA that is chelated to metals, including cobalt, iron, zinc, aluminum, copper, and nickel.[5]

Complexing agents in wastewater are of concern primarily because of their ability to solubilize heavy metals from plumbing, and from deposits containing heavy metals. Complexation may increase the leaching of heavy metals from waste disposal sites and reduce the efficiency with which heavy metals are removed with sludge in conventional biological waste treatment. Removal of chelated iron is difficult with conventional municipal water treatment processes. Iron(III) and perhaps several other essential micronutrient metal ions are kept in solution by chelation in algal cultures. The availability of chelating agents may be a factor in determining algal growth. The yellow-brown color of some natural waters is due to naturally-occurring chelates of iron.

3.11. BONDING AND STRUCTURE OF METAL COMPLEXES

This section discusses some of the fundamentals helpful in understanding complexation in water. A complex consists of a central metal atom to which neutral or negatively charged ligands possessing electron-donor properties are bonded. The resulting complex may be neutral or may have a positive or negative charge. The ligands are said to be contained within the **coordination sphere** of the central metal atom. Depending upon the type of bonding involved, the ligands within the coordination sphere are held in a definite structural pattern. However, in solution, ligands of many complexes exchange rapidly between solution and the coordination sphere of the central metal ion.

The **coordination number** of a metal atom, or ion, is the number of ligand electron-donor groups that are bonded to it. The most common coordination numbers are 2, 4, and 6. Polynuclear complexes contain two or more metal atoms joined together through bridging ligands, frequently OH, as shown for iron(III) in Reaction 3.9.6.

Selectivity and Specificity in Chelation

Although chelating agents are never entirely specific for a particular metal ion, some complicated chelating agents of biological origin approach almost complete specificity for certain metal ions. One example of such a chelating agent is ferrichrome, synthesized by and extracted from fungi, which forms extremely stable chelates with iron(III). It has been observed that cyanobacteria of the *Anabaena* species secrete appreciable quantities of iron-selective hydroxamate chelating agents during periods of heavy algal bloom.[6] These photosynthetic organisms readily take up iron chelated by hydroxamate-chelated iron, whereas some competing green algae, such as *Scenedesmus*, do not. Thus, the chelating agent serves a dual function of promoting the growth of certain cyanobacteria while suppressing the growth of competing species, allowing the cyanobacteria to exist as the predominant species

3.12. CALCULATIONS OF SPECIES CONCENTRATIONS

The stability of complex ions in solution is expressed in terms of **formation constants**. These can be **stepwise formation constants** (K expressions) representing the bonding of individual ligands to a metal ion, or **overall formation constants** (β expressions) representing the binding of two or more ligands to a metal ion. These concepts are illustrated for complexes of zinc ion with ammonia by the following:

$$Zn^{2+} + NH_3 \leftarrow\rightarrow ZnNH_3^{2+} \qquad (3.12.1)$$

$$K_1 = \frac{[ZnNH_3^{2+}]}{[Zn^{2+}][NH_3]} = 3.9 \times 10^2 \text{ (Stepwise formation constant)} \qquad (3.12.2)$$

$$ZnNH_3^{2+} + NH_3 \leftarrow\rightarrow Zn(NH_3)_2^{2+} \qquad (3.12.3)$$

$$K_2 = \frac{[Zn(NH_3)_2^{2+}]}{[ZnNH_3^{2+}][NH_3]} = 2.1 \times 10^2 \qquad (3.12.4)$$

$$Zn^{2+} + 2NH_3 \leftarrow\rightarrow Zn(NH_3)_2^{2+} \qquad (3.12.5)$$

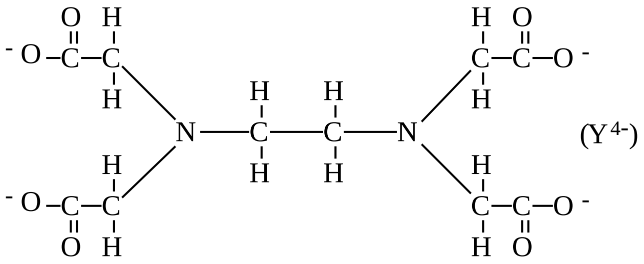
$$\beta_2 = \frac{[Zn(NH_3)_2^{2+}]}{[Zn^{2+}][NH_3]^2} = K_1K_2 = 8.2 \times 10^4 \text{ (Overall formation constant)} \qquad (3.12.6)$$

(For $Zn(NH_3)_3^{2+}$, $\beta_3 = K_1K_2K_3$ and for $Zn(NH_3)_4^{2+}$, $\beta_4 = K_1K_2K_3K_4$.)

The following sections show some calculations involving chelated metal ions in aquatic systems. Because of their complexity, the details of these calculations may be beyond the needs of some readers, who may choose to simply consider the results. In addition to the complexation itself, consideration must be given to competition of H^+ for ligands, competition among metal ions for ligands, competition among different ligands for metal ions, and precipitation of metal ions by various precipitants. Not the least of the problems involved in such calculations is the lack of accurately known values of equilibrium constants to be used under the conditions being considered, a factor which can yield questionable results from even the most elegant computerized calculations. Furthermore, kinetic factors are often quite important. Such calculations, however, can be quite useful to provide an overall view of aquatic systems in which complexation is important, and as general guidelines to determine areas in which more data should be obtained.

3.13. COMPLEXATION BY DEPROTONATED LIGANDS

In most circumstances, metal ions and hydrogen ions compete for ligands, making the calculation of species concentrations more complicated. Before going into such calculations, however, it is instructive to look at an example in which the ligand has lost all ionizable hydrogen. At pH values of 11 or above, EDTA is essentially all in the completely ionized tetranegative form, Y^{4-}, illustrated below:



Consider a wastewater with an alkaline pH of 11 containing copper(II) at a total level of 5.0 mg/L and excess uncomplexed EDTA at a level of 200 mg/L (expressed as the disodium salt, $Na_2H_2C_{10}H_{12}O_8N_2{\bullet}2H_2O$, formula weight 372). At this pH uncomplexed EDTA is present as ionized Y^{4-}. The questions to be asked are: Will most of the copper be present as the EDTA complex? If so, what will be the equilibrium concentration of the hydrated copper(II) ion, Cu^{2+}? To answer the former question it is first necessary to calculate the molar concentration of uncomplexed excess EDTA, Y^{4-}. Since disodium EDTA with a formula weight of 372 is present at 200 mg/L (ppm), the total molar concentration of EDTA as Y^{4-} is 5.4×10^{-4} M. The formation constant K_1 of the copper-EDTA complex CuY^{2-} is

$$K_1 = \frac{[CuY^{2-}]}{[Cu^{2+}][Y^{4-}]} = 6.3 \times 10^{18} \qquad (3.13.1)$$

The ratio of complexed copper to uncomplexed copper is

$$\frac{[CuY^{2-}]}{[Cu^{2+}]} = [Y^{4-}]K_1 = 5.4 \times 10^{-4} \times 6.3 \times 10^{18} = 3.3 \times 10^{15} \qquad (3.13.2)$$

and, therefore, essentially all of the copper is present as the complex ion. The molar concentration of total copper(II) in a solution containing 5.0 mg/L copper(II) is 7.9×10^{-5} M, which in this case is essentially all in the form of the EDTA complex. The very low concentration of uncomplexed, hydrated copper(II) ion is given by

$$[Cu^{2+}] = \frac{[CuY^{2-}]}{K_1[Y^{4-}]} = \frac{7.9 \text{ x } 10^{-5}}{6.3 \times 10^{18} \times 5.4 \times 10^{-4}} = 2.3 \times 10^{-20} \text{ M} \qquad (3.13.3)$$

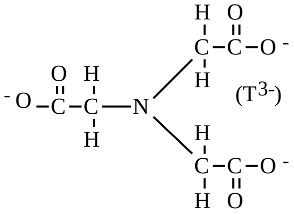
It is seen that in the medium described, the concentration of hydrated copper(II) ion is extremely low compared to total copper(II) ion. Any phenomenon in solution that depends upon the concentration of the hydrated copper(II) ion (such as a physiological effect or an electrode response) would be very different in the medium described, as compared to the effect observed if all of the copper at a level of 5.0 mg/L were present as Cu^{2+} in a more acidic solution and in the absence of complexing agent. The phenomenon of reducing the concentration of hydrated metal ion to very low values through the action of strong chelating agents is one of the most important effects of complexation in natural aquatic systems.

3.14. COMPLEXATION BY PROTONATED LIGANDS

Generally, complexing agents, particularly chelating compounds, are conjugate bases of Brönsted acids; for example, glycinate anion, $H_2NCH_2CO_2^-$, is the conjugate base of glycine, $^+H_3NCH_2CO_2^-$. Therefore, in many cases hydrogen ion competes with metal ions for a ligand, so that the strength of chelation depends upon pH. In the nearly neutral pH range usually encountered in natural waters, most organic ligands are present in a conjugated acid form.

In order to understand the competition between hydrogen ion and metal ion for a ligand, it is useful to know the distribution of ligand species as a function of pH. Consider nitrilotriacetic acid, commonly designated H_3T, as an example. The trisodium salt of this compound, (NTA) is used as a detergent phosphate substitute and is a strong chelating agent. Biological processes are required for NTA degradation, and under some conditions it persists for long times in water. Given the ability of NTA to solubilize and transport heavy metal ions, this material is of considerable environmental concern.

Nitrilotriacetic acid, H_3T, loses hydrogen ion in three steps to form the nitrilotriacetate anion, T^{3-}, the structural formula of which is



The T^{3-} species may coordinate through three $-CO_2^-$ groups and through the nitrogen atom, as shown in Figure 3.10. Note the similarity of the NTA structure to that of EDTA, discussed in Section 3.13. The stepwise ionization of H_3T is described by the following equilibria:

$$H_3T \rightleftarrows H^+ + H_2T^- \qquad (3.14.1)$$

$$K_{a1} = \frac{[H^+][H_2T^-]}{[H_3T]} = 2.18 \times 10^{-2} \qquad pK_{a1} = 1.66 \qquad (3.14.2)$$

$$H_2T^- \rightleftarrows H^+ + HT^{2-} \qquad (3.14.3)$$

$$K_{a2} = \frac{[H^+][HT^{2-}]}{[H_2T^-]} = 1.12 \times 10^{-3} \qquad pK_{a2} = 2.95 \qquad (3.14.4)$$

$$HT^{2-} \rightleftarrows H^{+} + T^{3-} \qquad (3.14.5)$$

$$K_{a3} = \frac{[H^{+}][T^{3-}]}{[HT^{2-}]} = 5.25 \times 10^{-11} \qquad pK_{a3} = 10.28 \qquad (3.14.6)$$

These expressions show that uncomplexed NTA may exist in solution as any one of the four species, H_3T, H_2T^-, HT^{2-}, or T^{3-}, depending upon the pH of the solution. As was shown for the $CO_2/HCO_3^-/CO_3^{2-}$ system in Section 3.7 and Figure 3.8, fractions of NTA species can be illustrated graphically by a diagram of the distribution-of-species with pH as a master (independent) variable. The key points used to plot such a diagram for NTA are given in Table 3.2, and the plot of fractions of species (α values) as a function of pH is shown in Figure 3.11. Examination of the plot shows that the complexing anion T^{3-} is the predominant species only at relatively high pH values, much higher than usually would be encountered in natural waters. The HT^{2-} species has an extremely wide range of predominance, however, spanning the entire normal pH range of ordinary fresh waters.

Table 3.2. Fractions of NTA Species at Selected pH Values

pH value	α_{H_3T}	$\alpha_{H_2T^-}$	$\alpha_{HT^{2-}}$	$\alpha_{T^{3-}}$
pH below 1.00	1.00	0.00	0.00	0.00
pH = pK_{a1}	0.49	0.49	0.02	0.00
pH = $\frac{1}{2}(pK_{a1} + pK_{a2})$	0.16	0.68	0.16	0.00
pH = pK_{a2}	0.02	0.49	0.49	0.00
pH = $\frac{1}{2}(pK_{a2} + pK_{a3})$	0.00	0.00	1.00	0.00
pH = pK_{a3}	0.00	0.00	0.50	0.50
pH above 12	0.00	0.00	0.00	1.00

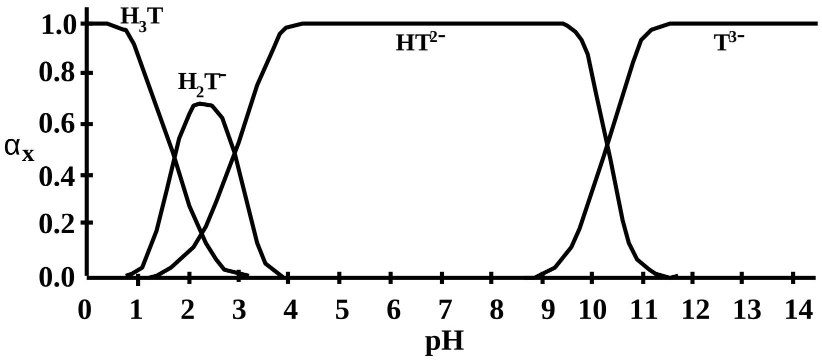


Figure 3.11. Plot of fraction of species α_x as a function of pH for NTA species in water.

3.15. SOLUBILIZATION OF LEAD ION FROM SOLIDS BY NTA

A major concern regarding the widespread introduction of strong chelating agents such as NTA into aquatic ecosystems from sources such as detergents or electroplating wastes is that of possible solubilization of toxic heavy metals from solids through the action of chelating agents. Experimentation is required to determine whether this may be a problem, but calculations are helpful in predicting probable effects. The extent of solubilization of heavy metals depends upon a number of factors, including the stability of the metal chelates, the concentration of the complexing agent in the water, pH, and the nature of the insoluble metal deposit. Several example calculations are given here.

Consider first the solubilization of lead from solid $Pb(OH)_2$ by NTA at pH 8.00. As illustrated in Figure 3.11, essentially all uncomplexed NTA is present as HT^{2-} ion at pH 8.00. Therefore, the solubilization reaction is

$$Pb(OH)_2(s) + HT^{2-} \rightleftarrows PbT^{-} + OH^{-} + H_2O \tag{3.15.1}$$

which may be obtained by adding the following reactions:

$$Pb(OH)_2(s) \rightleftarrows Pb^{2+} + 2OH^{-} \tag{3.15.2}$$

$$K_{sp} = [Pb^{2+}][OH^{-}]^2 = 1.61 \times 10^{-20} \tag{3.15.3}$$

$$HT^{2-} \rightleftarrows H^{+} + T^{3-} \tag{3.15.4}$$

$$K_{a3} = \frac{[H^+][T^{3-}]}{[HT^{2-}]} = 5.25 \times 10^{-11} \tag{3.15.5}$$

$$Pb^{2+} + T^{3-} \rightleftarrows PbT^{-} \tag{3.15.6}$$

$$K_f = \frac{[PbT^-]}{[Pb^{2+}][T^{3-}]} = 2.45 \times 10^{11} \tag{3.15.7}$$

$$H^{+} + OH^{-} \rightleftarrows H_2O \tag{3.15.8}$$

$$\frac{1}{K_w} = \frac{1}{[H^+][OH^-]} = \frac{1}{1.00 \times 10^{-14}} \tag{3.15.9}$$

$$Pb(OH)_2(s) + HT^{2-} \rightleftarrows PbT^{-} + OH^{-} + H_2O \tag{3.15.1}$$

$$K = \frac{[PbT^-][OH^-]}{[HT^{2-}]} = \frac{K_{sp}K_{a3}K_f}{K_w} = 2.07 \times 10^{-5} \tag{3.15.10}$$

Assume that a sample of water contains 25 mg/L of $N(CH_2CO_2Na)_3$, the trisodium NTA salt, formula weight 257. The total concentration of both complexed and uncomplexed NTA is 9.7×10^{-5} mmol/mL. Assuming a system in which NTA at pH 8.00 is in equilibrium with solid $Pb(OH)_2$, the NTA may be primarily in the uncomplexed form, HT^{2-}, or in the lead complex, PbT^{-}. The predominant species may be determined by calculating the $[PbT^-]/[HT^{2-}]$ ratio from the expression for K, noting that at pH 8.00, $[OH^-] = 1.00 \times 10^{-6}$ M:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[OH^-]} = \frac{2.07 \times 10^{-5}}{1.00 \times 10^{-6}} = 20.7 \qquad (3.15.11)$$

Since $[PbT^-]/[HT^{2-}]$ is approximately 20 to 1, most of the NTA in solution is present as the lead chelate. The molar concentration of PbT^- is just slightly less than the 9.7×10^{-5} mmols/mL total NTA present. The atomic weight of lead is 207, so the concentration of lead in solution is approximately 20 mg/L. This reaction is pH-dependent such that the fraction of NTA chelated decreases with increasing pH.

Reaction of NTA with Metal Carbonate

Carbonates are common forms of heavy metal ion solids. Solid lead carbonate, $PbCO_3$, is stable within the pH region and alkalinity conditions often found in natural waters and wastewaters. An example similar to the one in the preceding section may be worked, assuming that equilibrium is established with $PbCO_3$ rather than with solid $Pb(OH)_2$. In this example it is assumed that 25 mg/L of trisodium NTA is in equilibrium with $PbCO_3$ at pH 7.00 and a calculation is made to determine whether the lead will be complexed appreciably by the NTA. The carbonate ion, CO_3^{2-}, reacts with H^+ to form HCO_3^-. As discussed in Section 3.7, the acid-base equilibrium reactions for the $CO_2/HCO_3^-/CO_3^{2-}$ system are

$$CO_2 + H_2O \leftrightarrows HCO_3^- + H^+ \qquad (3.3.6)$$

$$K'_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK'_{a1} = 6.35 \qquad (3.3.7)$$

$$HCO_3^- \leftrightarrows CO_3^{2-} + H^+ \qquad (3.3.8)$$

$$K'_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK'_{a2} = 10.33 \qquad (3.3.9)$$

where the acid dissociation constants of the carbonate species are designated as K'_a to distinguish them from the acid dissociation constants of NTA. Figure 3.8 shows that within a pH range of about 7 to 10 the predominant carbonic species is HCO_3^-; therefore, the CO_3^{2-} released by the reaction of NTA with $PbCO_3$ will go into solution as HCO_3^-:

$$PbCO_3(s) + HT^{2-} \leftrightarrows PbT^- + HCO_3^- \qquad (3.15.12)$$

This reaction and its equilibrium constant are obtained as follows:

$$PbCO_3(s) \leftrightarrows Pb^{2+} + CO_3^{2-} \qquad (3.15.13)$$

$$K_{sp} = [Pb^{2+}][CO_3^{2-}] = 1.48 \times 10^{-13} \qquad (3.15.14)$$

$$Pb^{2+} + T^{3-} \leftrightarrows PbT^{-} \tag{3.15.6}$$

$$K_f = \frac{[PbT^-]}{[Pb^{2+}][T^{3-}]} = 2.45 \times 10^{11} \tag{3.15.7}$$

$$HT^{2-} \leftrightarrows H^+ + T^{3-} \tag{3.15.4}$$

$$K_{a3} = \frac{[H^+][T^{3-}]}{[HT^{2-}]} = 5.25 \times 10^{-11} \tag{3.15.5}$$

$$CO_3^{2-} + H^+ \leftrightarrows HCO_3^- \tag{3.15.15}$$

$$\frac{1}{K'_{a2}} = \frac{[HCO_3^-]}{[CO_3^{2-}][H^+]} = \frac{1}{4.69 \times 10^{-11}} \tag{3.15.16}$$

$$PbCO_3(s) + HT^{2-} \leftrightarrows PbT^- + HCO_3^- \tag{3.15.12}$$

$$K = \frac{[PbT^-][HCO_3^-]}{[HT^{2-}]} = \frac{K_{sp}K_{a3}K_f}{K'_{a2}} = 4.06 \times 10^{-2} \tag{3.15.17}$$

From the expression for K, Equation 3.15.17, it may be seen that the degree to which $PbCO_3$ is solubilized as PbT^- depends upon the concentration of HCO_3^-. Although this concentration will vary appreciably, the figure commonly used to describe natural waters is a bicarbonate ion concentration of 1.00×10^{-3}, as shown in Section 3.9. Using this value the following may be calculated:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.00 \times 10^{-3}} = 40.6 \tag{3.15.18}$$

Thus, under the given conditions, most of the NTA in equilibrium with solid $PbCO_3$ would be present as the lead complex. As in the previous example, at a trisodium NTA level of 25 mg/L, the concentration of soluble lead(II) would be approximately 20 mg/L. At relatively higher concentrations of HCO_3^-, the tendency to solubilize lead would be diminished, whereas at lower concentrations of HCO_3^-, NTA would be more effective in solubilizing lead.

Effect of Calcium Ion upon the Reaction of Chelating Agents with Slightly Soluble Salts

Chelatable calcium ion, Ca^{2+}, which is generally present in natural waters and wastewaters, competes for the chelating agent with a metal in a slightly soluble salt, such as $PbCO_3$. At pH 7.00, the reaction between calcium ion and NTA is

$$Ca^{2+} + HT^{2-} \leftrightarrows CaT^- + H^+ \tag{3.15.19}$$

described by the following equilibrium expression:

$$K' = \frac{[CaT^-][H^+]}{[Ca^{2+}][HT^{2-}]} = 1.48 \times 10^8 \times 5.25 \times 10^{-11} = 7.75 \times 10^{-3} \qquad (3.15.20)$$

The value of K' is the product of the formation constant of CaT^-, (1.48×10^8), and K_{a3} of NTA, 5.25×10^{-11}. The fraction of NTA bound as CaT^- depends upon the concentration of Ca^{2+} and the pH. Typically, $[Ca^{2+}]$ in water is 1.00×10^{-3} M. Assuming this value and pH 7.00, the ratio of NTA present in solution as the calcium complex to that present as HT^{2-} is:

$$\frac{[CaT^-]}{[HT^{2-}]} = \frac{[Ca^{2+}]}{[H^+]} K' = \frac{1.00 \times 10^{-3}}{1.00 \times 10^{-7}} \times 7.75 \times 10^{-3} \qquad (3.15.21)$$

$$\frac{[CaT^-]}{[HT^{2-}]} = 77.5$$

Therefore, most of the NTA in equilibrium with 1.00×10^{-3} M Ca^{2+} would be present as the calcium complex, CaT^-, which would react with lead carbonate as follows:

$$PbCO_3(s) + CaT^- + H^+ \leftarrow\rightarrow Ca^{2+} + HCO_3^- + PbT^- \qquad (3.15.22)$$

$$K'' = \frac{[Ca^{2+}][HCO_3^-][PbT^-]}{[CaT^-][H^+]} \qquad (3.15.23)$$

Reaction 3.15.22 may be obtained by subtracting Reaction 3.15.19 from Reaction 3.15.12, and its equilibrium constant may be obtained by dividing the equilibrium constant of Reaction 3.15.19 into that of Reaction 3.15.12:

$$PbCO_3(s) + HT^{2-} \leftarrow\rightarrow PbT^- + HCO_3^- \qquad (3.15.12)$$

$$K = \frac{[PbT^-][HCO_3^-]}{[HT^{2-}]} = \frac{K_s K_{a3} K_f}{K'_{a2}} = 4.06 \times 10^{-2} \qquad (3.15.17)$$

$$-(Ca^{2+} + HT^{2-} \leftarrow\rightarrow CaT^- + H^+) \qquad (3.15.19)$$

$$K' = \frac{[CaT^-][H^+]}{[Ca^{2+}][HT^{2-}]} = 7.75 \times 10^{-3} \qquad (3.15.20)$$

$$PbCO_3(s) + CaT^- + H^+ \leftarrow\rightarrow Ca^{2+} + HCO_3^- + PbT^- \qquad (3.15.22)$$

$$K'' = \frac{K}{K'} = \frac{4.06 \times 10^{-2}}{7.75 \times 10^{-3}} = 5.24 \qquad (3.15.24)$$

Having obtained the value of K", it is now possible to determine the distribution of NTA between PbT^- and CaT^-. Thus, for water containing NTA chelated to calcium at pH 7.00, a concentration of HCO_3^- of 1.00×10^{-3}, a concentration of Ca^{2+} of 1.00×10^{-3}, and in equilibrium with solid $PbCO_3$, the distribution of NTA between the lead complex and the calcium complex is:

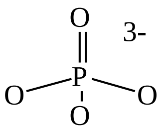
$$\frac{[PbT^-]}{[CaT^-]} = \frac{[H^+]K''}{[Ca^{2+}][HCO_3^-]} = \frac{1.00 \times 10^{-7} \times 5.24}{1.00 \times 10^{-3} \times 1.00 \times 10^{-3}} = 0.524$$

It may be seen that only about 1/3 of the NTA would be present as the lead chelate, whereas under the identical conditions, but in the absence of Ca^{2+}, approximately all of the NTA in equilibrium with solid $PbCO_3$ was chelated to NTA. Since the fraction of NTA present as the lead chelate is directly proportional to the solubilization of $PbCO_3$, differences in calcium concentration will affect the degree to which NTA solubilizes lead from lead carbonate.

3.16. POLYPHOSPHATES IN WATER

Phosphorus occurs as many oxoanions, anionic forms in combination with oxygen. Some of these are strong complexing agents. Since about 1930, salts of polymeric phosphorus oxoanions have been used for water treatment, for water softening, and as detergent builders. When used for water treatment, polyphosphates "sequester" calcium ion in a soluble or suspended form. The effect is to reduce the equilibrium concentration of calcium ion and prevent the precipitation of calcium carbonate in installations such as water pipes and boilers. Furthermore, when water is softened properly with polyphosphates, calcium does not form precipitates with soaps or interact detrimentally with detergents.

The simplest form of phosphate is orthophosphate, PO_4^{3-}:

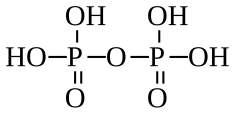


The orthophosphate ion possesses three sites for attachment of H^+. Orthophosphoric acid, H_3PO_4, has a pK_{a1} of 2.17, a pK_{a2} of 7.31, and a pK_{a3} of 12.36. Because the third hydrogen ion is so difficult to remove from orthophosphate, as evidenced by the very high value of pK_{a3}, very basic conditions are required for PO_4^{3-} to be present at significant levels in water. It is possible for orthophosphate in natural waters to originate from the hydrolysis of polymeric phosphate species.

Pyrophosphate ion, $P_2O_7^{4-}$, is the first of a series of unbranched chain polyphosphates produced by the condensation of orthophosphate:

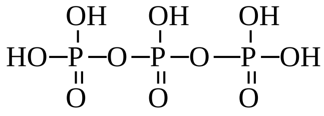
$$2PO_4^{3-} + H_2O \rightleftarrows P_2O_7^{4-} + 2OH^- \qquad (3.16.1)$$

A long series of linear polyphosphates may be formed, the second of which is triphosphate ion, $P_3O_{10}^{5-}$. These species consist of PO_4 tetrahedra with adjacent tetrahedra sharing a common oxygen atom at one corner. The structural formulas of the acidic forms, $H_4P_2O_7$ and $H_5P_3O_{10}$, are:



$$\mathrm{HO{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}OH}$$

Pyrophosphoric (diphosphoric) acid

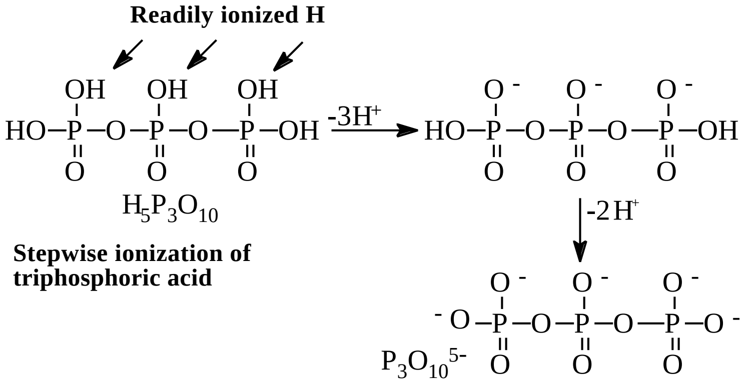


$$\mathrm{HO{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}OH}$$

Triphosphoric acid

It is easy to visualize the longer chains composing the higher linear polyphosphates. **Vitreous sodium phosphates** are mixtures consisting of linear phosphate chains with from 4 to approximately 18 phosphorus atoms each. Those with intermediate chain lengths comprise the majority of the species present.

The acid-base behavior of the linear-chain polyphosphoric acids may be explained in terms of their structure by comparing them to orthophosphoric acid. Pyrophosphoric acid, $H_4P_2O_7$, has four ionizable hydrogens. The value of pK_{a1} is quite small (relatively strong acid), whereas pK_{a2} is 2.64, pK_{a3} is 6.76, and pK_{a4} is 9.42. In the case of triphosphoric acid, $H_5P_3O_{10}$, the first two pK_a values are small, pK_{a3} is 2.30, pK_{a4} is 6.50, and pK_{a5} is 9.24. When linear polyphosphoric acids are titrated with base, the titration curve has an inflection at a pH of approximately 4.5 and another inflection at a pH close to 9.5. To understand these phenomena, consider the following ionization of triphosphoric acid:



$$\mathrm{HO{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{OH}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}OH} \xrightarrow{-3H^+} \mathrm{HO{-}\overset{O^-}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{O^-}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{O^-}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}OH} \xrightarrow{-2H^+} \mathrm{{}^-O{-}\overset{O^-}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{O^-}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O{-}\overset{O^-}{\underset{\underset{O}{\|}}{\overset{|}{P}}}{-}O^-} \tag{3.16.2}$$

Stepwise ionization of triphosphoric acid

Each P atom in the polyphosphate chain is attached to an -OH group that has one readily ionizable hydrogen that is readily removed in titrating to the first equivalence point. The end phosphorus atoms have two OH groups each. One of the OH groups on an end phosphorus atom has a readily ionizable hydrogen, whereas the other loses its hydrogen much less readily. Therefore, one mole of triphosphoric acid, $H_5P_3O_{10}$, loses three moles of hydrogen ion at a relatively low pH (below 4.5), leaving the $H_2P_3O_{10}^{3-}$ species with two ionizable hydrogens. At intermediate pH values (below 9.5), an additional two moles of “end hydrogens” are lost to form the $P_3O_{10}^{5-}$ species. Titration of a linear-chain polyphosphoric acid up to pH 4.5 yields the number of moles of phosphorus atoms per mole of acid, and titration from pH 4.5 to pH 9.5 yields the number of end phosphorus atoms. Orthophosphoric acid, H_3PO_4, differs from the linear chain polyphosphoric acids in that it has a third ionizable hydrogen which, as noted earlier, is removed in only extremely basic media.

Hydrolysis of Polyphosphates

All of the polymeric phosphates hydrolyze to simpler products in water. The rate of hydrolysis depends upon a number of factors, including pH, and the ultimate product is always some form of orthophosphate. The simplest hydrolytic reaction of a polyphosphate is that of pyrophosphoric acid to produce orthophosphoric acid:

$$H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4 \qquad (3.16.3)$$

Researchers have found evidence that algae and other microorganisms catalyze the hydrolysis of polyphosphates. Even in the absence of biological activity, polyphosphates hydrolyze chemically at a significant rate in water. Therefore, there is much less concern about the possibility of polyphosphates binding to heavy metal ions and transporting them than is the case with organic chelating agents such as NTA or EDTA, which must depend upon microbial degradation for their decomposition.

Complexation by Polyphosphates

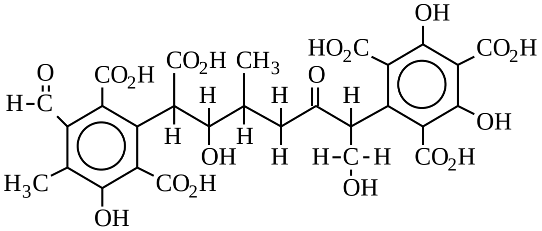
In general, chain phosphates are good complexing agents and even form complexes with alkali-metal ions. Ring phosphates form much weaker complexes than do chain species. The different chelating abilities of chain and ring phosphates are due to structural hindrance of bonding by the ring polyphosphates.

3.17. COMPLEXATION BY HUMIC SUBSTANCES

The most important class of complexing agents that occur naturally are the **humic substances**.[7] These are degradation-resistant materials formed during the decomposition of vegetation that occur as deposits in soil, marsh sediments, peat, coal, lignite, or in almost any location where large quantities of vegetation have decayed. They are commonly classified on the basis of solubility. If a material containing humic substances is extracted with strong base, and the resulting solution is acidified, the products are (a) a nonextractable plant residue called **humin**; (b) a material that precipitates from the acidified extract, called **humic acid**; and (c) an organic material that remains in the acidified solution, called **fulvic acid**. Because of their acid-base, sorptive, and complexing properties, both the soluble and insoluble humic substances have a strong effect upon the properties of water. In general, fulvic acid dissolves in water and exerts its effects as the soluble species. Humin and humic acid remain insoluble and affect water quality through exchange of species, such as cations or organic materials, with water.

Humic substances are high-molecular-weight, polyelectrolytic macromolecules. Molecular weights range from a few hundred for fulvic acid to tens of thousands for the humic acid and humin fractions. These substances contain a carbon skeleton with a high degree of aromatic character and with a large percentage of the molecular weight incorporated in functional groups, most of which contain oxygen. The elementary composition of most humic substances is within the following ranges: C, 45-55%; O, 30-45%, H, 3-6%; N, 1-5%; and S, 0-1%. The terms *humin, humic acid,* and *fulvic acid* do not refer to single compounds but to a wide range of compounds of generally similar origin with many properties in common. Humic substances have been known since before 1800, but their structural and chemical characteristics are still being explained.

Some feeling for the nature of humic substances may be obtained by considering the structure of a hypothetical molecule of fulvic acid shown below:



This structure is typical of the type of compound composing fulvic acid. The compound has a formula weight of 666, and its chemical formula may be represented by $C_{20}H_{15}(CO_2H)_6(OH)_5(CO)_2$. As shown in the hypothetical compound, the functional groups that may be present in fulvic acid are carboxyl, phenolic hydroxyl, alcoholic hydroxyl, and carbonyl. The functional groups vary with the particular acid sample. Approximate ranges in units of milliequivalents per gram of acid are: total acidity, 12-14; carboxyl, 8-9; phenolic hydroxyl, 3-6; alcoholic hydroxyl, 3-5; and carbonyl, 1-3. In addition, some methoxyl groups, $-OCH_3$, may be encountered at low levels.

The binding of metal ions by humic substances is one of the most important environmental qualities of humic substances. This binding can occur as chelation between a carboxyl group and a phenolic hydroxyl group, as chelation between two carboxyl groups, or as complexation with a carboxyl group (see below):

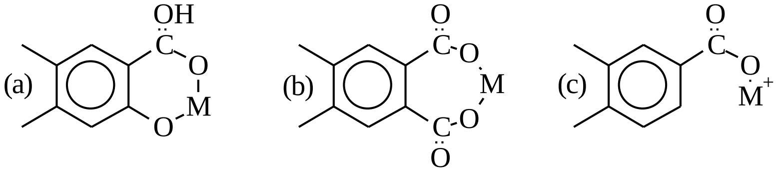


Figure 3.1. Binding of a metal ion, M^{2+}, by humic substances (a) by chelation between carboxyl and phenolic hydroxyl, (b) by chelation between two carboxyl groups, and (c) by complexation with a carboxyl group.

Iron and aluminum are very strongly bound to humic substances, whereas magnesium is rather weakly bound. Other common ions, such as Ni^{2+}, Pb^{2+}, Ca^{2+}, and Zn^{2+}, are intermediate in their binding to humic substances.

The role played by soluble fulvic acid complexes of metals in natural waters is not well known. They probably keep some of the biologically important transition-metal ions in solution, and are particularly involved in iron solubilization and transport. Yellow fulvic acid-type compounds called **Gelbstoffe** and frequently encountered along with soluble iron, are associated with color in water.

Insoluble humins and humic acids, effectively exchange cations with water and may accumulate large quantities of metals. Lignite coal, which is largely a humic acid material, tends to remove some metal ions from water.

Special attention has been given to humic substances since about 1970, following the discovery of **trihalomethanes** (THMs, such as chloroform and dibromochloromethane) in water supplies. It is now generally believed that these suspected carcinogens can be formed in the presence of humic substances during the disinfection of raw municipal drinking water by chlorination (see Chapter 8). The humic substances produce THMs by reaction with chlorine. The formation of THMs can be reduced by removing as much of the humic material as possible prior to chlorination.

3.18. COMPLEXATION AND REDOX PROCESSES

Complexation may have a strong effect upon oxidation-reduction equilibria by shifting reactions, such as that for the oxidation of lead,

$$\mathrm{Pb} \leftarrow\rightarrow \mathrm{Pb}^{2+} + 2e^- \qquad (3.18.1)$$

strongly to the right by binding to the product ion, thus cutting its concentration down to very low levels. Perhaps more important is the fact that upon oxidation,

$$\mathrm{M} + {}^{1}\!/_{2}\mathrm{O}_2 \leftarrow\rightarrow \mathrm{MO} \qquad (3.18.2)$$

many metals form self-protective coatings of oxides, carbonates, or other insoluble species which prevent further chemical reaction. Copper and aluminum roofing and structural iron are examples of materials which are thus self-protecting. A chelating agent in contact with such metals can result in continual dissolution of the protective coating so that the exposed metal corrodes readily. For example, chelating agents in wastewater may increase the corrosion of metal plumbing, thus adding heavy metals to effluents. Solutions of chelating agents employed to clean metal surfaces in metal plating operations have a similar effect.

LITERATURE CITED

1. Stevens, William K., “Expectation Aside, Water Use in U.S. Is Showing Decline,” *New York Times*, November 10, 1998, p. 1.
2. Martell, A. E., “Principles of Complex Formation,” in *Organic Compounds in Aquatic Environments*, S. D. Faust and J. V. Hunter, Eds., Marcell Dekker, Inc., New York, 1971, pp. 262–392.
3. Means, J. L., D. A. Crerar, and J. O. Duguid, “Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents,” *Science*, **200**, 1978, pp. 1477-81.
4. Cleveland, K. J. M. and T. F. Rees, “Characterization of Plutonium in Ground Water near the Idaho Chemical Processing Plant,” *Environmental Science and Technology*, **16**, 1982, pp. 437–439.

5. Bolton, Harvey, Jr., Don C. Girvin, Andrew E. Plymale, Scott D. Harvey, and Darla J. Workman, “Degradation of Metal-Nitrilotriacetate Complexes by *Chelatobacter heintzii*,” *Environmental Science and Technology*, **30**, 931-938 (1996).

6. Murphy, T. P., D. R. S. Lean, and C. Nalewajko, “Blue–Green Algae: Their Excretion of Iron–Selective Chelators Enables them to Dominate other Algae,” *Science*, **192**, 1976, pp. 900-2.

7. Manahan, Stanley E., “Humic Substances and the Fates of Hazardous Waste Chemicals,” Chapter 6 in *Influence of Aquatic Humic Substances on Fate and Treatment of Pollutants*, Advances in Chemistry Series **219**, American Chemical Society, Washington, D.C., 1989, pp. 83-92

SUPPLEMENTARY REFERENCES

Appelo, C.A.J., and D. Postma, *Geochemistry, Groundwater, and Pollution*, A. A. Balkema Publishers, Rotterdam, 1993.

Baker, Lawrence A., Ed., *Environmental Chemistry of Lakes and Reservoirs*, American Chemical Society, Washington, D.C., 1994.

Brownlow, Arthur H., *Geochemistry*, 2nd ed., Prentice Hall, Upper Saddle River, NJ, 1996.

Butler, James N., *Ionic Equilibrium: Solubility and pH Calculations*, John Wiley & Sons, New York, 1998.

Drever, James I., *The Geochemistry of Natural Waters: Surface and Groundwater Environments*, 3rd ed., Prentice Hall, Upper Saddle River, NJ, 1997.

Faure, Gunter, *Principles and Applications of Geochemistry: A Comprehensive Textbook for Geology Students*, 2nd ed., Prentice Hall, Upper Saddle River, NJ, 1998.

Gilbert, Janine, Dan L. Danielopol, and Jack Stanford, Eds., *Groundwater Ecology*, Academic Press, Orlando, FL, 1994.

Hem, J. D., *Study and Interpretation of the Chemical Characteristics of Natural Water*, 2nd ed., U.S. Geological Survey Paper **1473**, Washington, D.C., 1970.

Hessen, D. O. and L. J. Tranvik, Eds., *Aquatic Humic Substances: Ecology and Biogeochemistry*, Springer Verlag, Berlin, 1998.

Howard, Alan G., *Aquatic Environmental Chemistry*, Oxford University Press, Oxford, UK, 1998.

Kegley, Susan E. and Joy Andrews, *The Chemistry of Water*, University Science Books , Mill Valley, CA, 1997.

Knapp, Brian, *Air and Water Chemistry*, Atlantic Europe, Henley-on-Thames, UK, 1998).

Langmuir, Donald, *Aqueous Environmental Geochemistry*, Prentice Hall, Upper Saddle River, NJ, 1997.

Matshullat, Jorg, Heinz Jurgen Tobschall, and Hans-Jurgen Voigt, Eds., *Geochemistry and the Environment: Relevant Processes in the Atmosphere*, Springer, Berlin, 1997.

Oceanography in the Next Decade, National Academy Press, Washington, D.C. 1992.

Patrick, Ruth, *Surface Water Quality*, Princeton University Press, Princeton, NJ, 1992.

Sigg, Laura and Werner Stumm, *Aquatische Chemie: Eine Einfuehrung in die Chimie Waessriger Loesungen und Natuerlicher Gewaesser*, Tuebner, Stuttgart, Germany, 1994.

Snoeyink, Vernon L., and David Jenkins, *Water Chemistry*, John Wiley and Sons, Inc., New York, 1980.

Stumm, Werner and James J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed., John Wiley and Sons, Inc., New York, 1995.

Stumm, Werner, *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*, John Wiley and Sons, Inc., New York, 1992.

Stumm, Werner, Ed., *Aquatic Chemical Kinetics: Reaction Rates of Processes in Natural Waters*, John Wiley and Sons, Inc., New York, 1990.

Suffet, I. H., and Patrick MacCarthy, Eds., *Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants*, Advances in Chemistry Series **219**, American Chemical Society, Washington, D.C., 1989.

U. S. Environmental Protection Agency, *Ground Water Handbook*, 2nd ed., Government Institutes, Rockville, MD, 1992.

van der Leeden, Frits, Fred L. Troise, and David K. Todd, Eds., *The Water Encyclopedia*, Water Information Center, Plainview, NY, 1991.

QUESTIONS AND PROBLEMS

1. Alkalinity is determined by titration with standard acid. The alkalinity is often expressed as mg/L of $CaCO_3$. If V_p mL of acid of normality N are required to titrate V_s mL of sample to the phenolphthalein endpoint, what is the formula for the phenolphthalein alkalinity as mg/L of $CaCO_3$?

2. Exactly 100 pounds of cane sugar (dextrose), $C_{12}H_{22}O_{11}$, were accidentally discharged into a small stream saturated with oxygen from the air at 25˚C. How many liters of this water could be contaminated to the extent of removing all the dissolved oxygen by biodegradation?

3. Water with an alkalinity of 2.00×10^{-3} equivalents/liter has a pH of 7.00. Calculate $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[OH^-]$.

4. Through the photosynthetic activity of algae, the pH of the water in Problem 3 was changed to 10.00. Calculate all the preceding concentrations and the weight of biomass, $\{CH_2O\}$, produced. Assume no input of atmospheric CO_2.

5. Calcium chloride is quite soluble, whereas the solubility product of calcium fluoride, CaF_2, is only 3.9×10^{-11}. A waste stream of 1.00×10^{-3} M HCl is injected into a formation of limestone, $CaCO_3$, where it comes into equilibrium. Give the chemical reaction that occurs and calculate the hardness and alkalinity of the water at equilibrium. Do the same for a waste stream of 1.00×10^{-3} M HF.

6. For a solution having 1.00×10^{-3} equivalents/liter total alkalinity (contributions from HCO_3^-, CO_3^{2-}, and OH^-) at $[H^+] = 4.69 \times 10^{-11}$, what is the percentage contribution to alkalinity from CO_3^{2-}?

7. A wastewater disposal well for carrying various wastes at different times is drilled into a formation of limestone ($CaCO_3$), and the wastewater has time to come to complete equilibrium with the calcium carbonate before leaving the formation through an underground aquifer. Of the following components in the wastewater, the one that would not cause an increase in alkalinity due either to the component itself or to its reaction with limestone, is (a) NaOH, (b) CO_2, (c) HF, (d) HCl, (e) all of the preceding would cause an increase in alkalinity.

8. Calculate the ratio $[PbT^-]/[HT^{2-}]$ for NTA in equilibrium with $PbCO_3$ in a medium having $[HCO_3^-] = 3.00 \times 10^{-3}$ M.

9. If the medium in Problem 8 contained excess calcium such that the concentration of uncomplexed calcium, $[Ca^{2+}]$, were 5.00×10^{-3} M, what would be the ratio $[PbT^-]/[CaT^-]$ at pH 7?

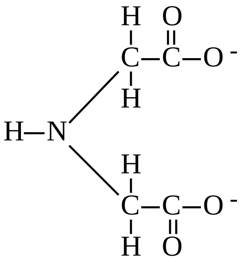
10. A wastewater stream containing 1.00×10^{-3} M disodium NTA, Na_2HT, as the only solute is injected into a limestone ($CaCO_3$) formation through a waste disposal well. After going through this aquifer for some distance and reaching equilibrium, the water is sampled through a sampling well. What is the reaction between NTA species and $CaCO_3$? What is the equilibrium constant for the reaction? What are the equilibrium concentrations of CaT^-, HCO_3^-, and HT^{2-}? (The appropriate constants may be looked up in this chapter.)

11. If the wastewater stream in Problem 10 were 0.100 M in NTA and contained other solutes that exerted a buffering action such that the final pH were 9.00, what would be the equilibrium value of HT^{2-} concentration in moles/liter?

12. Exactly 1.00×10^{-3} mole of $CaCl_2$, 0.100 mole of NaOH, and 0.100 mole of Na_3T were mixed and diluted to 1.00 liter. What was the concentration of Ca^{2+} in the resulting mixture?

13. How does chelation influence corrosion?

14. The following ligand has more than one site for binding to a metal ion. How many such sites does it have?



15. If a solution containing initially 25 mg/L trisodium NTA is allowed to come to equilibrium with solid $PbCO_3$ at pH 8.50 in a medium that contains 1.76×10^{-3} M HCO_3^- at equilibrium, what is the value of the ratio of the concentration of NTA bound with lead to the concentration of unbound NTA, $[PbT^-]/[HT^{2-}]$?

16. After a low concentration of NTA has equilibrated with $PbCO_3$ at pH 7.00, in a medium having $[HCO_3^-] = 7.50 \times 10^{-4}$ M, what is the ratio $[PbT^-]/[HT^{2-}]$?

17. What detrimental effect may dissolved chelating agents have upon conventional biological waste treatment?

18. Why is chelating agent usually added to artificial algal growth media?

19. What common complex compound of magnesium is essential to certain life processes?

20. What is always the ultimate product of polyphosphate hydrolysis?

21. A solution containing initially 1.00×10^{-5} M CaT^- is brought to equilibrium with solid $PbCO_3$. At equilibrium, pH = 7.00, $[Ca^{2+}] = 1.50 \times 10^{-3}$ M, and $[HCO_3^-] = 1.10 \times 10^{-3}$ M. At equilibrium, what is the fraction of total NTA in solution as PbT^- ?

22. What is the fraction of NTA present after HT^{2-} has been brought to equilibrium with solid $PbCO_3$ at pH 7.00, in a medium in which $[HCO_3^-] = 1.25 \times 10^{-3}$ M?

23. Describe ways in which measures taken to alleviate water supply and flooding problems might actually aggravate such problems.

24. The study of water is known as _____________________, _________________, is the branch of the science dealing with the characteristics of fresh water, and the science that deals with about 97% of all Earth's water is called ___________.

25. Consider the hydrologic cycle in Figure 3.1. List or discuss the kinds or classes of environmental chemistry that might apply to each major part of this cycle.

26. Consider the unique and important properties of water. What molecular or bonding characteristics of the water molecules are largely responsible for these properties. List or describe one of each of the following unique properties of water related to (a) thermal characteristics, (b) transmission of light, (c) surface tension, (d) solvent properties.

27. Discuss how thermal stratification of a body of water may affect its chemistry.

28. Relate aquatic life to aquatic chemistry. In so doing, consider the following: autotrophic organisms, producers, heterotrophic organisms, decomposers, eutrophication, dissolved oxygen, biochemical oxygen demand.