Chapter 2

The Hydrosphere and Water Chemistry

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2.2 Sources and Uses of Water

- **The most important issue in dealing with water is simply getting it**, a problem largely attributed to the uneven distribution of water around the globe.
- *United states' Rainfall*: 1.48 x 10^{13} L/day, *evaporation and transpiration*: 1.02 x 10^{13} L/day
- *Available water*: 4.6 x 10^{12} L/day , *United states' water use*: 1.6 x 10^{12} L/day
- people in areas with low precipitation often consume more water than people in regions with more rainfall. The two largest consumers of water are **irrigation** and **industrial use** (including cooling water for **electrical power generation**). Most of the rest of the water used is for **municipal water supply**.

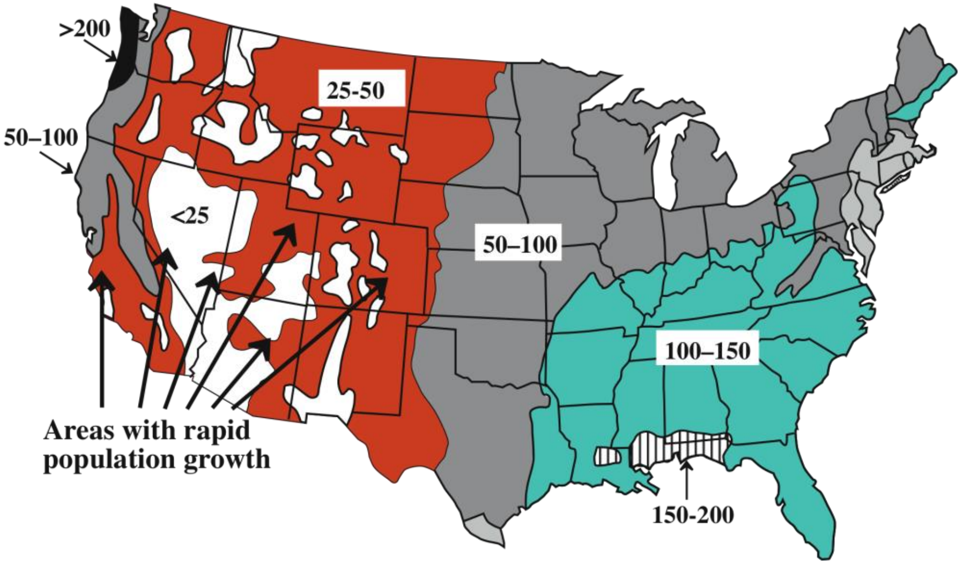

Figure 2.3 average annual rainfall in continental U.S. in the unit of cm/year

Conservation and recycling have accounted for much of the decreased use in the industrial sector.

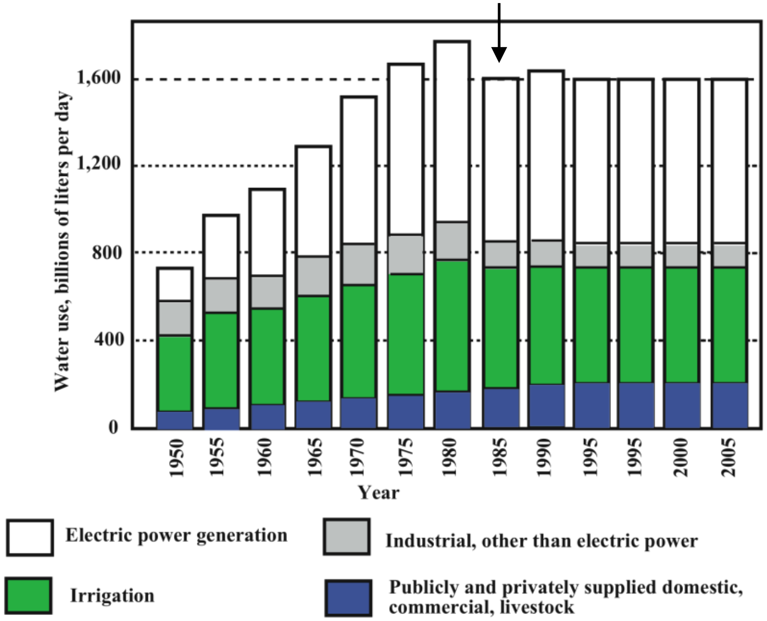

Figure 2.4 Trends in U.S. Water Use, which has stabilized

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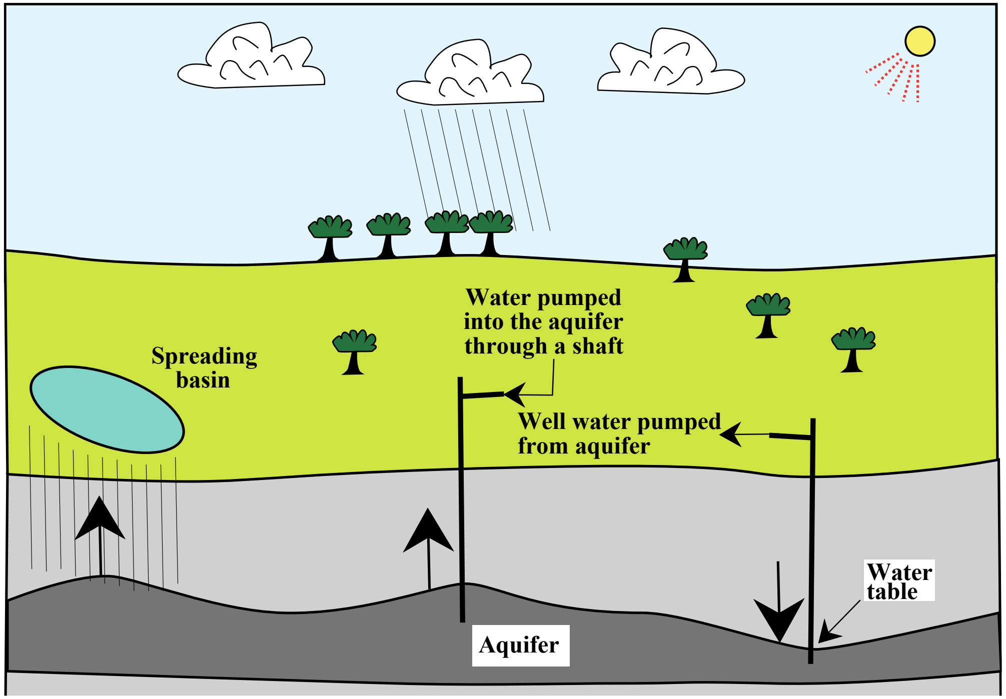
2.2 Sources and Uses of Water

- **Groundwater** is a major source of municipal water supplies and in some rural areas, On average, approximately 190 billion L/day is used for irrigation in the United States.
- At the present time, groundwater resources are being depleted. So much water has been sucked from some underground aquifers that there is perceptible surface subsidence and even **damage to surface structures**. Groundwater depletion usually accompanies the phenomenon of **desertification** in which productive land reverts to desert.



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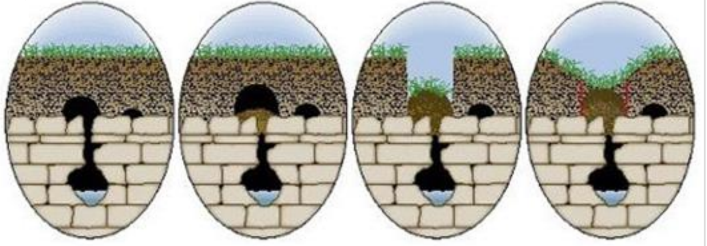

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FIGURE 2.5 Groundwater is contained in underground aquifers beneath Earth's surface. The water table can be lowered by pumping water from an aquifer and raised by pumping water into an aquifer or from natural infiltration of water in a spreading basin on the surface.

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2.3 H_2O: Simple Formula, Remarkable Molecule

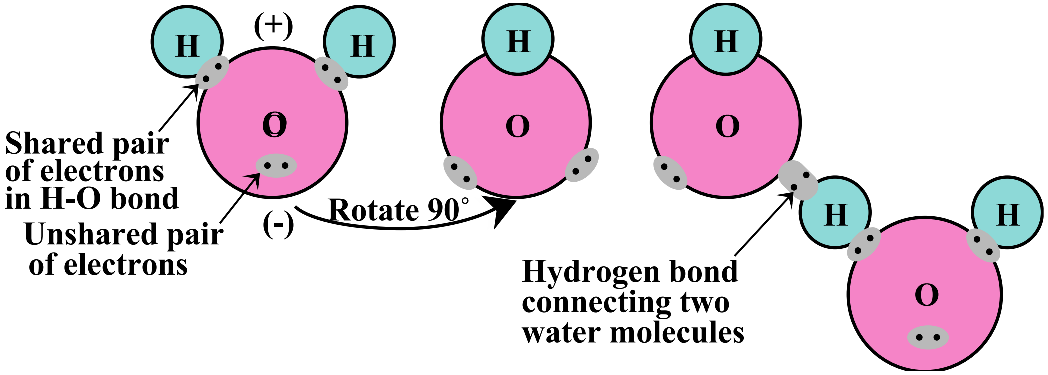

FIGURE 2.6 Because of the arrangement of the two bonding pairs and the two nonbonding pairs of electrons as far as possible from each other around the sphere of the oxygen atom in the water molecule, **the molecule is polar**. The nonbonding pairs of electrons can form **hydrogen bonds** with hydrogen atoms in other water molecules. This hydrogen bonding and the polar nature of the water molecule are responsible for **the unique solvent properties, heat/temperature behavior, and other characteristics of water.**

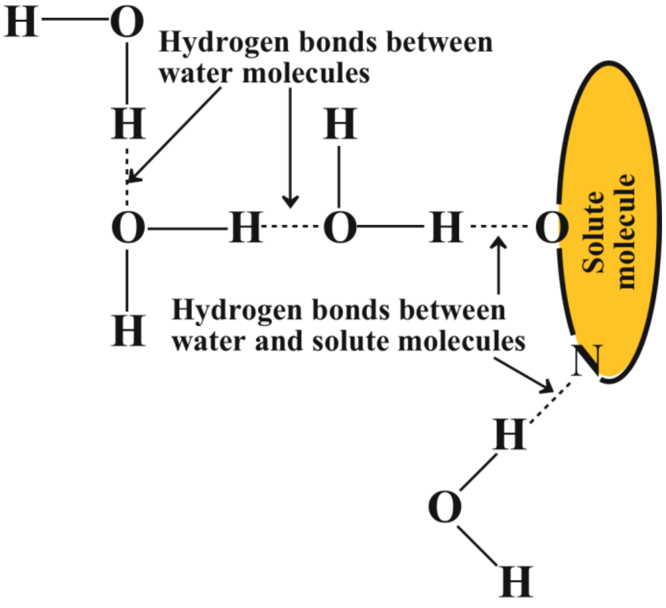

FIGURE Hydrogen bonding with solute molecules and between water molecules

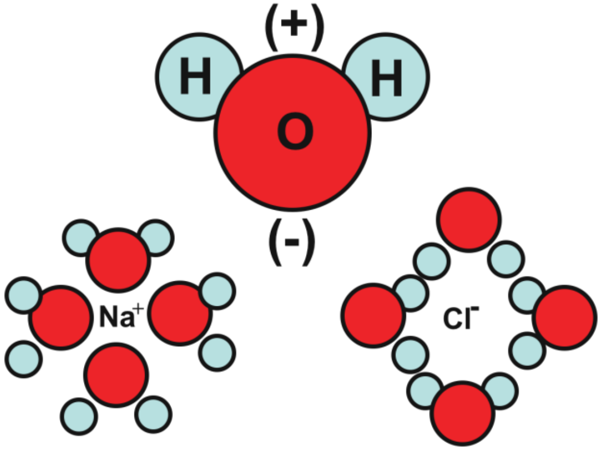

FIGURE Polar water molecule and solvent effects on ions

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2.3 H_2O: Simple Formula, Remarkable Molecule

Table 2.1 Important Properties of Water

Property	Effects
Excellent solvent	Transport of nutrients and waste products enabling biological processes to occur 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 ultraviolet light	Colorless, allowing light required for photosynthesis to reach considerable depths in
Maximum density as a liquid at 4℃	Ice floats and vertical circulation is 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	The temperature of water in a body of water is stabilized at the freezing point of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

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2.4 Life in Water

- **Autotrophic organisms** utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. *(ex) Algae and photosynthetic cyanobacteria generate biomass from* CO_2 *and others*
- **Heterotrophic organisms** utilize the organic substances produced by autotrophic organisms as the raw materials for the synthesis of their own biomass.
- **Decomposers** are a subclass of the heterotrophic organisms consisting chiefly of bacteria and fungi, which ultimately break down material 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**. High productivity requires an adequate supply of carbon (CO_2), nitrogen (nitrate), phosphorus (orthophosphate), and trace elements such as iron.
- Excessive productivity results in decay of the biomass produced, consumption of dissolved oxygen, and odor production, a condition called **eutrophication**.
- **Temperature, transparency, and turbulence** are the three main physical properties affecting aquatic life. Very low water temperatures result in very slow biological processes, whereas excessively high temperatures can be fatal to organisms. The transparency of water determines the growth of algae. Turbulence mix processes and transports nutrients and waste products in water.
- **Dissolved oxygen (DO)** frequently is the key substance in determining the extent and kinds of life. **Biochemical oxygen demand(BOD)** refers to the amount of oxygen utilized when the organic matter is degraded biologically.

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2.5 Chemistry of Water

- To understand water pollution, it is first necessary to have an appreciation of chemical phenomena that occur in water.
- *<u>an exact description of the chemistry of a natural water system</u>* based on acid–base, solubility, and complexation equilibrium constants, redox potential, pH, and other chemical parameters *<u>is not possible</u>*.
- ***<u>the systems must be described by simplified models, often based around equilibrium</u>*** chemical concepts. Though not exact or 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

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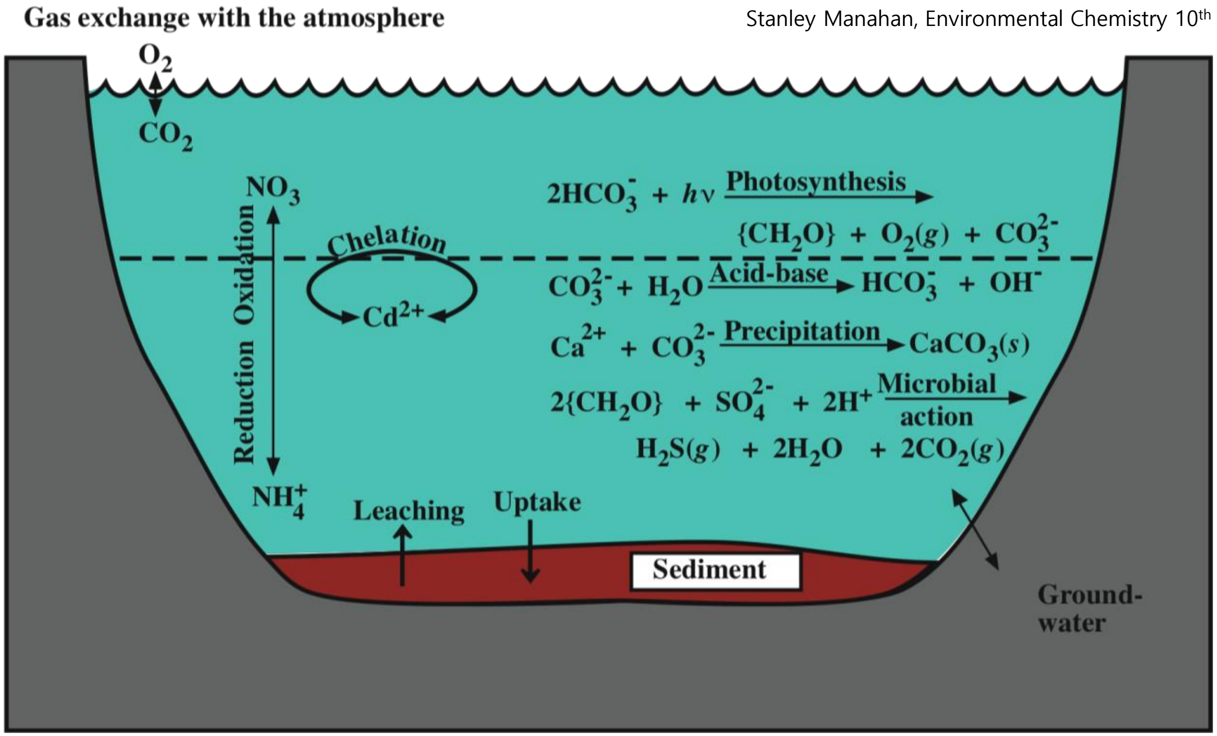

FIGURE 2.7 Major aquatic chemical processes.

2.6 Gases in Water

- *Dissolved gases—O_2 for fish and CO_2 for algae*—are crucial to the living species.
- Many fish kills are caused not by the direct toxicity of pollutants but by a deficiency of oxygen because of its consumption in the biodegradation of pollutants or organic matter.

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

the microorganism-mediated degradation of only 7 or 8 mg of organic material can completely consume the O_2 in 1 L of water initially saturated with air at 25 ℃.

- a body of water re-oxygenate itself by contact with the atmosphere of 21% oxygen.
- **The solubility of oxygen** in water depends on **water temperature**, **the partial pressure of oxygen in the atmosphere**, and **the salt content of the water**, based on 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* (details will be discussed in Chapter 4)
- **At higher temperatures**, the decreased solubility of oxygen, combined with the increased respiration rate of aquatic organisms, frequently causes a **severe oxygen depletion**.

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2.7 Water Acidity and Carbon Dioxide in Water

- *Acidity: capacity to neutralize* OH^- / *Alkalinity: capacity to neutralize* H^+
- *Weak acid:* CO_2, $H_2PO_4^-$, H_2S, *proteins, fatty acids, acidic metal ions* (Fe^{3+})

$$\mathrm{Al(H_2O)_6^{3+}} \leftrightarrow \mathrm{Al(H_2O)_5OH^{2+}} + \mathrm{H^+}$$

- *Strong acid:* H_2SO_4 *and HCl, called free mineral acid, which come from acid mine water*
- *Some industrial wastes, such as spent steel pickling liquor, contain acidic metal ions and often some excess strong acid.*

- *Carbon dioxide and its ionization products, bicarbonate ion* HCO_3^- *and carbonate ion* CO_3^{2-}, *have an extremely important influence on the chemistry of water.*

  - *The equilibrium of dissolved* CO_2 *with gaseous carbon dioxide in the atmosphere*
  - *Many minerals are deposited as salts of the carbonate ion.*
  - *Algae in water utilize dissolved* CO_2 *in the synthesis of biomass.*
  - *A large share of the* CO_2 *is a product of the breakdown of organic matter by bacteria.*
  - *a strong buffering effect on the pH of water.*

$$\mathrm{CO_2(water)} \leftrightarrow \mathrm{CO_2(atmosphere)}$$

$$\mathrm{CO_2}(aq) + \mathrm{H_2O} \leftrightarrow \mathrm{H_2CO_3}$$

$$\mathrm{CO_2}(aq) + \mathrm{H_2O} \leftrightarrow \mathrm{H^+} + \mathrm{HCO_3^-}$$

$$\mathrm{HCO_3^-} \leftrightarrow \mathrm{CO_3^{2-}} + \mathrm{H^+}$$

$$\mathrm{MCO_3(slightly\ soluble\ carbonate\ salt)} \leftrightarrow \mathrm{M^{2+}} + \mathrm{CO_3^{2-}}$$

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2.7 Water Acidity and Carbon Dioxide in Water

- a small fraction of the dissolved carbon dioxide is actually present as H_2CO_3

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \qquad K = 2 \times 10^{-3} \text{ at } 25\ ℃$$

- Aqueous CO_2 molecule hydrated by water is dominant and can be transformed into other carbon species based on the equilibria below. *The predominant species formed by CO_2 dissolved in water depends on pH*.

$$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^- \qquad HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

$$K'_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35 \qquad K'_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK_{a2} = 10.33$$

$$\alpha CO_2 = \frac{[CO_2]}{[CO_2]+[HCO_3^-]+[CO_3^{2-}]}$$

$$\alpha HCO_3^- = \frac{[HCO_3^-]}{[CO_2]+[HCO_3^-]+[CO_3^{2-}]}$$

$$\alpha CO_3^{2-} = \frac{[CO_3^{2-}]}{[CO_2]+[HCO_3^-]+[CO_3^{2-}]}$$

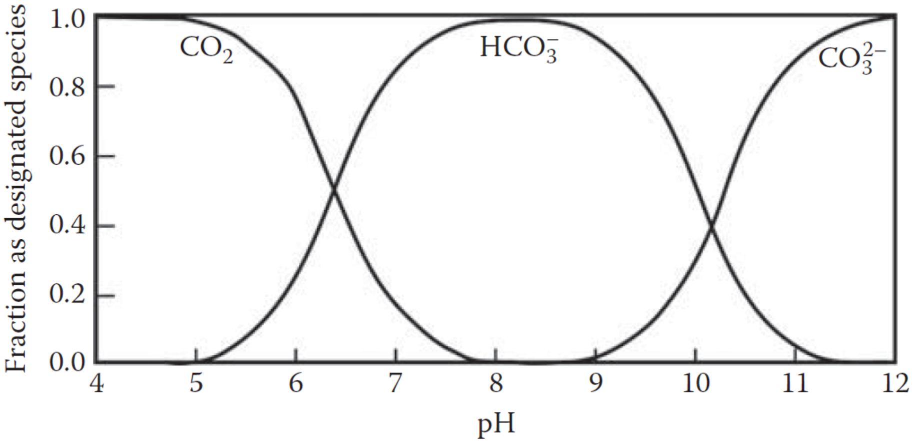

FIGURE 2.8 Distribution of species diagram for the CO_2, HCO_3^- and CO_3^{2-} system in water.

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2.7 Water Acidity and Carbon Dioxide in Water

- 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:

$$\alpha CO_2 = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \qquad \alpha HCO_3^- = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \qquad \alpha CO_3^{2-} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

- For pH significantly below pK_{a1}, αCO_2 is essentially 1
- When $pH = pK_{a1}$, $\alpha CO_2 = \alpha HCO_3^-$
- When $pH = ½(pK_{a1} + pK_{a2})$, αHCO_3^- is at its maximum of 0.98
- When $pH = pK_{a2}$, $\alpha HCO_3^- = \alpha CO_3^{2-}$
- For pH significantly above pK_{a2}, αCO_3^{2-} is essentially 1

The distribution of species diagram shows that *bicarbonate ion is the predominant species in the pH range found in most waters* (seawater pH 7.5 to 8.4)

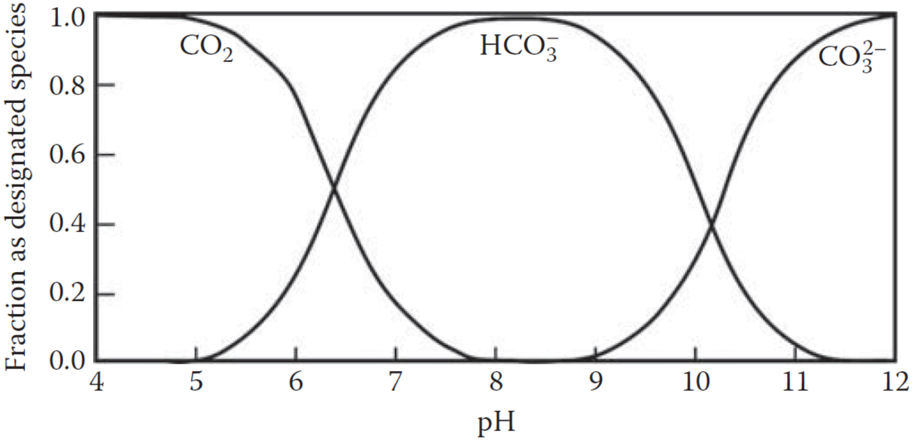

FIGURE 2.8 Distribution of species diagram for the CO_2, HCO_3^- and CO_3^{2-} system in water.

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2.7 Water Acidity and Carbon Dioxide in Water

- *What is the pH of pure water in ambient condition ?*
- the value of [CO_2(*aq*)] in water at 25°C in equilibrium with air that is 400 ppm CO_2 is 1.309×10^{-5} M.
- The carbon dioxide dissociates partially in water to produce equal concentrations of H^+ and HCO_3^-. The concentrations of H^+ and HCO_3^- are calculated from K_{a1}:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{[H^+]^2}{1.309 \times 10^{-5}} = 4.45 \times 10^{-7}$$

$$[H^+] = [HCO_3^-] = (1.309 \times 10^{-5} \times 4.45 \times 10^{-7})^{1/2} = 2.41 \times 10^{-6}$$

$$\text{pH} = 5.61$$

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

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2.8 Alkalinity

- *The capacity of water to accept H+ ions (protons)* is called **alkalinity**.
- the alkalinity must be known to calculate the quantities of chemicals to be added in treating the water to be used in boilers, food processing, and municipal water systems. It helps to *determine the ability of water to support algal growth*, e.g. **water fertility**
- ***Basic species*** *responsible for alkalinity:* ***bicarbonate, carbonate, hydroxide***
- ***Minor contribution****: ammonia, conjugate bases of phosphoric, silicic, boric, organic acids.*

$$[\text{alk}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

- *Whereas pH is an intensity factor, alkalinity is a capacity factor.*

(ex) 10^{-3} M NaOH vs 0.1 M $NaHCO_3$

The sodium hydroxide solution is very basic, pH 11, but a liter of it will neutralize only 1.00 x 10^{-3} mol of acid. The pH of the $NaHCO_3$ solution is 8.34, much lower than that of the NaOH. However, a liter of the sodium bicarbonate solution will neutralize 0.100 mol of acid; therefore, its alkalinity is 100 times that of the more basic NaOH solution.

Alkalinity is expressed with the number of moles of H^+ that can be neutralized in a liter of solution, e.g. ***equivalents per liter***

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2.8 Alkalinity

- **Natural water** typically has an alkalinity ("[alk]") of **10^{-3} equivalents per liter (eq/L)**, meaning that the alkaline solutes in 1 L of water will neutralize 10^{-3} mol of acid.
- The contributions made by different species to alkalinity depend on pH.
- *At **pH 7**, $[OH^-]$ is too low to make any significant contribution and $[HCO_3^-] >> [CO_3^{2-}]$*

  $HCO_3^- = 1.00 \times 10^{-3}$ M $\quad$ $CO_2(aq) = 2.25 \times 10^{-4}$ M
- *At **pH 10**, significant contributions from HCO_3^-, CO_3^{2-}, OH^-*

  $HCO_3^- = 4.64 \times 10^{-4}$ M and $CO_3^{2-} = 2.18 \times 10^{-4}$ M and $OH^- = 10^{-4}$ M

$$[\text{alk}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad = 1 \times 10^{-3}$$

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

$$\boxed{\begin{array}{l} 4.64 \times 10^{-4}\ \text{eq/L from } HCO_3^- \\ 4.36 \times 10^{-4}\ \text{eq/L from } CO_3^{2-} \\ 1.00 \times 10^{-4}\ \text{eq/L from } OH^- \\ \hline \text{alk} = 1.00 \times 10^{-3}\ \text{eq/L} \end{array}}$$

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

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2.8.2 Dissolved Inorganic Carbon and Alkalinity

- Total **inorganic carbon concentration [C]** represents a significant potential source of carbon for algae growing in water that fix carbon. It is described as follows:

$$[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

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

$$[C]pH\ 10 = 0 + 4.64 \times 10^{-4} + 2.18 \times 10^{-4} = 6.82 \times 10^{-4}$$

- *As dissolved inorganic carbon is used up to synthesize biomass*, $\{CH_2O\}$, *the water becomes more basic with a change in pH but none in 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

$$CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2$$

$$HCO_3^- + H_2O + h\nu \rightarrow \{CH_2O\} + OH^- + O_2$$

$$[C]pH\ 7 \times 1\ L - [C]pH\ 10 \times 1\ L = 1.22 \times 10^{-3}\ mol - 6.82 \times 10^{-4}\ mol = 5.4 \times 10^{-4}\ mol$$

- This translates to an increase of **5.4×10^{-4} mol/L of biomass (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*.

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2.9 Calcium and Other Metals in Water

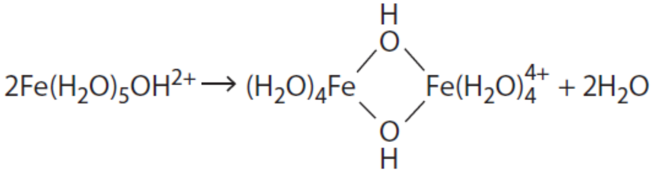
- **metal ions** in water solution are present in forms such as the **hydrated metal cation** or coordinated to other species. And these ions undergo various chemical reactions:

Acid dissociation reaction: $\mathrm{Fe(H_2O)_6^{3+} \leftrightarrow FeOH(H_2O)_5^{2+} + H^+}$

Precipitation reaction: $\mathrm{Fe(H_2O)_6^{3+} \leftrightarrow Fe(OH)_3(\mathit{s}) + 3H_2O + 3H^+}$

Oxidation-reduction reaction: $\mathrm{Fe(H_2O)_6^{2+} \leftrightarrow Fe(OH)_3(\mathit{s}) + 3H_2O + e^- + 3H^+}$

dehydration-dimerization:



- Of the cations found in most freshwater systems, **calcium** generally has **the highest concentration** because the concentration is largely determined by the rocks (*primary contributing minerals:* $CaSO_4 \bullet 2H_2O$; $CaSO_4$; $CaMg(CO_3)_2$; $CaCO_3$)
- **microorganisms** degrading organic matter in water, sediments, and soil accounts for the very *high levels of* CO_2 observed in water: $\mathrm{\{CH_2O\} + O_2 \leftrightarrow CO_2 + H_2O}$
- Water containing a high level of carbon dioxide readily *dissolves calcium* from its carbonate minerals. For the reverse reaction, CO_2 is lost from the water, *calcium carbonate deposits are formed*

$$\mathrm{CaCO_3(\mathit{s}) + CO_2(\mathit{g}) + H_2O}$$
$$\mathrm{\leftrightarrow Ca^{2+} + 2HCO_3^-}$$

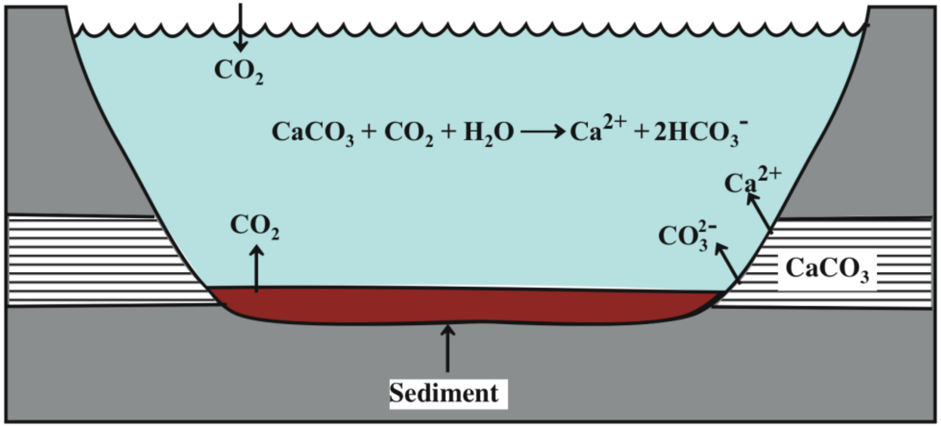


Figure 2.9 Carbon dioxide-calcium carbonate equilibria

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2.9 Calcium and Other Metals in Water

- 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.
- *for water in equilibrium with solid calcium carbonate and atmospheric CO_2 (400 ppm CO_2), the following concentrations are calculated:*

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

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

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

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

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

$$[HCO_3^-] = 2\,[Ca^{2+}]$$

$$[CO_2] = 1.309 \times 10^{-5}\ M \qquad [Ca^{2+}] = 5.18 \times 10^{-4}\ M$$

$$[HCO_3^-] = 1.04 \times 10^{-3}\ M \quad [H^+] = 5.63 \times 10^{-4}\ M$$

$$[CO_3^{2-}] = 8.63 \times 10^{-6}\ M \quad pH = 8.25$$

- Factors such as nonequilibrium conditions, high CO_2 concentrations in bottom regions, and increased pH owing 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.

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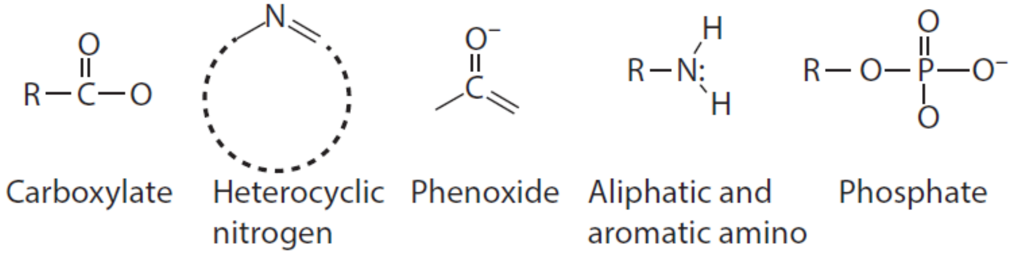
2.10 Complexation and Chelation

- In addition to the hydrated metal ions, metals may exist chelated to inorganic anions or to organic compounds as metal complexes.

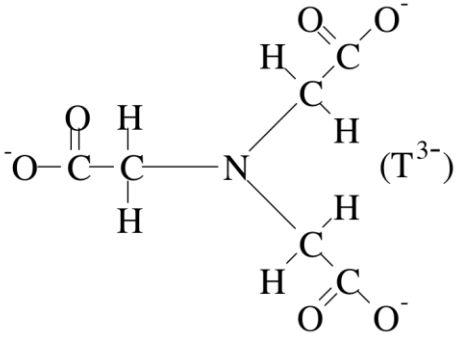
$$Fe(H_2O)_6^{3+} + CN^- \leftrightarrow FeCN(H_2O)_5^{2+} + H_2O$$

an unidentate ligand

- *The ligands found in natural waters and wastewaters contain a variety of functional groups that can donate the electrons required to bond the ligand to a metal ion. The most common are as follows:*



- In general, since a chelating agent may bond to a metal ion in *more than one place* simultaneously, *chelates are more stable* than complexes with unidentate ligands.



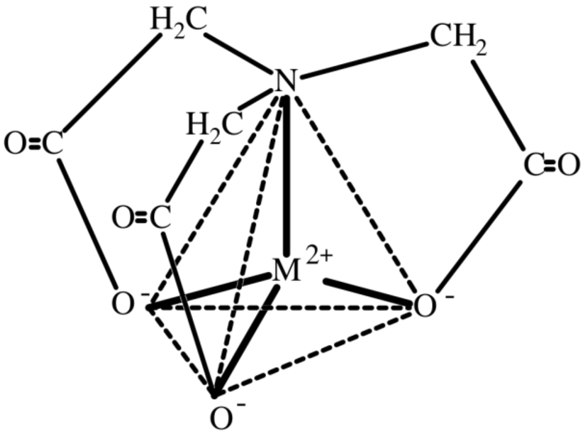


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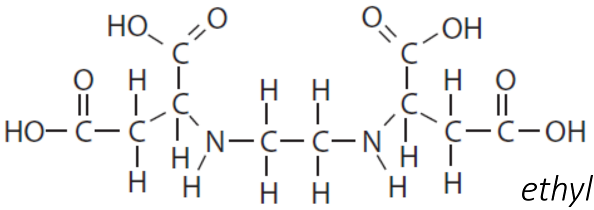
FIGURE 2.10 Nitrilotriacetate chelate of a divalent metal ion in a tetrahedral configuration.

2.10.1 Occurrence and Importance of Chelating Agents

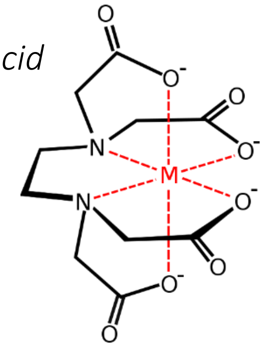
- Complexation may cause changes in oxidation state of the metal and may result in a metal becoming solubilized from an insoluble compound. The formation of insoluble complex compounds removes metal ions from solution. Complexation may strongly influence metals' adsorption, distribution, transport, etc.

- A natural chelating agent is **ethylenediaminedisuccinic acid** which is biodegradable and has been used for uptake of waste substances by plants from soil (**phytoremediation**)



ethylenediaminedisuccinic acid

ethylenediaminetetraacetic acid



- *The most important pollutant chelating agents: NTA and EDTA*

- **Complexation** may increase the *<u>leaching of heavy metals</u>* from waste disposal sites and reduce the efficiency with which heavy metals are removed with sludge in conventional biological waste treatment.

- *<u>Removal of chelated iron is difficult with conventional municipal water treatment processes</u>*.

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2.12 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:*

$$Zn^{2+} + NH_3 \leftrightarrow ZnNH_3^{2+}$$

$$ZnNH_3^{2+} + NH_3 \leftrightarrow Zn(NH_3)_2^{2+}$$

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

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

$$Zn^{2+} + 2NH_3 \leftrightarrow Zn(NH_3)_2^{2+}$$

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

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

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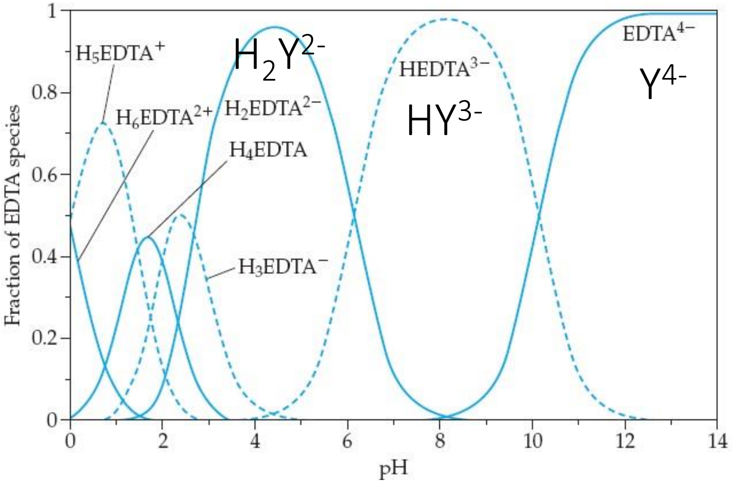
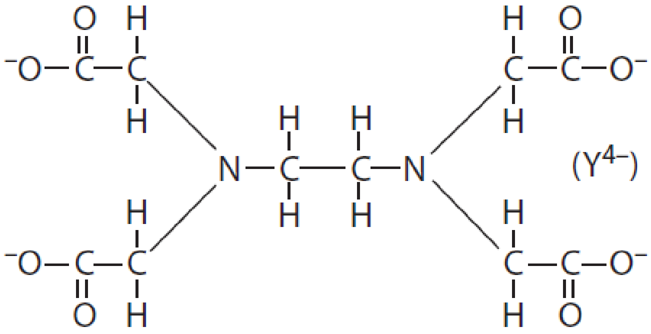
2.13 Complexation by Deprotonated Ligands

- Generally, calculation of complex species concentrations is complicated *by competition between metal ions and H^+ for ligands*. For example, At pH values of 11 or above, **EDTA** is essentially all in the **completely ionized tetranegative form**, Y^{4-}:



- *Consider a wastewater with an alkaline pH of 11 containing copper(II) at a total level of 7.9×10^{-5} M and excess uncomplexed EDTA at a level of 5.4×10^{-4} M. If so, what will be the equilibrium concentration of the hydrated copper(II) ion, Cu^{2+}?*



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

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

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

- *the concentration of hydrated Cu^{2+} ion is extremely low. The Cu(II) is all in the form of the EDTA complex.*

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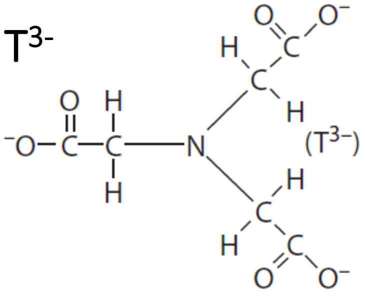
2.14 Complexation by Protonated Ligands

- hydrogen ion competes with metal ions for a ligand, so that *the strength of chelation depends on pH*. In the neutral pH range usually encountered in natural waters, most organic ligands are present in a conjugated acid form.
- **Nitrilotriacetic acid, H_3T**, loses hydrogen ion in three steps to form the **NTA anion, T^{3-}**. The T^{3-} species may coordinate through three –CO2$^-$ groups and the nitrogen atom.
- In near-neutral natural waters, *the predominant unchelated NTA species is HT^{2-}*.

T^{3-}



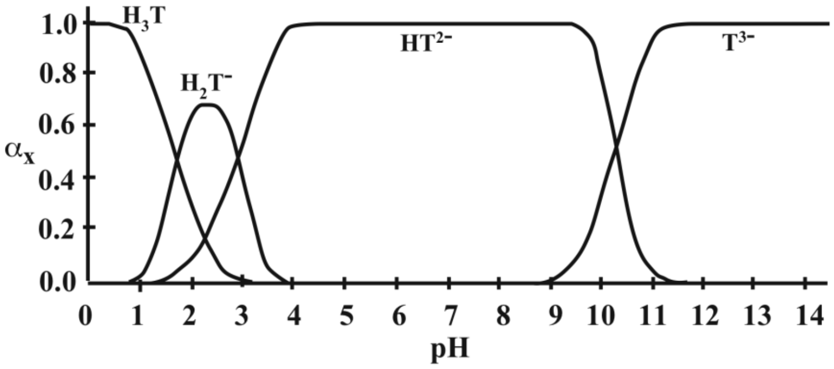


Figure 2.11 Distribution of species as a function of pH for unchelated nitrilotriacetic acid (NTA)

$$H_3T \leftrightarrow H^+ + H_2T^-$$

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

$$H_2T^- \leftrightarrow H^+ + HT^{2-}$$

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

$$HT^{2-} \leftrightarrow H^+ + T^{3-}$$

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

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2.15 Solubilization of Lead Ion from Solids by NTA

- A major concern regarding the widespread introduction of strong chelating agents such as NTA 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.
- *Consider first the solubilization of lead from solid* $Pb(OH)_2$ *by NTA at pH 8.00. Essentially all uncomplexed NTA is present as* HT^{2-} *ion (The total concentration is* 9.7×10^{-5} *M)*
- *<u>most of the NTA in solution is present as the lead chelate</u>* → *[Pb] = 20 mg/L*

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

$$K = \frac{[PbT^-][OH^-]}{[HT^{2-}]} = \frac{K_{sp}K_{a3}K_f}{K_w} = 2.07\times10^{-5} \longrightarrow \frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[OH^-]} = \frac{2.07\times10^{-5}}{1.00\times10^{-6}} = 20.7$$

$$Pb(OH)_2(s) \leftrightarrow Pb^{2+} + 2OH^-$$

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

$$HT^{2-} \leftrightarrow H^+ + T^{3-}$$

$$K_{a3} = \frac{[H^+][T^{3-}]}{[HT^{2-}]} = 5.25\times10^{-11} \quad pK_{a3} = 10.28$$

$$H^+ + OH^- \leftrightarrow H_2O$$

$$\frac{1}{K_w} = \frac{1}{[H^+][OH^-]} = \frac{1}{1.00\times10^{-14}}$$

$$Pb^{2+} + T^{3-} \leftrightarrow PbT^-$$

$$K_f = \frac{[PbT^-]}{[Pb^{2+}][T^{3-}]} = 2.45\times10^{11}$$

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2.15.1 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 often found in natural waters and wastewaters.
- *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.*
- *At pH 7, the predominant carbonic species is HCO_3^-; therefore, the reaction of* ***NTA*** *with* ***$PbCO_3$*** *will lead to the formation of* ***HCO_3^-***. *It may be seen that* *<u>the degree to which $PbCO_3$ is solubilized as PbT^- depends on the concentration of HCO_3^-</u>*

$$PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$$

$$K = \frac{[PbT^-][HCO_3^-]}{[HT^{2-}]} = \frac{K_{sp}K_{a3}K_f}{K'_{a2}} = 4.06 \times 10^{-2} \longrightarrow \frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{\underset{\text{assume}}{[HCO_3^-]}} = \frac{4.06 \times 10^{-2}}{1.00 \times 10^{-3}} = 40.6$$

- *under the given conditions, most of the NTA in equilibrium with solid $PbCO_3$ would be present as the lead complex.*
- *<u>At relatively higher concentrations of HCO_3^-</u>*, the tendency to solubilize lead would be diminished, whereas *<u>at lower concentrations of HCO_3^-</u>*, NTA would be more effective in solubilizing lead.

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2.15.2 Effect of Calcium Ions on the Chelation Reaction

- Chelatable Ca^{2+} ion competes with a metal in a slightly soluble salt, such as $PbCO_3$.
- *Typically, $[Ca^{2+}]$ in water is 1.00×10^{-3} M. Assuming this value and pH 7.00,*

$$Ca^{2+} + HT^{2-} \leftrightarrow CaT^- + H^+$$

$$K' = \frac{[CaT^-][H^+]}{[Ca^{2+}][HT^{2-}]} = 1.48\times10^{8} \times 5.25\times10^{-11} = 7.75\times10^{-3}$$

$$\frac{[CaT^-]}{[HT^{2-}]} = \frac{[Ca^{2+}]}{[H^+]}K' = \frac{1.00\times10^{-3}}{1.00\times10^{-7}} \times 7.75\times10^{-3} = 77.5$$

- *most of the NTA would be present as the calcium complex, CaT^-, which would react with $PbCO_3$. Only approximately **1/3 of the NTA** would be present as the lead chelate.*

$$PbCO_3(s) + CaT^- + H^+ \leftrightarrow Ca^{2+} + HCO_3^- + PbT^-$$

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

pH = 7
$[Ca^{2+}] = 10^{-3}$ M
$[HCO_3^-] = 10^{-3}$ M

$$\longrightarrow \quad \frac{[PbT^-]}{[CaT^-]} = \frac{[H^+]K''}{[Ca^{2+}][HCO_3^-]} = 0.524$$

$$PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$$

$$-(Ca^{2+} + HT^{2-} \leftrightarrow CaT^- + H^+)$$

$$PbCO_3(s) + CaT^- + H^+ \leftrightarrow Ca^{2+} + HCO_3^- + PbT^-$$

$$K'' = \frac{K}{K'} = \frac{4.06\times10^{-2}}{7.75\times10^{-3}} = 5.24$$

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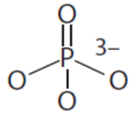
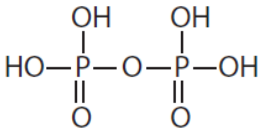
2.16 Polyphosphates and Phosphonates in Water

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

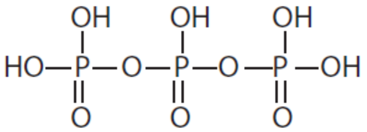


- ***Pyrophosphate ion, $P_2O_7^{4-}$***, *is the first of a series of unbranched chain polyphosphates produced by the condensation of orthophosphate. The second of which is* ***triphosphate ion, $P_3O_{10}^{5-}$***.

$$2PO_4^{3-} + H_2O \leftrightarrow P_2O_7^{4-} + 2OH^-$$



Pyrophosphoric
(diphosphoric) acid

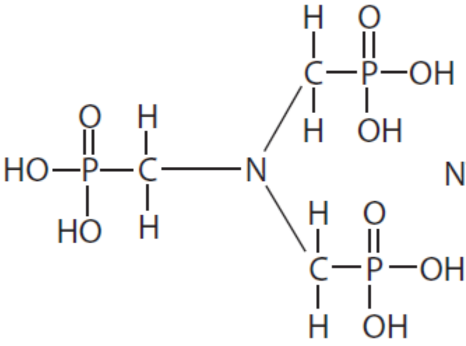


Triphosphoric acid

- *All of the polymeric phosphates hydrolyze to simpler products in water. The rate of hydrolysis depends on a number of factors, including pH, and the ultimate product is always some form of orthophosphate*

$$H_4P_2O_7 + H_2O \leftrightarrow 2H_3PO_4$$

- **Phosphonate chelating agents** are organic compounds structurally analogous to the aminopolycarboxylate chelating agents such as NTA and EDTA.
- nitrilotris(methylenephosphonic) acid, **NTMP**, is :



NTMP

- Phosphonate chelating agents are used for applications that include inhibition of scale and corrosion,metal finishing, cleaning and laundry agents, ore recovery, etc.

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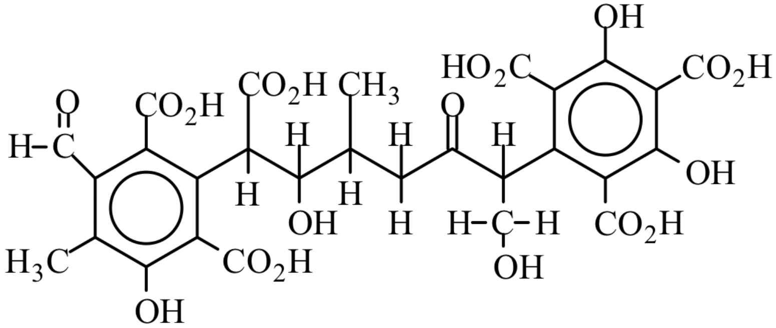
2.17 Complexation by Humic Substances

- Humic substances are biodegradation-resistant residues remaining from the biodegradation of plant biomass.
- 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**.



Structural formula of a hypothetical fulvic acid molecule

- fulvic acid dissolves in water and chelate metal ions. Insoluble humins and humic acids effectively exchange cations with water and may accumulate large quantities of metals.

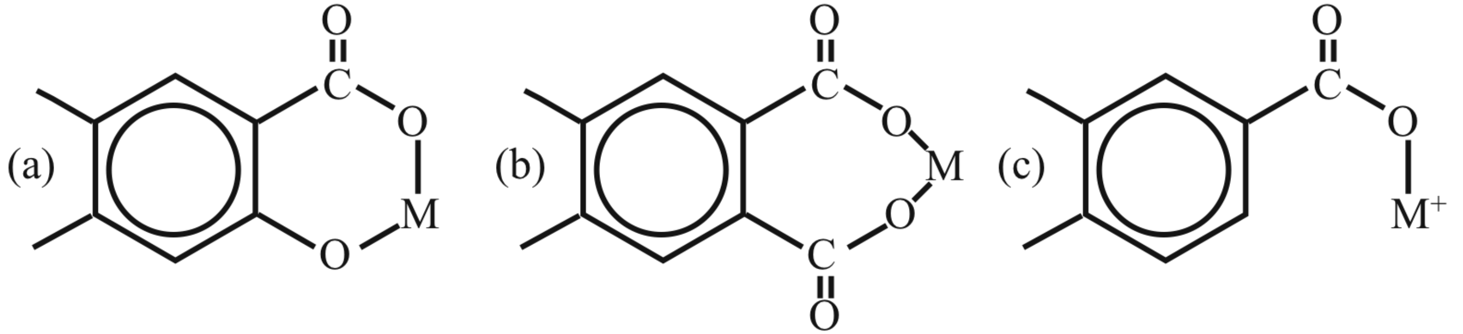


FIGURE 2.13 Binding of a metal ion, M2+, by humic substances (a) by chelation between carboxyl and phenolic hydroxyl, (b) by chelation between two carboxyl groups, and (c) by complexation with a carboxyl group.

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