Solutions for Environmental Chemistry 10th Edition by Manahan

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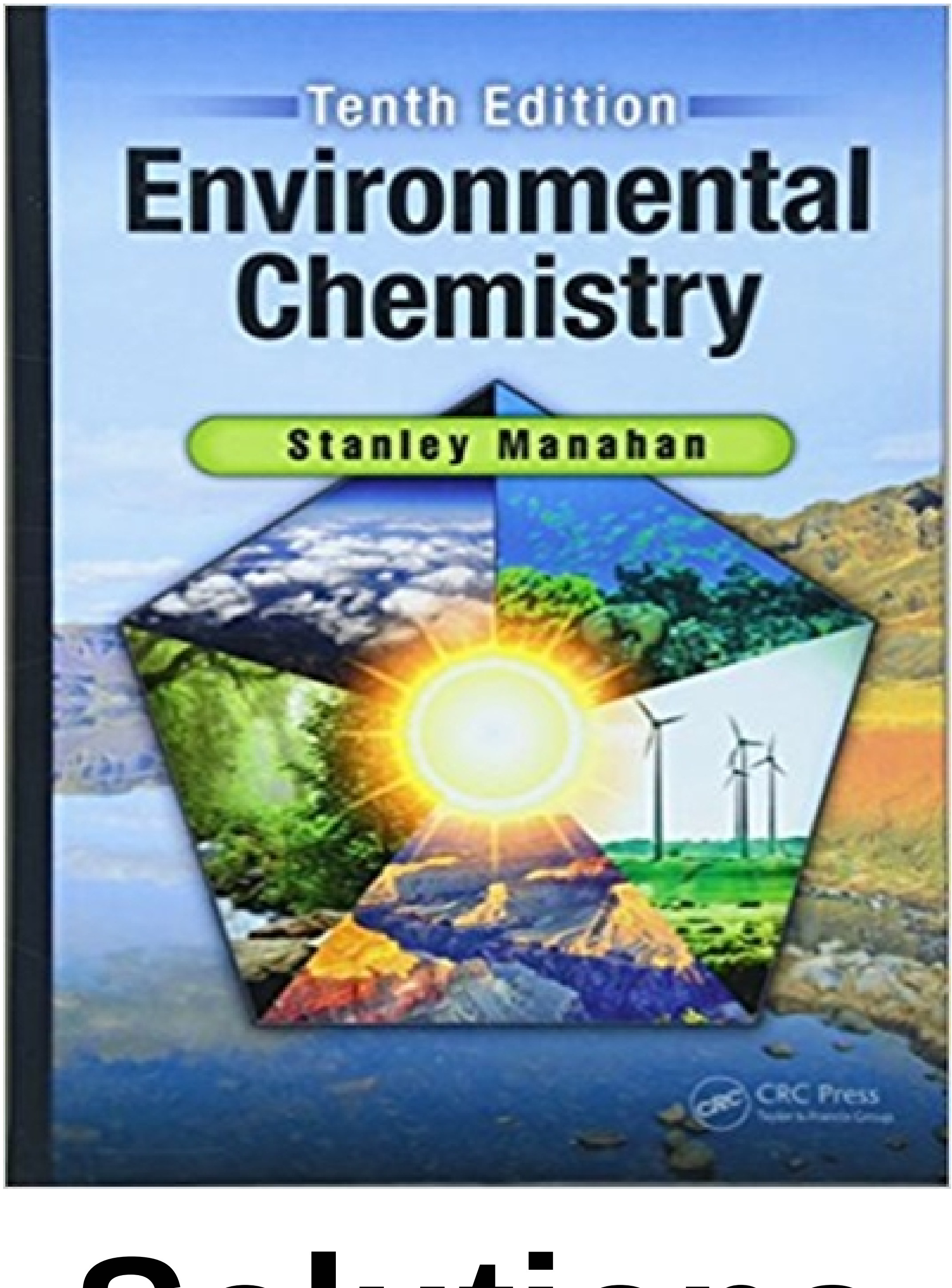


Solutions

Chapter 2
The Hydrosphere and Water Chemistry

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 $CaCO_3$?

   Answer: $(V_p \times N)/V_S$

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?

   Answer: The calculation is the following, where Dx is dextrose

$$4.54 \times 10^4 \text{ g Dx} \times \frac{1 \text{ mol Dx}}{342 \text{ g Dx}} \times \frac{12 \text{ mol } O_2}{1 \text{ mol Dx}} \times \frac{3.20 \times 10^4 \text{ mg } O_2}{1 \text{ mol } O_2} \times \frac{1 \text{ L}}{8.32 \text{ mg } O_2} = 6.13 \times 10^6 \text{ L}$$

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 $[OH^-]$.

   Answer: At pH = 7.00, the alkalinity is due to the $[HCO_3^-]$ and hence $[HCO_3^-] = 2.00 \times 10^{-3}$ eq/l. The $[OH^-] = 1.00 \times 10^{-7}$ eq/l and the $[CO_2]$ can be calculated by substituting the values of $[HCO_3^-]$ and $[H^+]$ in the k_{a1} expression and then solving for $[CO_2]$. The $[CO_3^{2-}]$ can be calculated by substituting the values of $[HCO_3^-]$ and $[H^+]$ in the k_{a1} expression:

$$K_{a1} = 4.45\times10^{-7} = \frac{[1.00\times10^{-7}]\times[2.00\times10^{-3}]}{[CO_2]}$$
$$[CO_2] = 4.49\times10^{-4}$$

$$K_{a2} = 4.69\times10^{-11} = \frac{[1.00\times10^{-7}]\times[CO_3^{2-}]}{2.00\times10^{-3}}$$
$$[CO_3^{2-}] = 9.38\times10^{-7}$$

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.

   Answer: Since the pH has changed to 10.00, $[H^+] = 1 \times 10^{-10}$ and $[OH^-] = 1.00 \times 10^{-4}$ The alkalinity is calculated by the formula:

   $[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] = 2.00 \times 10^{-3}$. The values of $[CO_3^{2-}]$ and $[HCO_3^-]$ are related by the formula

$$[CO_3^{2-}] = \frac{K_{a2}\times[HCO_3^-]}{[H^+]} = 0.469[HCO_3^-]$$

   Substitute this expression for $[CO_3^{2-}]$ into the alkalinity formula in which $[OH^-] = 1.00 \times 10^{-4}$ to solve for $[HCO_3^-] = 9.8 \times 10^{-4}$. The value of $[CO_3^{2-}]$ can be calculated by the K_{a2} formula giving $[CO_3^{2-}] = 4.60 \times 10^{-4}$.

   The amount of biomass produced can be calculated by finding out the difference between the amounts of total dissolved inorganic carbon at the 2 pH values as follows $[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$

   At pH= 7.00, $[C] = 2.45 \times 10^{-3}$ and at pH = 10.00 $[C] = 1.44 \times 10^{-3}$. $[C]_{pH7} \times 1L - [C]_{pH10} \text{ x } 1L = 1.01 \times 10^{-3}$. Since the molar mass of biomass $\{CH_2O\}$ = 30 g/mol, this number can be converted to the amount of biomass produced by the following calculation:

$$1.01\times10^{-3}\frac{\text{mol}}{\text{L}}\times30\frac{\text{g}}{\text{mol}} = 3.03\times10^{-2}\frac{\text{g}}{\text{L}} = 30.3\frac{\text{mg}}{\text{L}}$$

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.

   Answer: The reaction with HCl is:
   $CaCO_3 + HCl \rightarrow Ca^{2+} + Cl^- + HCO_3^-$, the hardness = $[Ca^{2+}] = 1.00 \times 10^{-3}$ and the alkalinity = $[HCO_3^-] = 1.00 \times 10^{-3}$
   In the presence of the HF the reaction becomes:
   $2CaCO_3 + 2HF \rightarrow CaF_2 + 2HCO_3^- + Ca^{2+}$
   Based upon the stoichiometry of this reaction $[HCO_3^-] = 1.00 \times 10^{-3}$ = alkalinity and $[Ca^{2+}] = 5.00 \times 10^{-4}$ = hardness. A slightly higher value of $[Ca^{2+}]$ and hardness results from the dissociation of CaF_2.

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-}? 2.62+2.62+2.62+2.13

   Answer: Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$
   Since $[H^+] = 4.69 \times 10^{-11}$, $[OH^-] = 2.13 \times 10^{-4}$. Since $[H^+] = 4.69 \times 10^{-11}$, from the expression for K_{a1}, $[HCO_3^-] = [CO_3^{2-}]$. Thus
   Alkalinity = $1.00 \times 10^{-3} = [HCO_3^-] + 2[HCO_3^-] + 2.13 \times 10^{-4}$
   $[HCO_3^-] = 2.62 \times 10^{-4}$ and $[CO_3^{2-}] = 2.62 \times 10^{-4}$
   The % contribution of the $CO_3^{2-} = (5.24 \times 10^{-4}/1.00 \times 10^{-3}) \times 100\% = 52.4\%$

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.

   Answer: (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.

   Answer: The reaction is $PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$ and, designating the equilibrium constant of this reaction as K, the following applies:

   $$\mathbf{\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06\times10^{-2}}{3.00\times10^{-3}} = 13.5}$$

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?

Answer: The reaction is $PbCO_3(s)$ + CaT^- + HT^2 ↔ Ca^{2+} + HCO_3^- + PbT^- for which the equilibrium constant may be designated K", which has a value of 5.24, and the following applies when $[HCO_3^-] = 3.00 \times 10^{-3}$ M and $[Ca^{2+}] = 5.00 \times 10^{-3}$ M and the ratio is 0.0349:

$$\mathbf{\frac{[PbT^-]}{[CaT^-]} = \frac{[H^+]\,K''}{[Ca^{2+}][HCO_3^-]} = 0.0349}$$

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.)

    Answer: The reaction is $CaCO_3(s) + HT^{2-} \leftrightarrow CaT^- + HCO_3^-$ from which the following may be calculated:

$$K = \frac{[CaT^-]\,[HCO_3^-]}{[HT^{2-}]} = \frac{K_{sp}\times K'}{K_{a2}} = \frac{4.47\times10^{-9}\times7.75\times10^{-3}}{4.69\times10^{-11}} = 0.739$$

$$[CaT^-] = [HCO_3^-] = 1.00\times10^{-3} \text{ and } [HT^{2-}] = 1.35\times10^{-6}$$

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?

    Answer: At equilibrium $[CaT^-] = [HCO_3^-]$ and $[HT^{2-}] = 0.100 - [CaT^-]$

$$K = 0.739 = \frac{[CaT^-][CaT^-]}{0.100 - [CaT^-]} \quad \text{so} = [CaT^-] = 0.0892 \text{ and } [HT^{2-}] = 0.0108$$

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?

    Answer: Under these conditions all the Ca is bound to the NTA and excess NTA is present as T^{3-} so that:

$$[CaT^-] = 1.00 \times 10^{-3} \qquad [T^{3-}] = 0.100 - [CaT^-] = 0.099$$

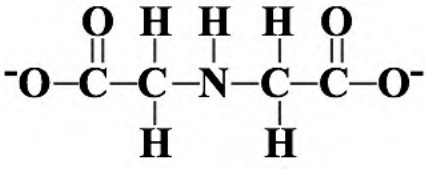
$$K_f = \frac{[CaT^-]}{[Ca^{2+}][T^{3-}]} = 1.48 \times 10^8$$

$$[Ca^{2+}] = 6.83 \times 10^{-11}$$

13. How does chelation influence corrosion?

    Answer: Chelation tends to increase corrosion by shifting redox potentials toward oxidation and by dissolving protective metal oxide coatings.

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



$^{-}O{-}C({=}O){-}CH_2{-}NH{-}CH_2{-}C({=}O){-}O^{-}$

Answer: There are three binding sites, one to each of the two carboxylate groups and one to the N atom

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, $[PbT^-]/[HT^{2-}]$?

Answer: The reaction is $PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$ for which K = 0.046 and from which the following may be calculated:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.76 \times 10^{-3}} = 23.1$$

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 of $[PbT^-]/[HT^{2-}]$?

Answer: 54.1

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

Answer: The presence of chelating agents in the sewage may prevent heavy metals from being removed by the sewage sludge (biosolids)

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

Answer: To keep micronutrient iron in solution

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

Answer: Chlorophyll, which conducts photosynthesis

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

Answer: Orthophosphate, usually as $H_2PO_4^-$ or HPO_4^{2-}

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^-?

Answer: The reaction is $PbCO_3(s) + CaT^- + H^+ \leftrightarrow Ca^{2+} + HCO_3^- + PbT^-$ for which the equilibrium constant may be designated K", which has a value of 5.24, and the following applies at pH 7.00 when $[HCO_3^-] = 1.10 \times 10^{-3}$ M and $[Ca^{2+}] = 1.50 \times 10^{-3}$ M.:

$$\text{Fraction of NTA as } PbT^- = \frac{[PbT^-]}{[CaT^-] + [PbT^-]} = \frac{[PbT^-]/[CaT^-]}{[CaT^-]/[CaT^-] + [PbT^-]/[CaT^-]} = 0.318$$

$$= \frac{0.318}{1.000 + 0.318} = 0.241$$

22. What is the fraction of NTA present as HT^{2-} 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.

Answer: The reaction is $PbCO_3(s) + HT^{2-} \longleftrightarrow PbT^- + HCO_3^-$ for which K = 0.046 and from which the following may be calculated:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.25 \times 10^{-3}} = 32.5$$

$$\text{Fraction of NTA as } HT^{2-} = \frac{[HT^{2-}]}{[PbT^-] + [HT^{2-}]} = \frac{[HT^{2-}]/[HT^{2-}]}{[PbT^-]/[HT^{2-}] + [HT^{2--}]/[HT^{2-}]}$$

$$= \frac{1.00}{32.5 + 1.00} = 0.030$$

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

Answer: Diversion of water to municipal and irrigation uses has resulted in depletion of water sources and degradation of water quality, such as by adding salinity. Construction of dikes along rivers to alleviate flooding has resulted in catastrophic flooding when these structures fail during extreme flooding events.

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 _________________.

Answer: Hydrology, limnology, and oceanography, respectively.

25. Consider the hydrologic cycle in Figure 2.1. List or discuss the kinds or classes of environmental chemistry that might apply to each major part of this cycle.

Answer: Oceanography applies to water in the ocean, by far the largest amount in the cycle; atmospheric chemistry interacts with water in the atmosphere, such as in formation of condensation nuclei around which cloud droplets form; limnology applies to fresh water in streams and lakes; chemistry of the geosphere interacts with aquatic chemistry in groundwater; water in soil is very much involved with soil chemistry.

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.

Answer: (a) The high heat capacity and high heats of vaporization and fusion of water are due largely to its hydrogen bonding tendencies; (b) the transmission of light is the result of the lack of chromophores that absorb visible light in the water molecule; (c) the high surface tension is largely due to the strong bonding of water molecules with each other; and (d) the solvent properties of water, such as the high solubility of ionic solutes in it, are due largely to the polar nature of the water molecule and its hydrogen bonding capability.

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

Answer: (a) The high heat capacity and high heats of vaporization and fusion of water are due largely to its hydrogen bonding tendencies; (b) the transmission of light is the result of the lack of chromophores that absorb visible light in the water molecule; (c) the high surface tension is largely due to the strong bonding of water molecules with each other; and (d) the solvent properties of water, such as the high solubility of ionic solutes in it, are due largely to the polar nature of the water molecule and its hydrogen bonding capability.

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.

    Answer: As several examples, photosynthetic autotrophic organisms are producers that generate biomass that provides the base of the aquatic food web; producers require adequate nutrients to generate biomass, but if the nutrients are excessive, eutrophication may result; too much biomass in water can result in excessive biochemical oxygen demand in water with depletion of dissolved oxygen.

29. Assuming levels of atmospheric CO_2 are 400 ppm CO_2, what is the pH of rainwater due to the presence of carbon dioxide? Some estimates are for atmospheric carbon dioxide levels to double in the future. What would be the pH of rainwater if this happens?

    Answer: As noted in Section 3.7, 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. In pure rainwater, the carbon dioxide dissociates partially in water to produce equal concentrations of H^+ and HCO_3^- and from the K_{a1} expression for CO_2, $[H^+] = 2.41 \times 10^{-6}$ and pH = 5.61. Doubling atmospheric CO_2 levels would double the concentration of CO_2 in rainwater to 2.618×10^{-5} M and, as shown in Section 2.7, this gives $[H^+] = 3.41 \times 10^{-6}$ and pH = 5.47.

30. Assume a sewage treatment plant processing 1 million liters of wastewater per day containing 200 mg/L of degradable biomass, $\{CH_2O\}$. Calculate the volume of dry air at 25°C that must be pumped into the wastewater per day to provide the oxygen required to degrade the biomass (Reaction 2.6.1).

    Answer: The reaction is $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$. The amount of biomass present in the 1 million liters of water is 2.00×10^8 mg = 2.00×10^5 g. The moles of O_2 required to react with this biomass are

$$2.00 \times 10^5 \text{ g } \{CH_2O\} \times \frac{1 \text{ mol } \{CH_2O\}}{30 \text{ g } \{CH_2O\}} \times \frac{1 \text{ mol } O_2}{1 \text{ mol } \{CH_2O\}} = 6.67 \times 10^3 \text{ mol } O_2$$

Since only 20.95% of dry air is O_2, the moles of air needed to supply this $O_2 = 3.18 \times 10^4$ mole. The volume of this amount of air at 25°C and 1 atm pressure can be calculated by the ideal gas law, PV = nRT, where R = 0.0821 L atm mol^{-1} giving 7.78×10^5 L of air. Only a fraction of the oxygen in the air is actually transferred into the sewage, so significantly more air would need to be pumped to supply the oxygen required.

31. Anoxic bacteria growing in a lake sediment produced equal molar amounts of carbon dioxide and carbon monoxide according to the biochemical reaction $2\{CH_2O\} \rightarrow CO_2 + CH_4$, so that the water in the lake was saturated with both CO_2 gas and CH_4 gas. In units of mol × L^{-1} × atm^{-1} the Henry's law constant for CO_2 is 3.38×10^{-2} and that of CH_4 has a value of 1.34×10^{-3}. At the depth at which the gas was being evolved, the total pressure was 1.10 atm and the temperature was 25°C, so the vapor pressure of water was 0.0313 atm. Calculate the concentrations of dissolved CO_2 and dissolved CH_4.

    Answer: Since equimolar amounts of CO_2 and CH_4 are evolved, the mole fraction of each gas = 0.500. The partial pressure of each gas = 0.500 × 1.10 = 0.550 atm. The corrected pressure of each gas = 0.550 - 0.0313 = 0.519. Using Henry's law, $[CO_2]$ = 0.519 atm × 3.38×10^{-2} mol

× L^{-1} × atm^{-1} = 1.75×10^{-2} M and $[CH_4] = 6.95 \times 10^{-4}$ M.

Chapter 2

THE HYDROSPHERE AND WATER CHEMISTRY

***Environmental Chemistry*, 10th Edition**
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Taylor and Francis/CRC Press
2017

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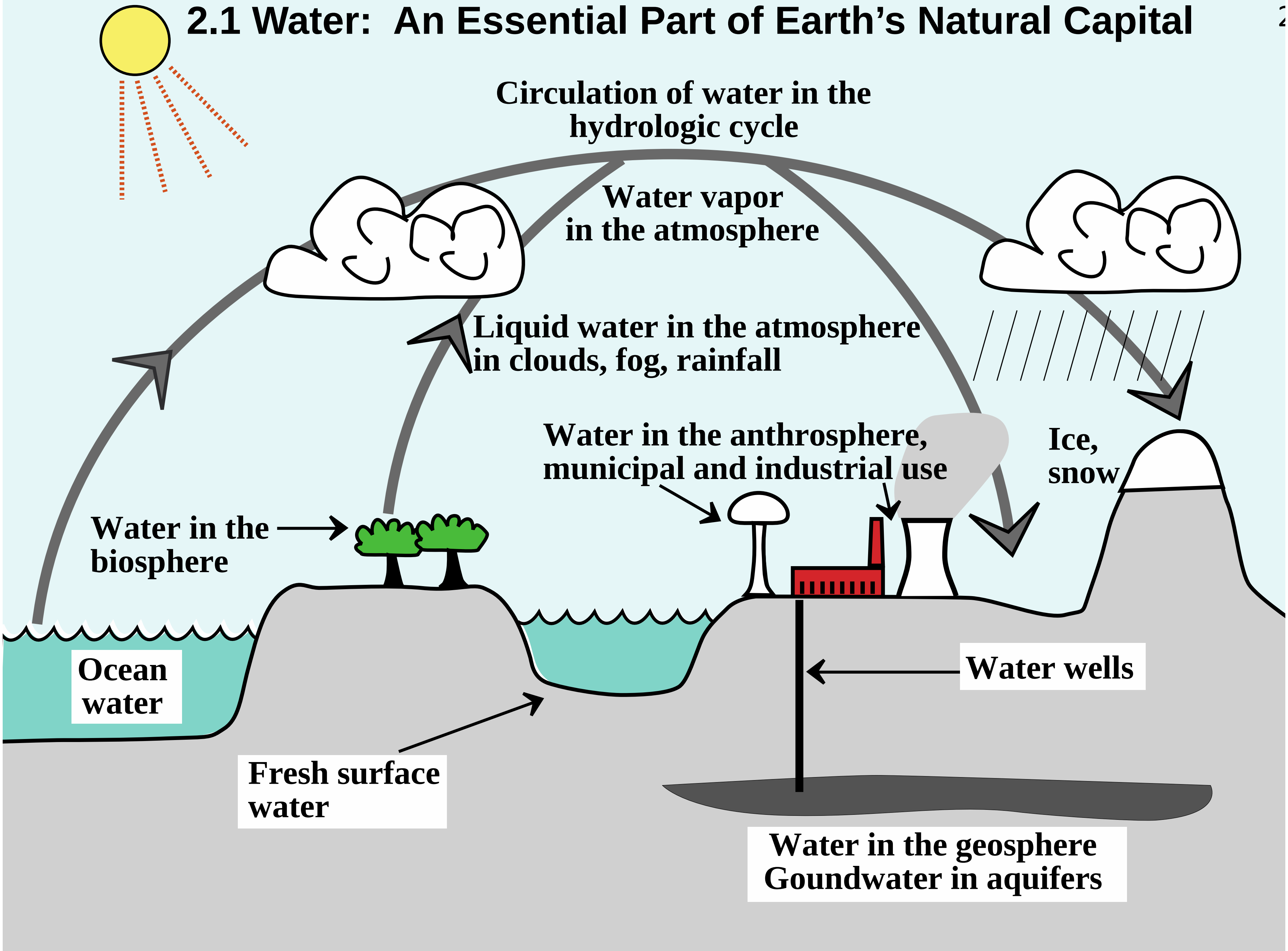
2.1 Water: An Essential Part of Earth’s Natural Capital



Circulation of water in the hydrologic cycle

Water vapor in the atmosphere

Liquid water in the atmosphere in clouds, fog, rainfall

Water in the biosphere

Water in the anthrosphere, municipal and industrial use

Ice, snow

Ocean water

Water wells

Fresh surface water

Water in the geosphere Goundwater in aquifers

Science of Water

Hydrology: **Study of water**

Limnology: **Science of fresh water**

Oceanography: **Science of oceans**

Environmental and resource problems with water

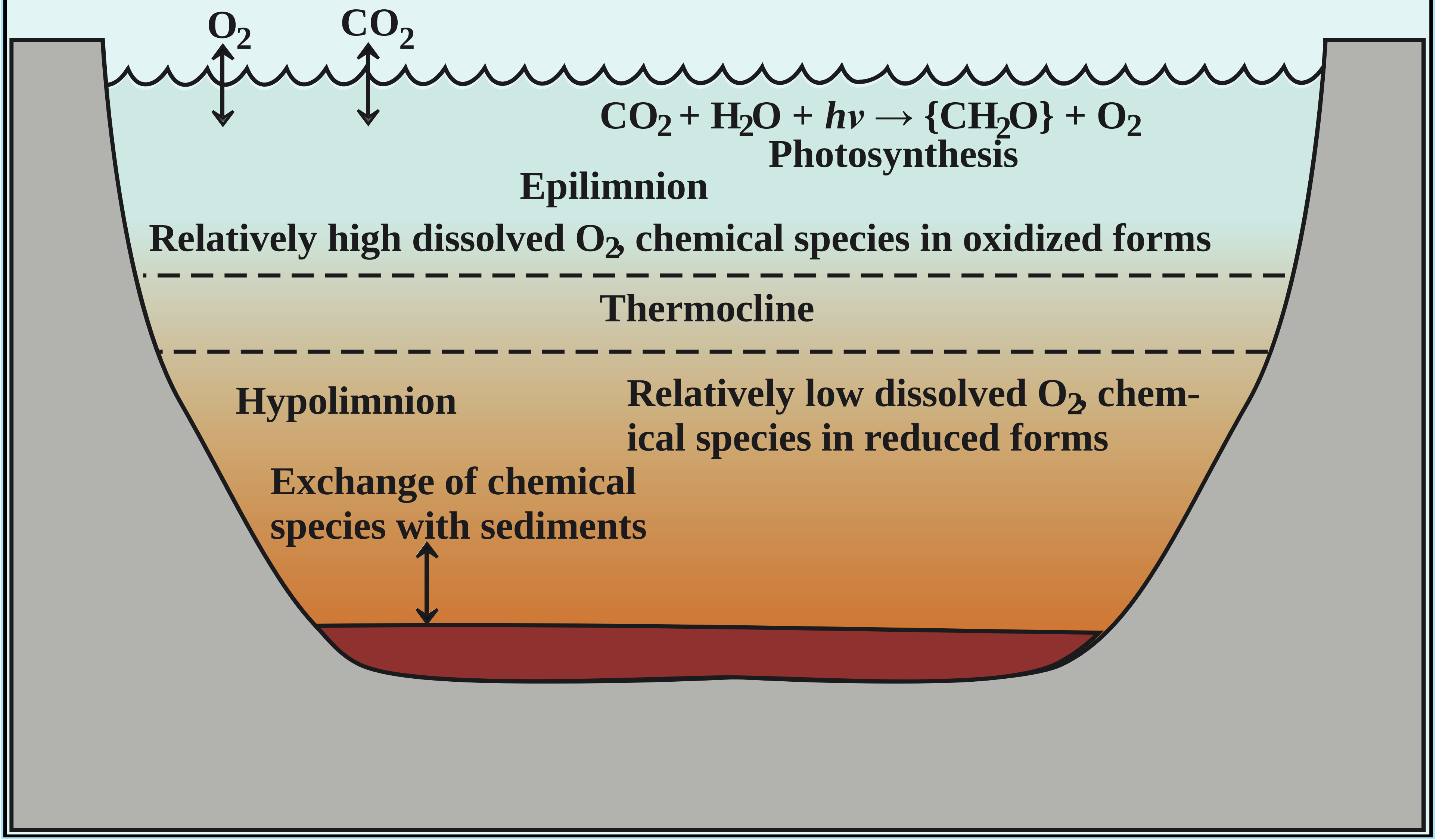
- **Too little water:** **Drought, global warming**
- **Too much water:** **Floods**
- **Waterborne diseases**
- **Contaminated water, water pollutants**

Water chemistry must consider many factors

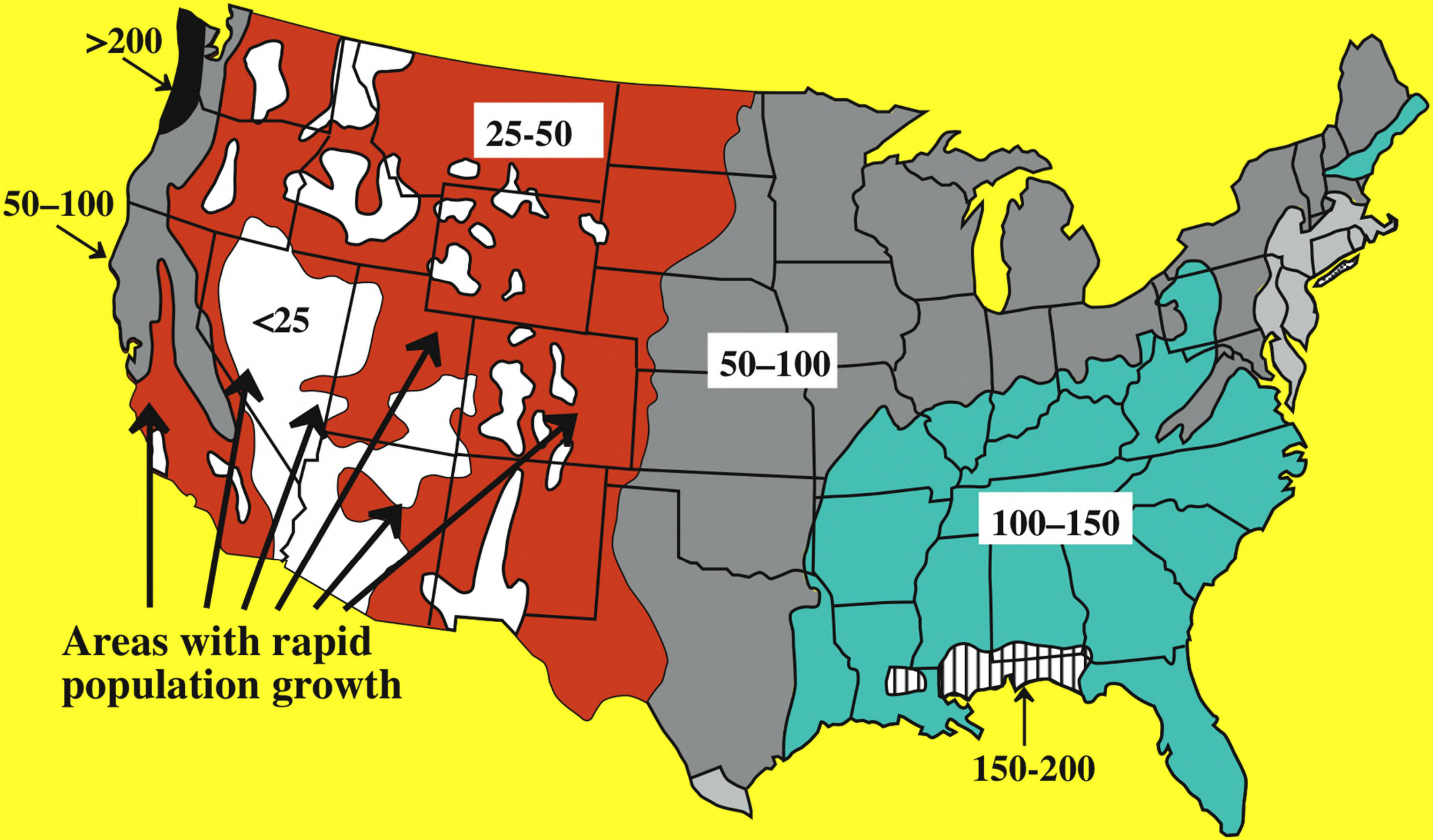
- **Where water is found**
- **Interactions with geosphere (especially groundwater)**
- **Organisms (especially microorganisms) in water**
- **Human influences (interaction with anthrosphere)**

Water very much involved with chemical fate and transport in the Earth System

Figure 2.2. The physical behavior of water has much to do with its chemical and environmental behavior and with aquatic life

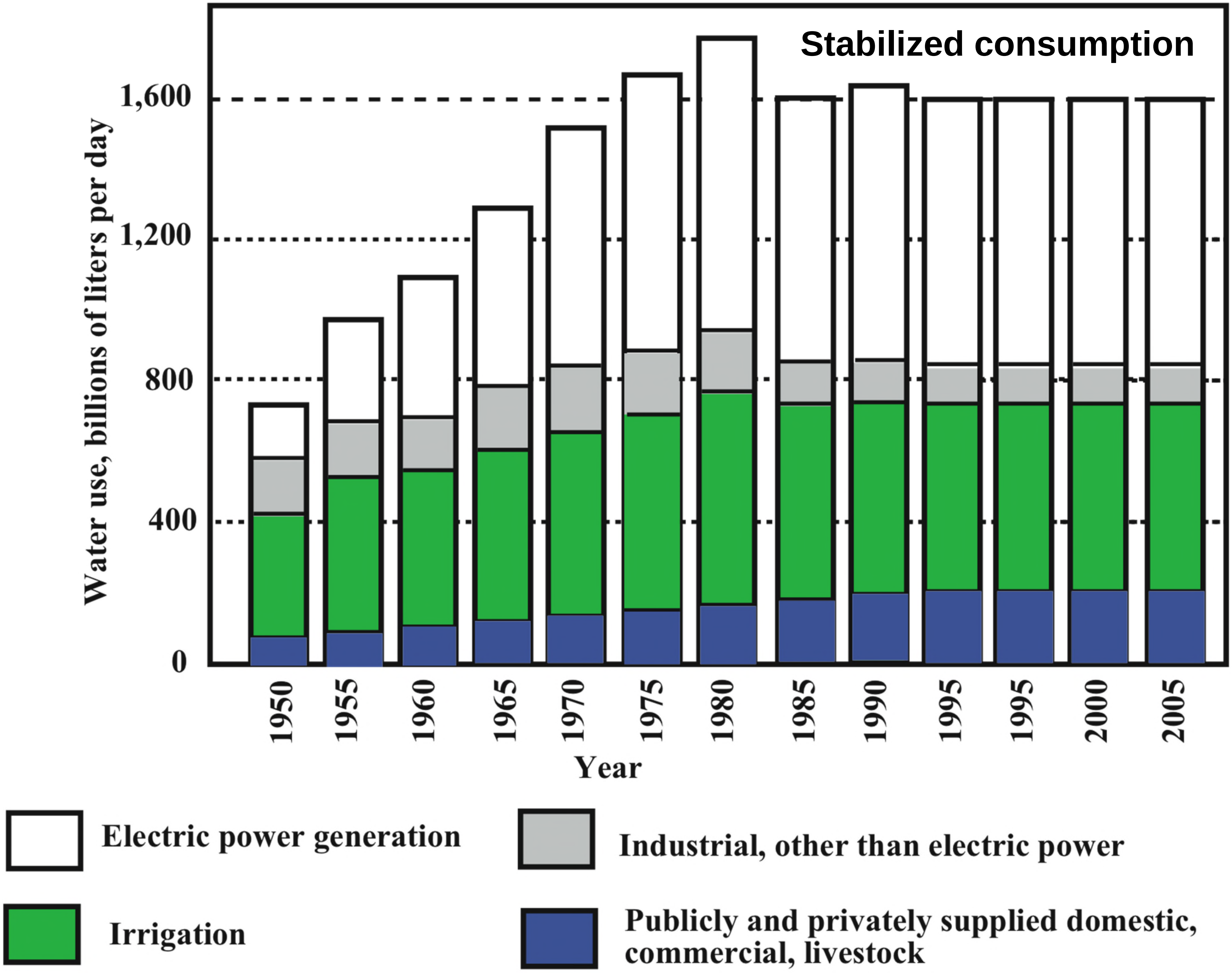


2.2 Sources and Uses of Water

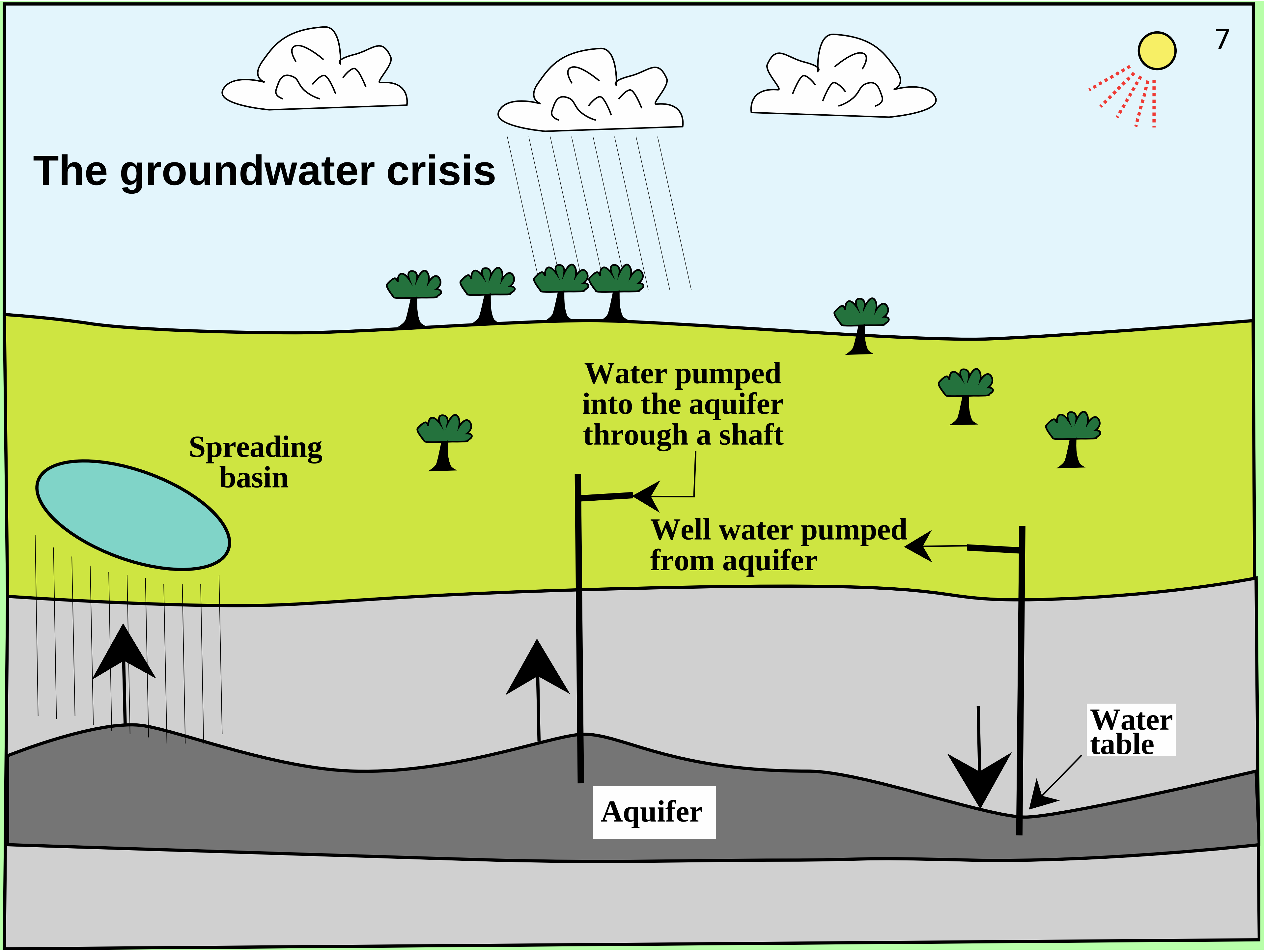


A major consideration regarding water sources is uneven distribution of water as shown by rainfall distribution in continental U.S., cm/year (Fig 2.3 showing average annual rainfall, cm/year)

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



The groundwater crisis



Groundwater is a major source of municipal water

- Only source in some areas
- About 190 billion liters per day for irrigation in the U.S.

Rapid depletion of groundwater in some areas

- Especially problematic in California's Central Valley–the vegetable garden of the U.S.
- Severe in many areas of Africa and Asia

Measures to alleviate groundwater shortages, especially deeper wells

- Lowered water table, no more water can be pumped
- Intrusions of saline water, especially in coastal areas
- Irreversible damage to aquifer compaction, cannot be recharged
- Surface subsidence, even structural damage
- Depletion of surface water in lakes and rivers
- Contributes to desertification–productive land becomes desert

2.3 H_2O: Simple Formula, Remarkable Molecule

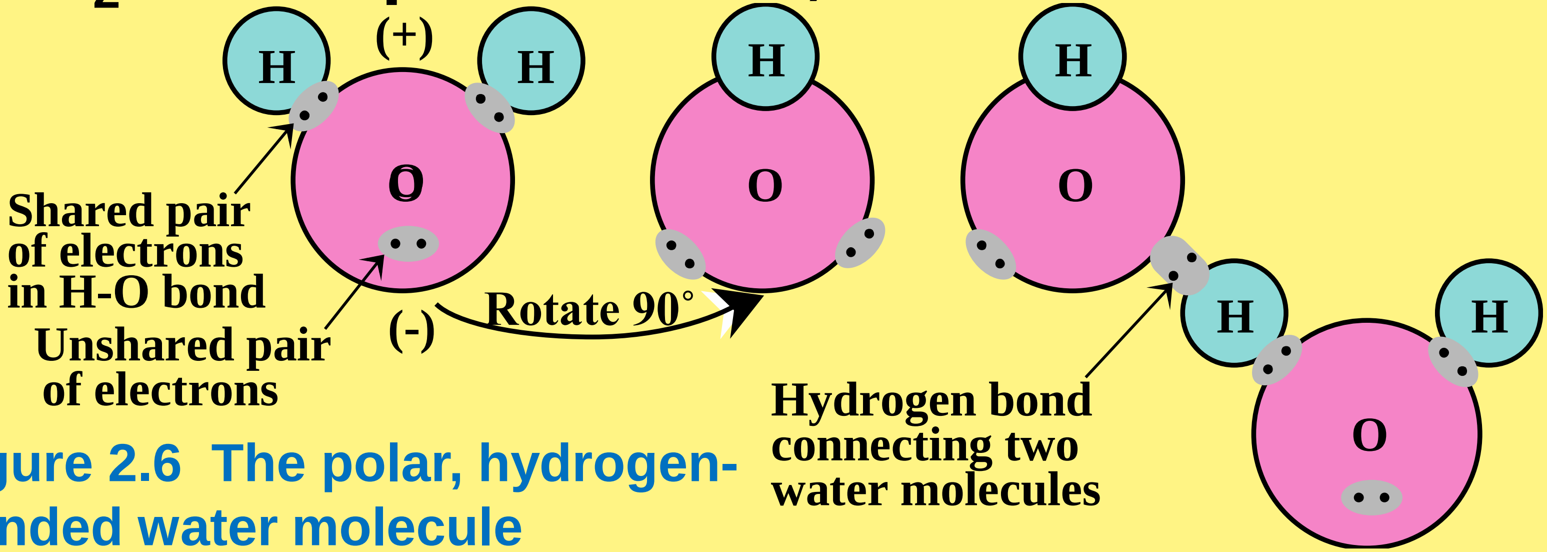


Figure 2.6 The polar, hydrogen-bonded water molecule

Characteristics of H_2O molecule

- Electron pairs as far apart as possible → angular configuration
- Non-bonded pairs of electrons form hydrogen bonds

Polarity and H-bonding give H_2O special properties

- Good solvent for polar and ionic species
- Unique heat/temperature/density behavior
  - High dielectric constant
  - High surface tension
  - High heat capacity
  - High heat of fusion
  - High heat of evaporation
  - Stratification of bodies of water

Transparency allows photosynthesis by algae, photosynthetic bacteria, plants in water

Hydrogen bonding with solute molecules and between water molecules

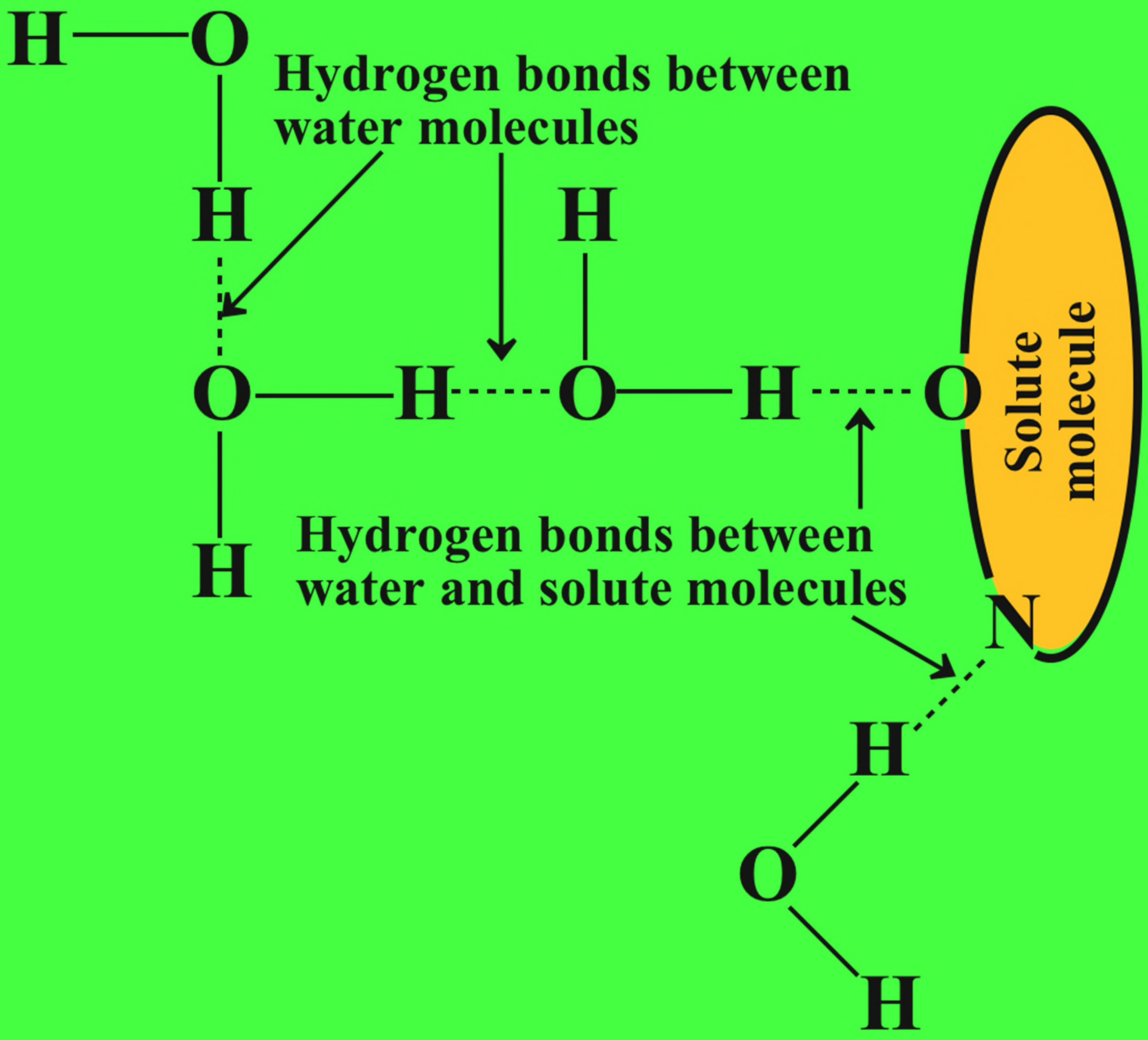


Table 2.1 Important Properties of Water

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°C	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

Polar water molecule and solvent effects on ions

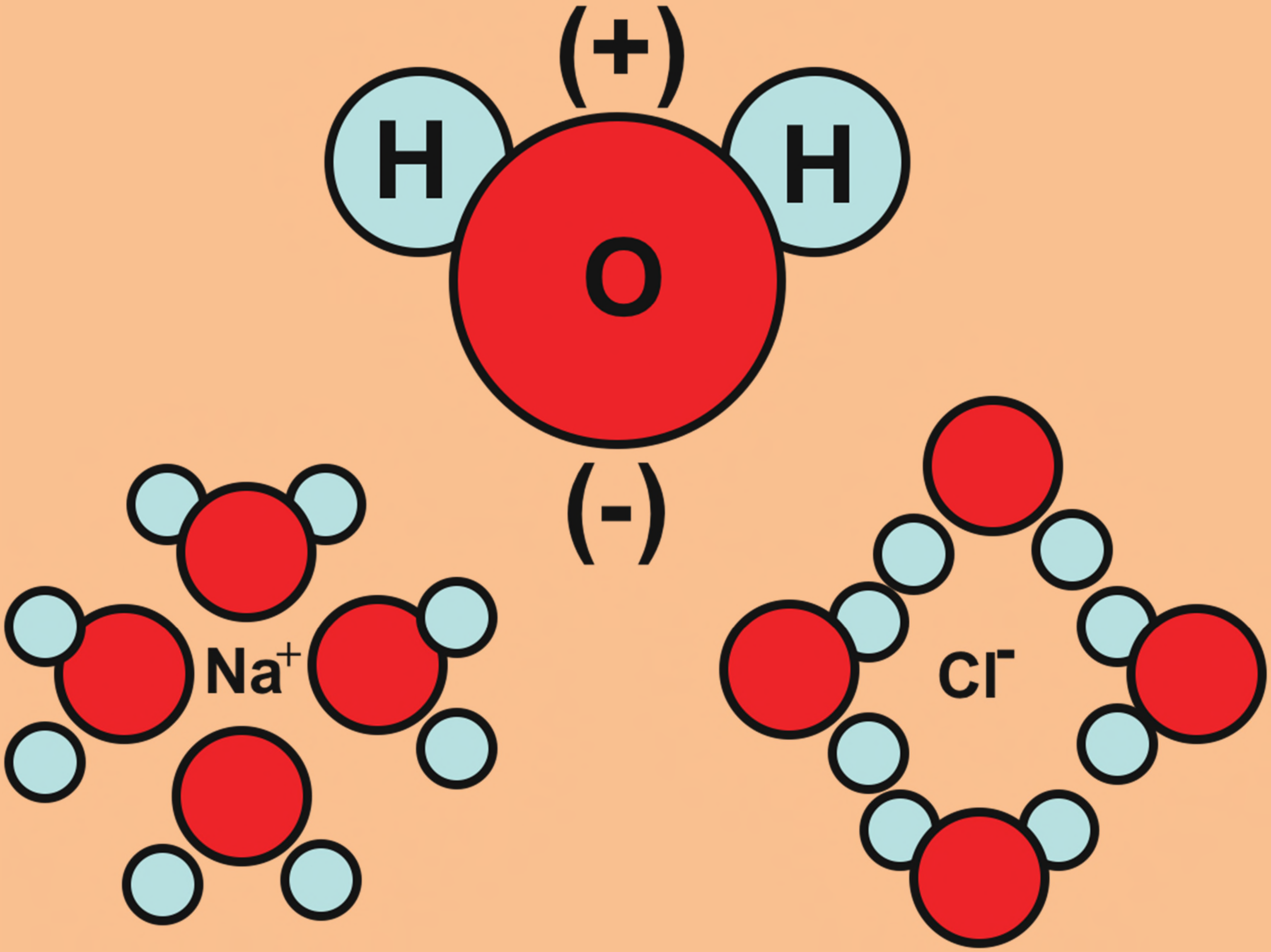
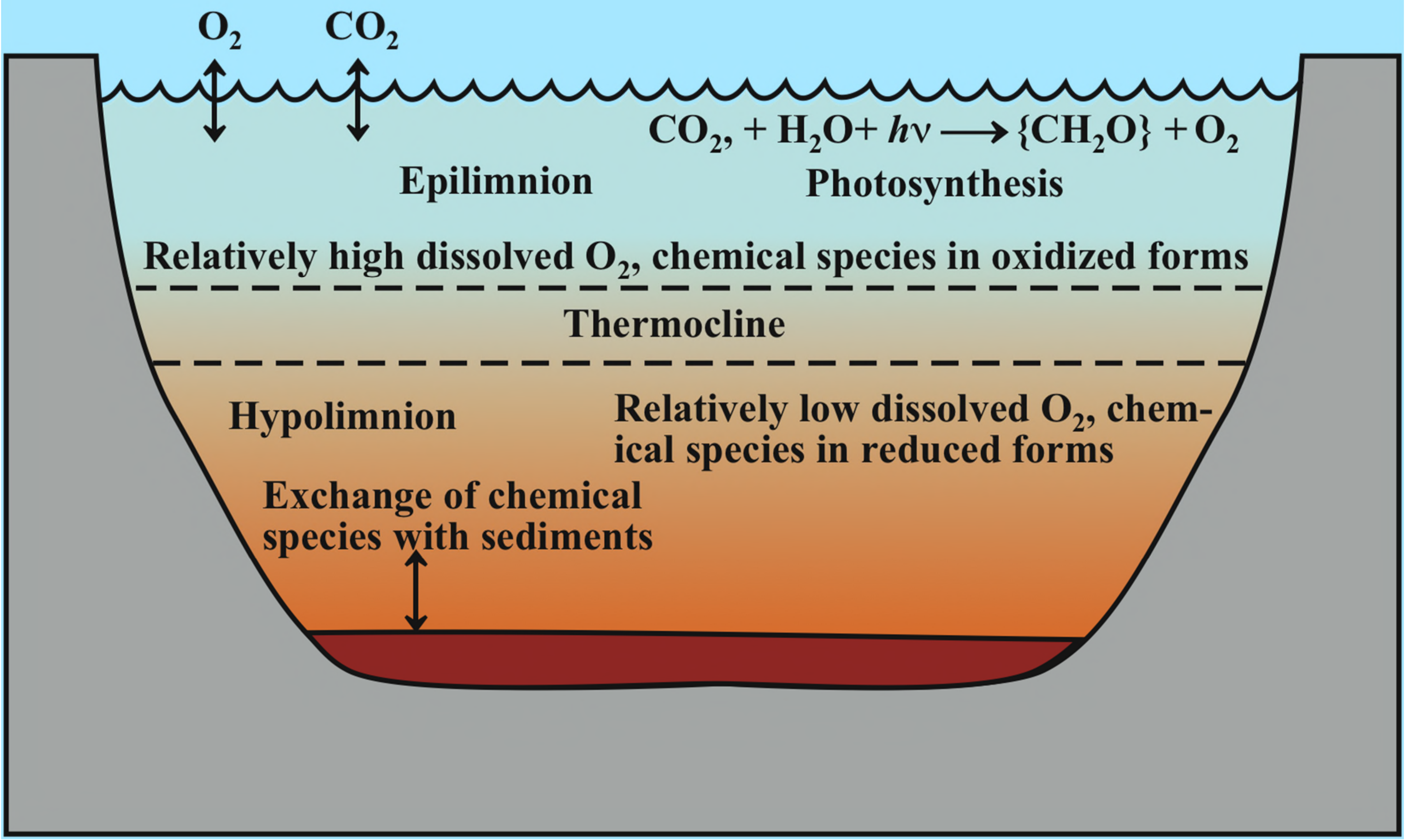


Figure 2.6. Thermal stratification of a lake

Overturn in fall tends to stir up bottom sediment



2.4 Life in Water (Biota)

Autotrophic organisms

- **Utilize solar or chemical energy**
- **Synthesize complex biochemicals from simple inorganic compounds**
- **Photosynthetic aquatic algae are producers that make biomass from CO_2 and other inorganic compounds**

Heterotrophic organisms metabolize organic materials

- **Decomposers (reducers) break down material of biological origin**

Productivity is the ability of organisms in a body of water to produce biomass that is the basis of the food chain

- **Eutrophication caused by excess productivity**

Decay of excess biomass

- **Consumption of oxygen**

Main physical factors affecting aquatic life

- **Temperature**
- **Transparency**
- **Turbulence**

Oxygen in water

- **Dissolved oxygen, DO**
- **Biochemical oxygen demand, BOD, from degradable substances**

2.5 Introduction to Aquatic Chemistry

Common chemical phenomena occur in water

- **Acid-base** • **Solubility** • **Oxidation-reduction**
- **Complexation** • **Biochemical (oxidation-reduction)**

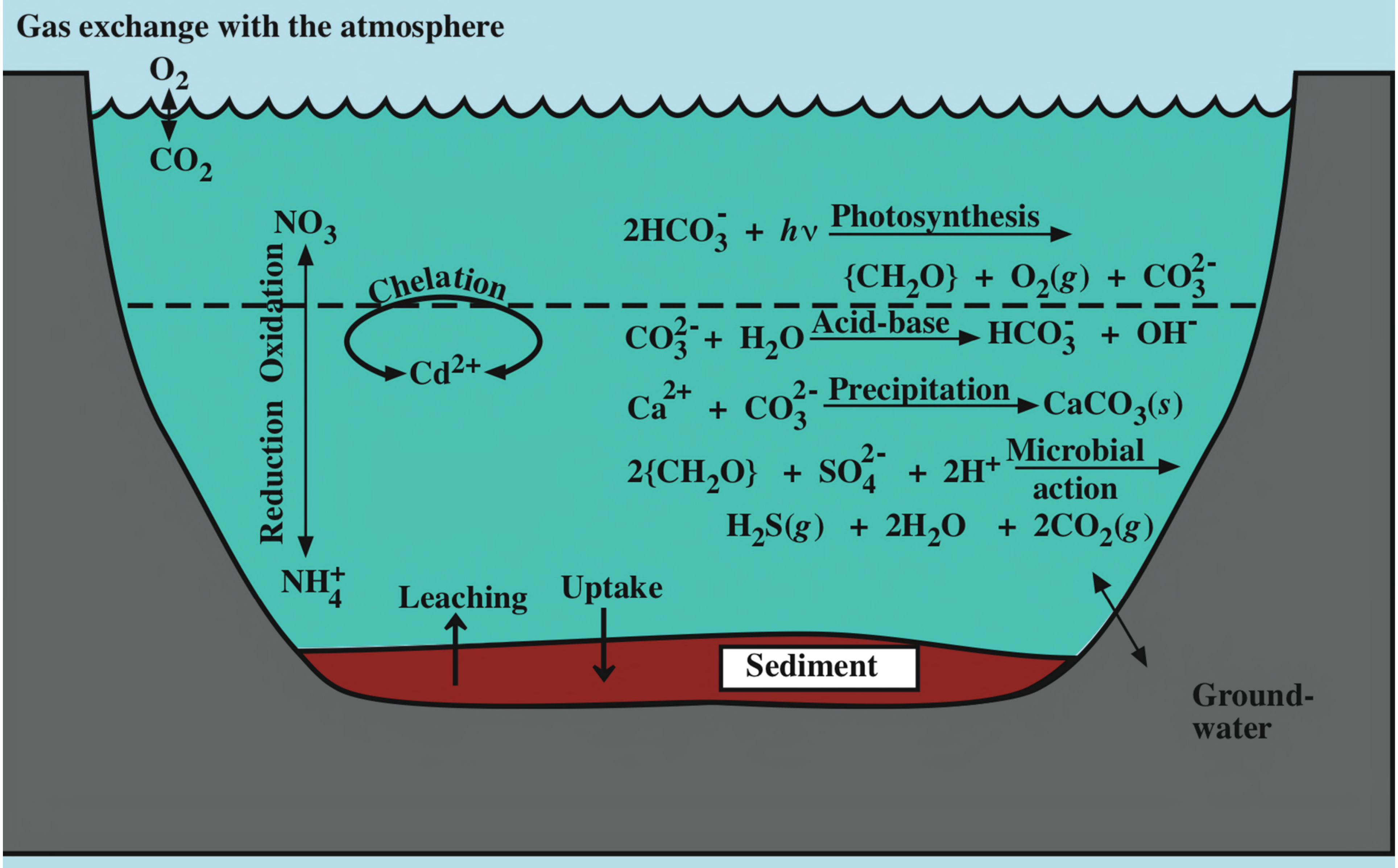
Aquatic systems are complicated, open, and dynamic

- **Solid phases** • **Gas phases** • **Organisms**

Simplified models based upon equilibrium conditions

- **Rates of processes (kinetics) also important**

Figure 2.7. Major aquatic chemical processes



Gas exchange with the atmosphere

O_2

CO_2

NO_3

Reduction Oxidation

NH_4^+

Chelation

Cd^{2+}

$$2HCO_3^- + h\nu \xrightarrow{\text{Photosynthesis}} \{CH_2O\} + O_2(g) + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \xrightarrow{\text{Acid-base}} HCO_3^- + OH^-$$

$$Ca^{2+} + CO_3^{2-} \xrightarrow{\text{Precipitation}} CaCO_3(s)$$

$$2\{CH_2O\} + SO_4^{2-} + 2H^+ \xrightarrow[\text{action}]{\text{Microbial}} H_2S(g) + 2H_2O + 2CO_2(g)$$

Leaching

Uptake

Sediment

Ground-water

2.6 Gases in Water

- O_2 for fish
- CO_2 to support algal growth

Henry's law: ***The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas in contact with the liquid.***

Oxygen in water

- From air (20.95% O_2 on basis of dry air)
- 8.32 mg/L O_2 in water in equilibrium with air at 25˚C
- Decreases with increasing temperature

Oxygen consumed by biodegradation of biomass, $\{CH_2O\}$

- $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$
- 8.3 mg O_2 consumed by only 7.8 mg $\{CH_2O\}$

2.7 Water Acidity and Carbon Dioxide in Water

Acidity: Capacity to neutralize OH^-

Alkalinity: Capacity to neutralize H^+

HCO_3^- as acid releases H^+

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

HCO_3^- as base accepts H^+

- $HCO_3^- + H^+ \leftrightarrow H_2O + CO_2$

Strong acids such as HCl contribute to free mineral acid, a pollutant

- Acid mine water from H_2SO_4

Hydrated metal ions as acids

- $Al(H_2O)_6^{3+} \leftrightarrow Al(H_2O)_5(OH)^{2+} + H^+$

Carbon Dioxide in Water

From air and as product of organic matter decay

- **In water mainly as $CO_2(aq)$**
- **Relatively little as H_2CO_3**

Acid-base equilibria for carbon dioxide species

- **$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$**

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

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

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

Slight acidity of unpolluted rainwater

Air is 406 parts per million CO_2 (in year 2017)

- **Water in equilibrium with this air has**

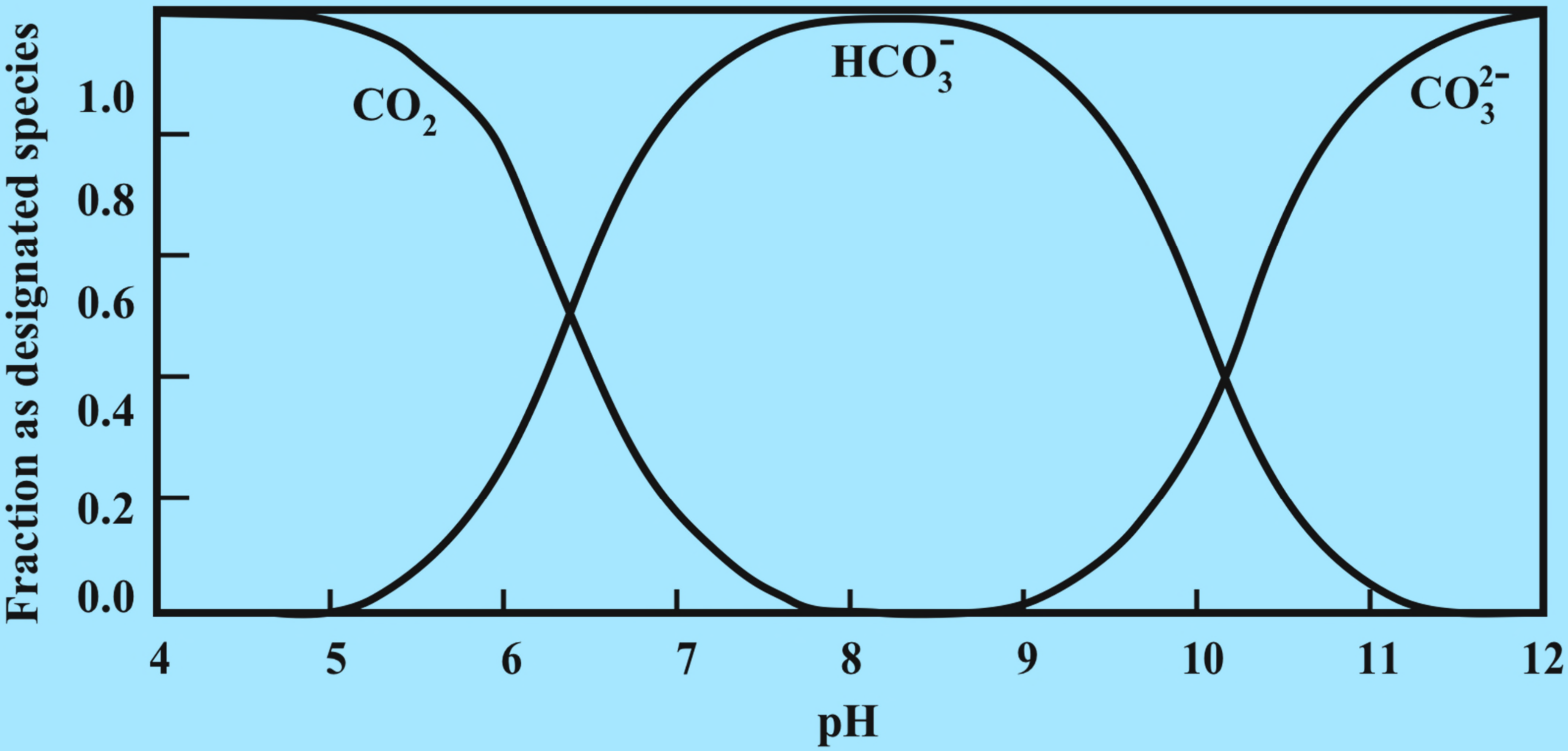
  $[CO_2(aq)] = 1.328 \times 10^{-5}$ mol/L
- **$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$**
- **$[H^+] = [HCO_3^-]$**

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

Solving the above gives

- **$[H^+] = 2.48 \times 10^{-6}$ mol/L**
- **pH = 5.61**

Figure 2.8. Distribution of CO_2 and carbonate species in water as a function of pH



2.8 Alkalinity

Alkalinity is the capacity to accept H^+ ion

- **Most commonly: $HCO_3^- + H^+ \leftrightarrow CO_2(\mathit{aq}) + H_2O$**
- **Other common contributors: OH^-, CO_3^{2-}**

Alkalinity

- **Buffers water pH**
- **Carbon source for algal growth**
- **Reacts with some water treatment chemicals**

Complete formula for alkalinity applicable over wide pH range: $[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

A common value to assume for alkalinity is

$1.00 \rightarrow 10^{-3}$ mol/L

At pH 7, essentially all alkalinity is from HCO_3^-

At pH 10 significant contributions from CO_3^{2-}, OH^-

- **About half the carbon at pH 10 as at pH 7**

2.9 Calcium and Other Metal Ions in Water

- Exist as hydrated metal ions such as $Al(H_2O)_6^{3+}$
- The +3 hydrated metal ions lose H^+ so are acidic

Dissolved Carbon Dioxide and Calcium Carbonate Minerals

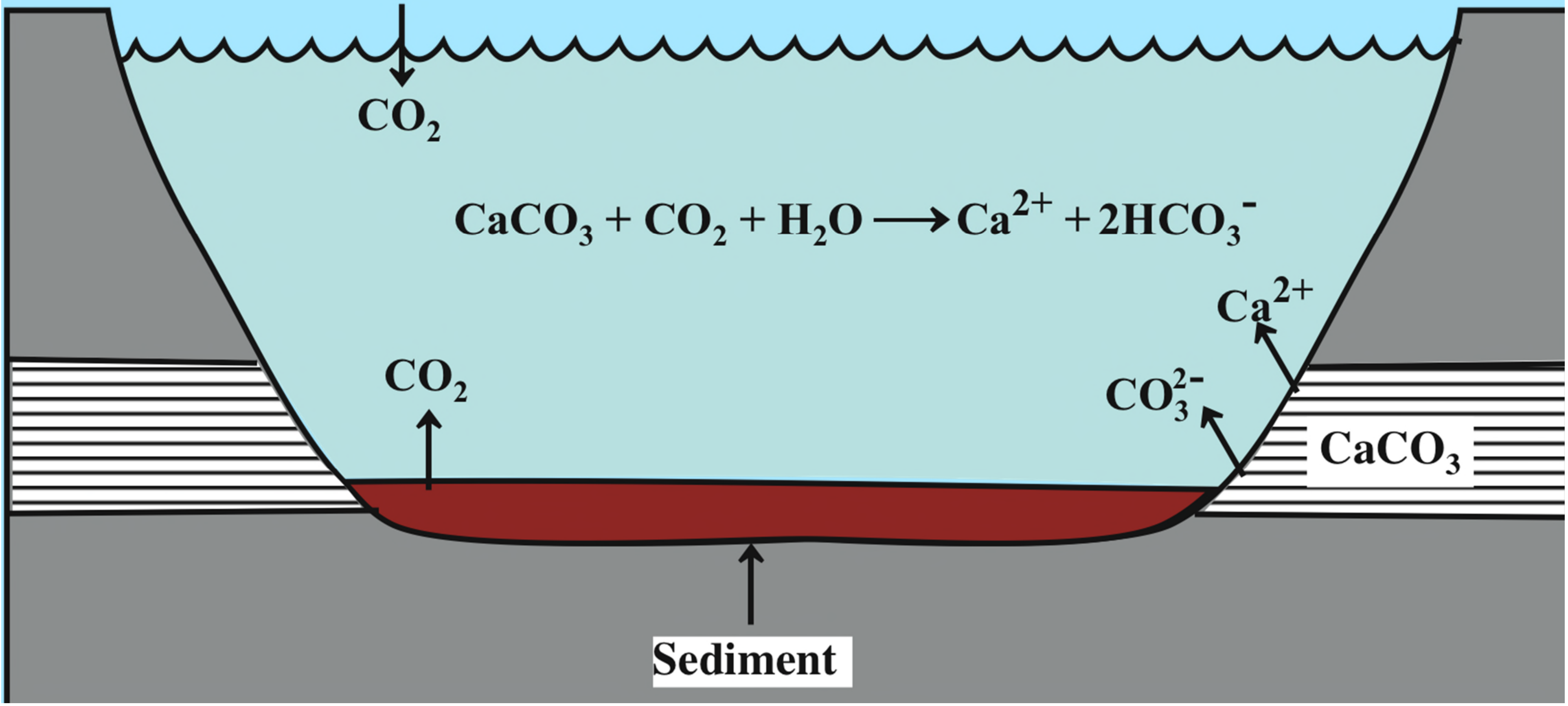
For water in equilibrium with air (400 ppm CO_2) and $CaCO_3$ (*s*) (see illustration on next slide):

$[CO_2] = 1.309 \times 10^{-5}$ mol/L $[Ca^{2+}] = 5.18 \times 10^{-4}$ mol/L

$[HCO_3^-] = 1.04 \times 10^{-3}$ mol/L $[H^+] = 5.63 \times 10^{-9}$ mol/L

$[CO_3^{2-}] = 8.63 \times 10^{-6}$ mol/L   pH = 8.25

Figure 2.9 Carbon dioxide-calcium carbonate equilibria



2.10 Complexation and Chelation

$Fe(H_2O)_6^{2+} + CN^- \leftrightarrow Fe(H_2O)_5CN^+ + H_2O$

$Fe(H_2O)_5CN^- + CN^- \leftrightarrow Fe(H_2O)_4(CN)_2 + H_2O$

The reactions above show

- Complexation
- A ligand (CN^-) binding to a metal ion, a reversible process
- Formation of a complex (ion), or coordination compound
- CN^- ion in the above example is a unidentate ligand

Chelation occurs with chelating agents that can bind in more than one place

Organometallic compounds are formed by irreversible binding of organic groups to metal atoms

Complexation and chelation affect ligands and metals

- Oxidation-reduction, decarboxylation, hydrolysis, and biodegradation of ligands
- Solubilization, precipitation, adsorption, distribution, transport, and effects of metal ions
- Biochemical effects of metals including bioavailability, toxicity, uptake by organisms

Occurrence of chelating agents

- Biocompounds such as hemoglobin
- Metabolic products of organisms
- Pollutants such as from metal plating wastes

Chelating agents in water may facilitate algal growth by making soluble nutrient iron available

2.10 Bonding and Structure of Metal Complexes

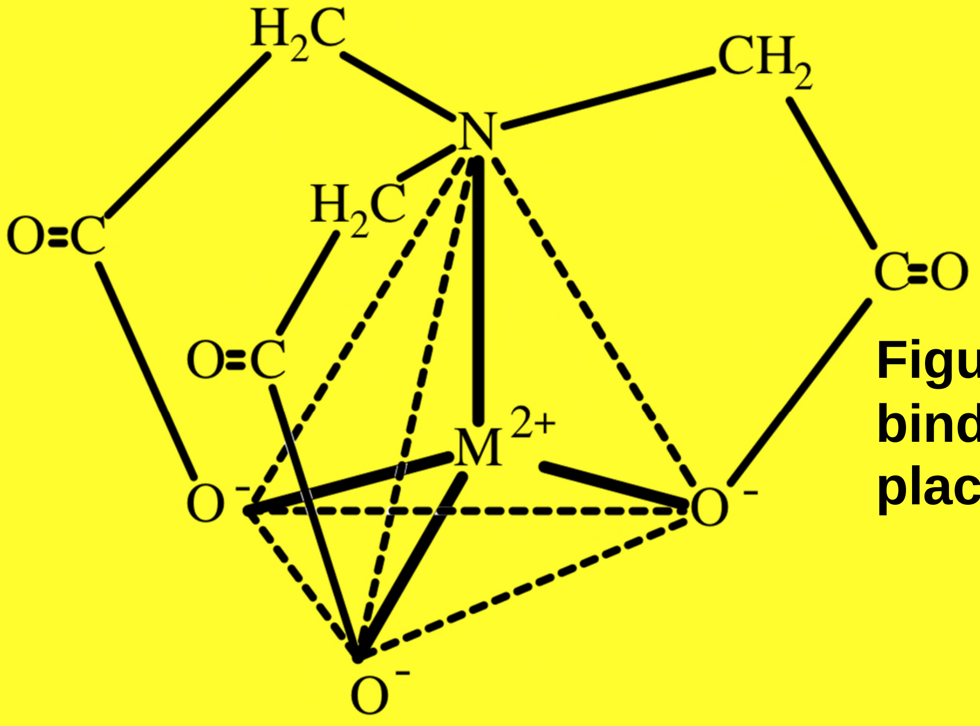
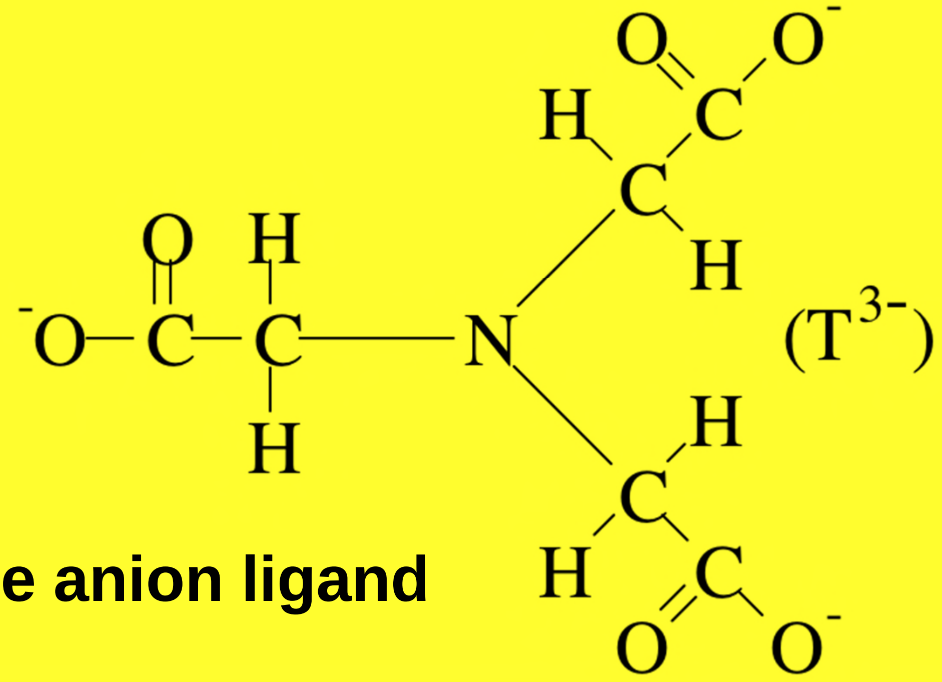


Figure 2.10 Nitrilotriacetate chelate binding a metal ion in four different places



Nitrilotriacetate anion ligand

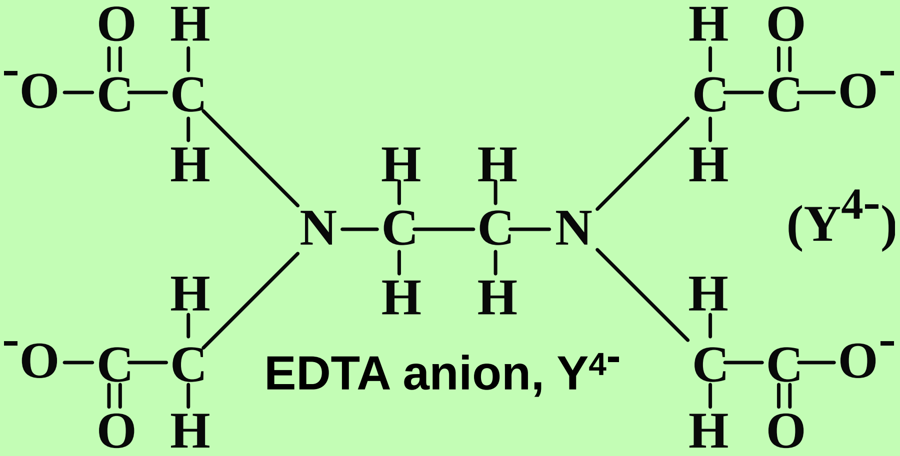
2.12 Calculations of Species Concentrations

Stepwise formation constants when multiple ligands may bond to metal ions

Overall formation constants for two or more ligands bonding

2.13 Complexation by Deprotonated Ligands

Textbook example of copper chelation by completely ionized EDTA



EDTA anion, Y^{4-}

At pH 11 at excess EDTA at 200 mg/L the concentration of unchelated EDTA is only

$[Cu^{2+}] = 2.3 \times 10^{-20}$ mol/L

$[CuY^{2-}] = 7.9 \times 10^{-5}$ mol/L

$[Cu^{2+}]/[CuY^{2-}] = 3.0 \times 10^{-14}$

- Vastly reduced free copper ion concentration in excess EDTA
- Influence chemical effects of Cu^{2+}
- Influence biochemical effects of Cu^{2+}

2.14 Complexation by Protonated Ligands

Examples shown with NTA, a triprotic acid chelating agent (structural formula of anion of NTA on an earlier slide)

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

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

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

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

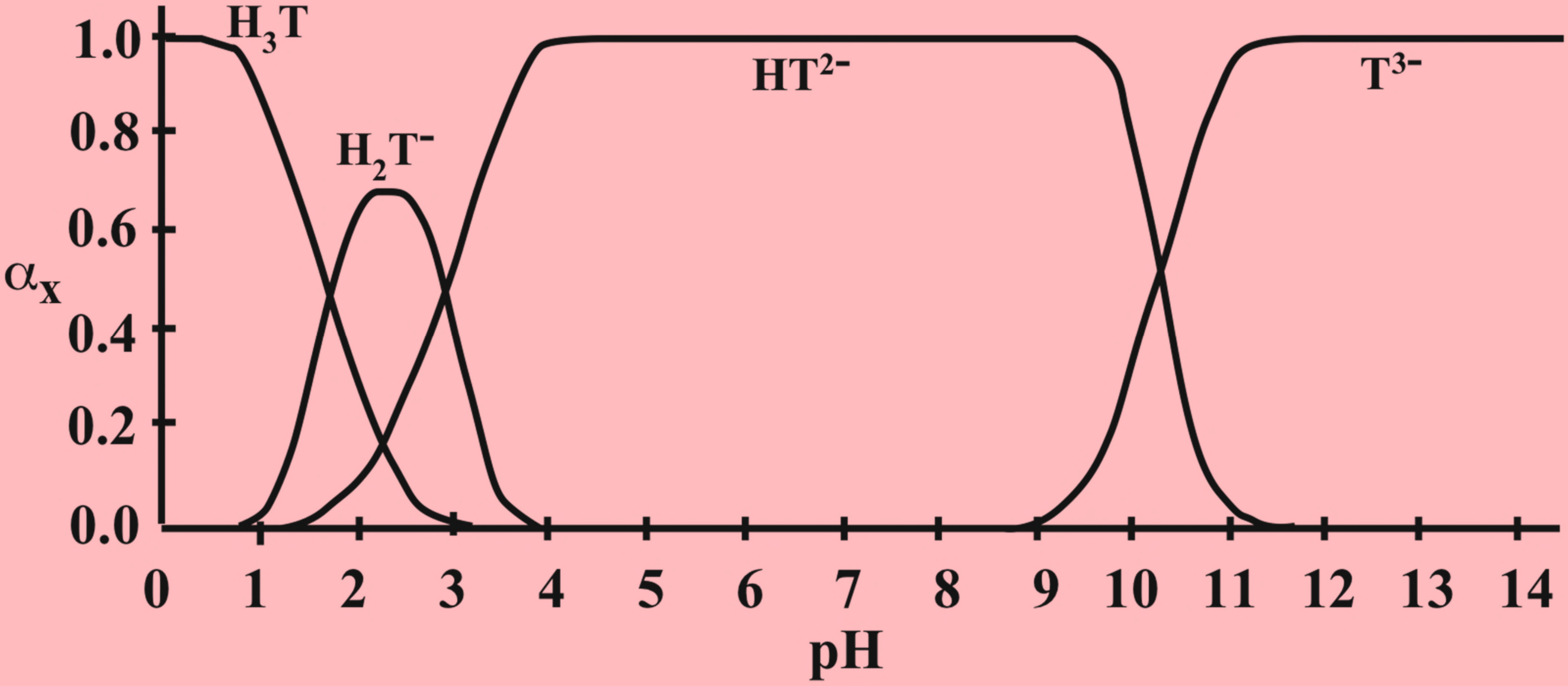
$HT^- \leftrightarrow H^+ + T^{3-}$

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

Throughout the normal range of pH in natural waters the predominant unchelated NTA species is HT^-

- **See distribution of species diagram on the next slide**

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



2.15 Solubilization of Lead Ion from Solids by NTA

A major concern with the introduction of pollutant chelating agents into water is their ability to dissolve and transport heavy metals. Several examples are presented for the chelating agent NTA reacting with lead-containing solids under various conditions. The first example is shown here and the results are given for the other examples, which are presented in the textbook. An approach is shown in which the overall reaction is broken down into its constituent reactions. These are then added together to get the overall reaction, then their equilibrium constant expressions are multiplied to give the expression for the overall reaction.

Assume a water sample contains 25 mg/L of the trisodium NTA salt, $N(CH_2CO_2Na)_3$ formula mass 257 in equilibrium with solid $Pb(OH)_2$. Under these conditions

- **Unchelated NTA is present as HT^{2-} (see diagram of distribution of NTA species as a function of pH)**
- **The other possible soluble form of NTA is the lead chelate, PbT^-**
- **At pH 8.00, $[OH^-] = 1.00 \times 10^{-6}$ mol/L**
- **The solubilization reaction is**

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

- **The degree of solubilization of lead is given by the ratio $[PbT^-]/[HT^{2-}]$**

The calculation of this ratio is shown on the following slide

- **$[PbT^-]/[HT^{2-}] = 20.7$ under the conditions given showing that essentially all the NTA is bound to lead as soluble PbT^-**

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

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

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

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

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

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

$$\mathrm{H^+ + OH^-} \rightleftarrows \mathrm{H_2O}$$

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

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

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

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

Reaction of NTA with Lead Carbonate

Lead carbonate, $PbCO_3$, is the predominant lead species in water under many conditions. The example shown in the text is for water containing 25 mg Na_3T in equilibrium with $PbCO_3$ at pH 7.00. The following apply (see equilibrium constant expressions in text):

- **Reaction:** $PbCO_3(s) + HT^{2-} \leftarrow\rightarrow PbT^- + HCO_3^-$

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

- **Assume a reasonable value of $[HCO_3^-] = 1.00 \times 10^{-3}$ mol/L**
- **Ratio of chelated to unchelated NTA:**

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

This ratio shows that under typical conditions NTA would dissolve lead from solid $PbCO_3$

CLICK HERE TO ACCESS THE COMPLETE Solutions

Reaction of NTA with $PbCO_3(s)$ in the presence of 1.00×10^{-3} mol/L Ca^{2+} at pH 7.00 and $[HCO_3^-] = 1.00 \times 10^{-3}$ mol/L

- **The reaction and its equilibrium constant are**

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

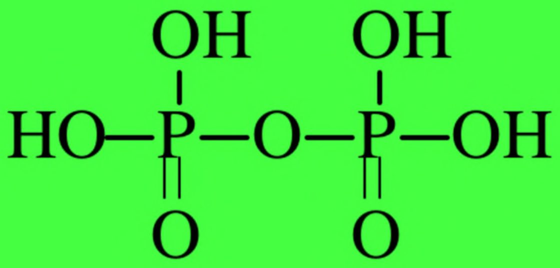
$$K'' = \frac{[Ca^{2+}][HCO_3^-][PbT^-]}{[CaT^-][H^+]} = 5.24$$

Putting the known concentrations into this expression and solving

- **$[PbT^-]/[HCO_3^-] = 0.524$**
- **About 1/3 of the NTA is bound with Pb^{2+} and 2/3 with Ca^{2+}**
- **Therefore, the presence of excess Ca^{2+} significantly inhibits NTA from dissolving lead from lead carbonate**

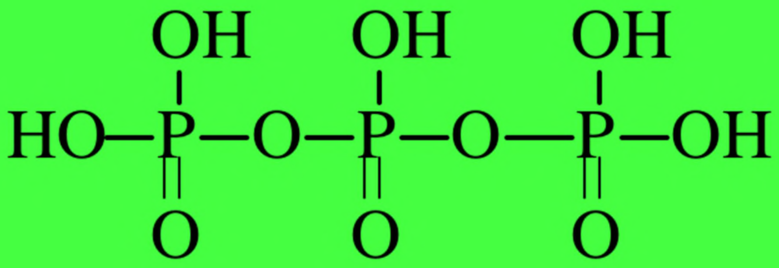
2.16 Polyphosphates and Phosphonates in Water

Figure 2.12. The first two members of the family of polyphosphoric acids which, in the partially ionized form chelate metals



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

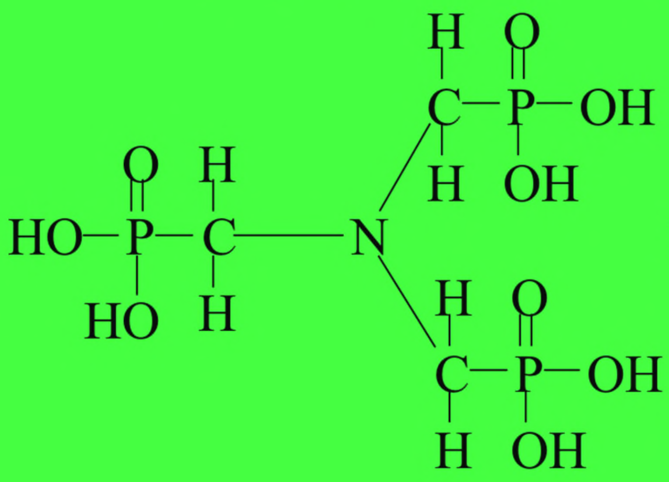
Pyrophosphoric (diphosphoric) acid



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

Triphosphoric acid

A phosphonate with chelating capabilities



NTMP

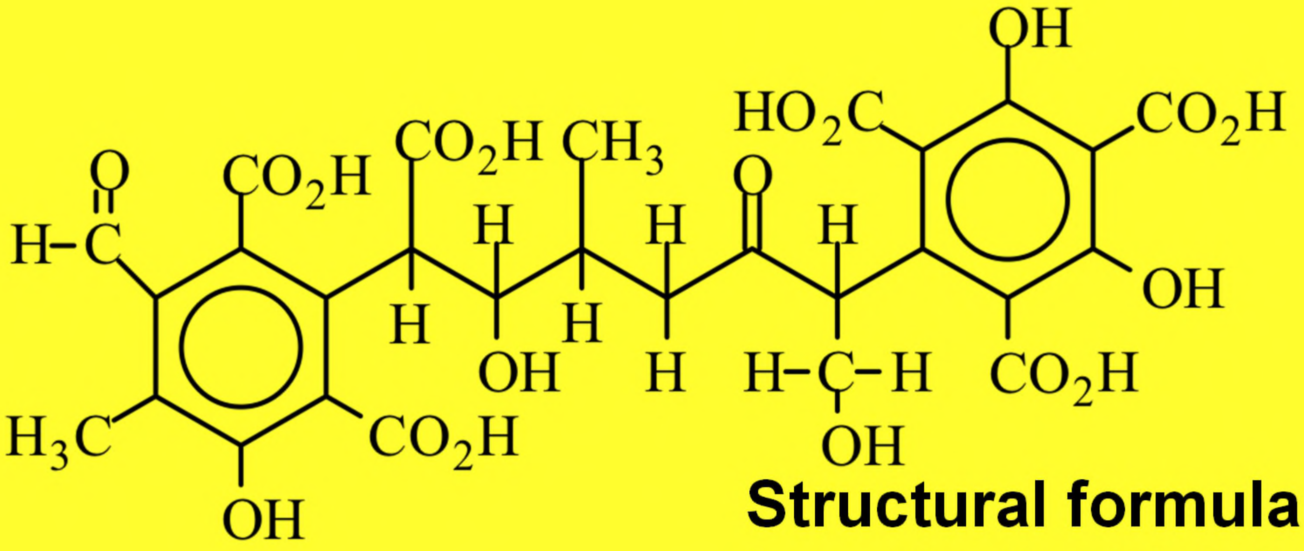
2.17 Complexation by Humic Substances

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

- **High-molecular mass polyelectrolytic macromolecules**

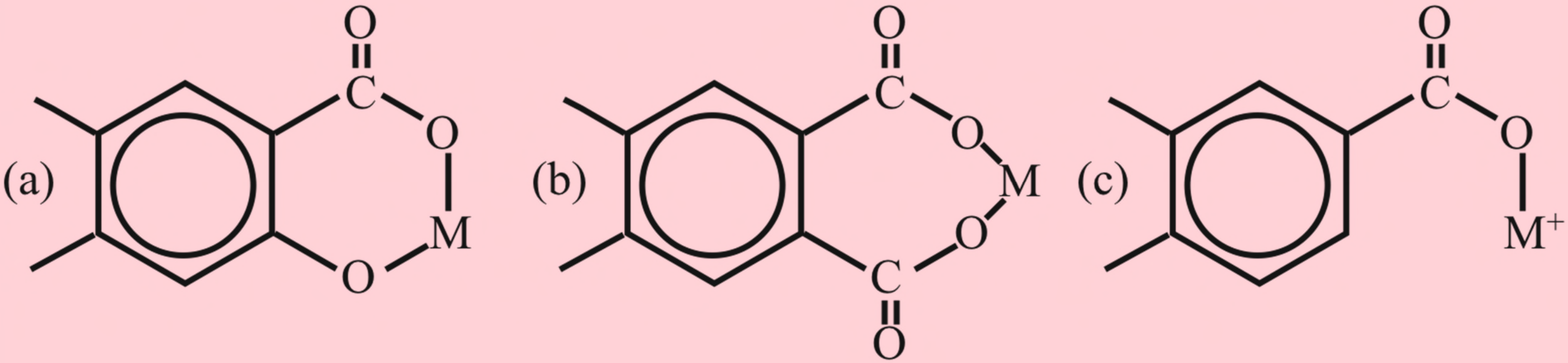
When a sediment or soil is treated with base solution

- **Humin material is humic substance not extracted**
- **Humic acid precipitates from acidified extract**
- **Fulvic acid remains in acidified solution**



Structural formula of a hypothetical fulvic acid molecule

Figure 2.13. Binding and chelation of a metal ion, M^{2+}, by humic substance



Humic substances are important in some natural waters

- **Chelate metals**
- **Cause problems with metals (iron) removal from water**
- **Water color, especially when bound to iron (gelbstoffe)**
- **Insoluble humin and humic acid remove metals from solution**
- **Precursors to trihalomethane ($CHCl_3$) production in water chlorination**

2.18 Complexation and Redox Processes

Complexation and chelation shift oxidation-reduction equilibria

- **Usually by stabilization of oxidized form of metal**
- **Dissolve protective oxide coatings**