Chapter 10

Chemistry of Natural Waters

1

Terminologies

Aquatic chemistry deals with chemical phenomena in water

- Mostly natural water (vs. water processed by humans)

Hydrology = study of water

Branches:

Limnology deals with characteristics (physical, chemical and biological) of freshwater

Oceanography deals with characteristics of the ocean

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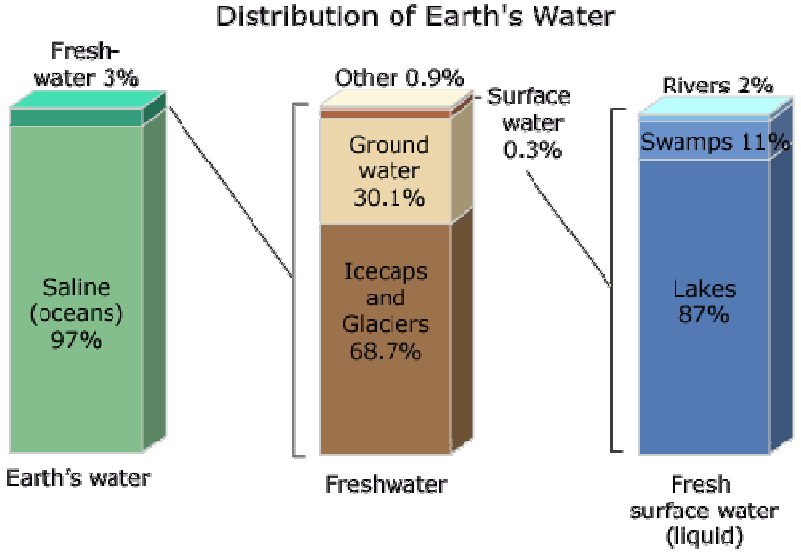

Image available at http://ga.water.usgs.gov/edu/graphics/earthwheredistribution.gif

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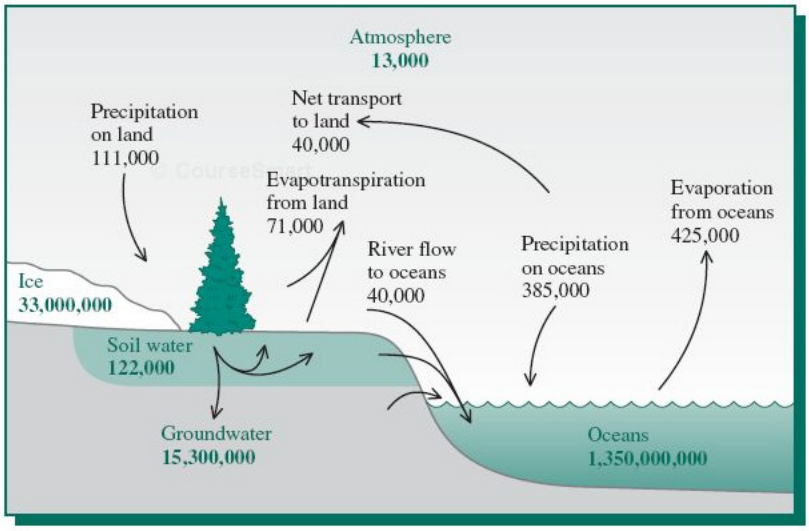
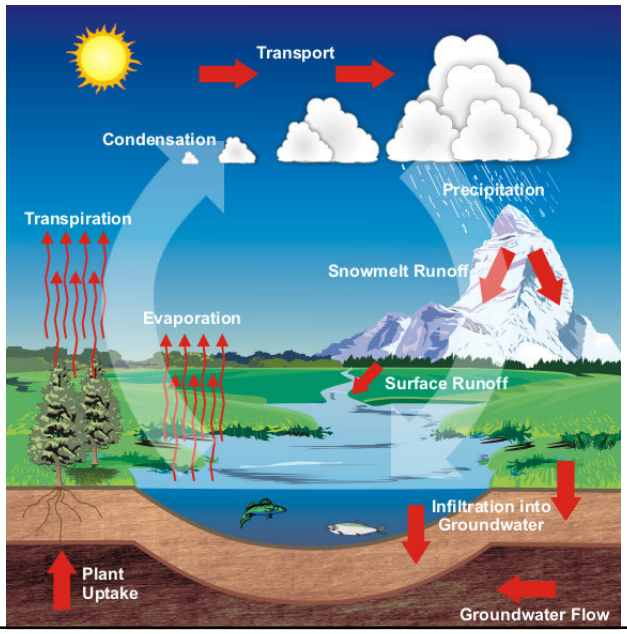


FIGURE 13- 1 Global pools and fluxes of water on Earth, showing the size of groundwater storage relative to other major water sources and fluxes. All pool volumes (green) are in cubic kilometers, and all fluxes (black) are in cubic kilometers per year. [Source: W. H. Schlesinger, Biogeochemistry An Analysis of Global Change, 2nd ed. (San Diego: Academic Press, 1997), Chapter 10.]

4

The Water (Hydrologic) Cycle

Image available at http://www.srh.noaa.gov/crp/weather/education/water_cycle.html



Key words:

- Evaporation
- Condensation
- Precipitation
- Infiltration
- Runoff
- Transpiration

5

The Hydrologic Cycle – Cont.

Source: Manahan, p. 56

Evaporation = involves vaporization of ocean water

Condensation = process of water changing from a vapor to a liquid

Clouds = water droplets suspended in air

Precipitation = water being released from clouds as rain, snow, sleet or hail

Evapotranspiration = evaporation of water from the ground and release of water from leaves of plants (transpiration)

Infiltration = seeping of rainwater/melted snow into the ground

6

Source: Manahan, p. 56

Runoff = surface flow of *water that does not infiltrate the ground*

- Drains into streams and rivers -> eventually empty into the ocean

Runoff happens when:

- Soil is *saturated with water* from too much precipitation, or
- There is too much *impervious surface* (Ex. parking lots)

7

Human Impact on the Water Cycle

- As the population increases, so will our need to withdraw more water from rivers, lakes and aquifers
  - Threatens local resources and future water supplies
- A larger population will not only use more water but will discharge more wastewater

Guo Liliang/ChinaFotoPress/Getty Images
The global water crisis affects the water supply all over the world, including China (right).
Image available at http://tlc.howstuffworks.com/home/gray-water.htm

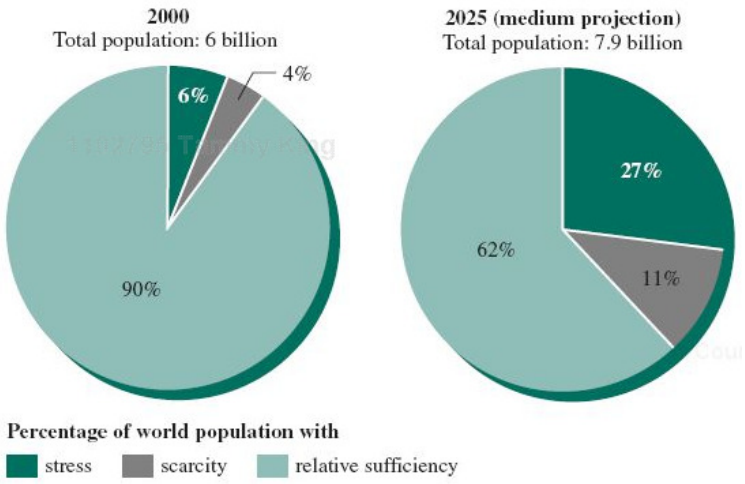
8

- Large cities, urban sprawl affect quality of streams and rivers
  - More impervious areas (e.g. roads, parking lots), less infiltration, more runoff into streams
  - Runoff can contain a lot of contaminants, such as oil and garbage.
  - This runoff often goes directly into streams
  - The replenishing of ground water aquifers occurs at a slower rate

Q. How do we protect our water resources?

9

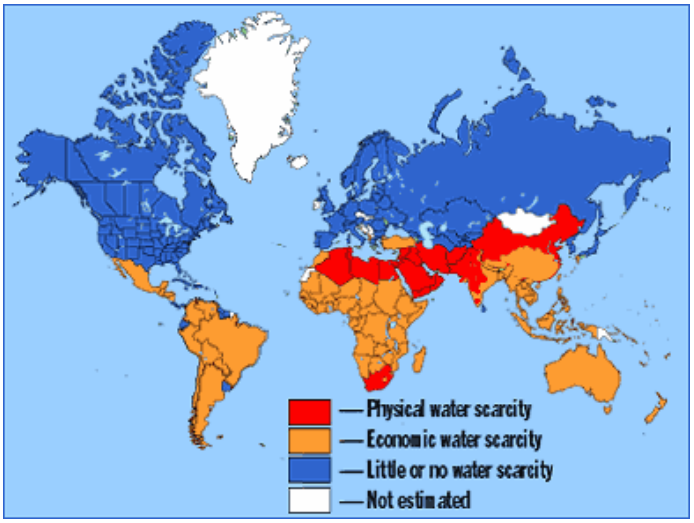
FIGURE 13- 2 **Global water supply in 2000 and projection for 2025.** [Source: R. Engelman et al., People in the Balance (Washington, DC: Popular Action International, 2000) as reproduced in Nature 422 (2003): 252.]



10

Bottomline: Projected increase in water scarcity and stress problems

Global water scarcity



Which areas of the world have water scarcity problem?

Image available at http://whyfiles.org/131fresh_water/2.html

11

Role of Chemistry

- Understanding chemical reactions in natural waters (Chapter 10)
  - Prevention or control of water pollution
- Purification of water for drinking purposes (Chapter 11)

12

Water Quality Parameters

Definition: **Water quality parameters** are properties of water that affect aquatic life

1. **Temperature (T)**
   - Low T slows biological processes
   - High T can be fatal; lowers dissolved oxygen (DO)

2. **Transparency to light** – affects:
   - Food for higher forms of life
   - Growth of *algae* (more transparent, better growth)

3. **Turbulence**
   - Affects mixing and transport of nutrients and waste

   Example: Planktons depend upon water current for their own mobility

13

Water Quality Parameters – Cont.

4. **Dissolved oxygen (DO)**
   - O_2 deficiency (very low DO) is fatal to fish, other aquatic animals

5. **Biochemical oxygen demand (BOD)**
   - BOD = the amount of O_2 used up during biological decomposition of organic matter (OM)

   High BOD + slow to replenish O_2 = unable to sustain life

6. **Carbon dioxide (CO_2)**
   - Needed by algae for photosynthesis *(& production of biomass)*

Too much ***decomposition*** ⟹ ↑**CO_2 levels** ⟹ Excessive algal growth, ↑***productivity***

14

Water Quality Parameters – Cont.

Productivity = ability of a body of water to produce living material

Productivity	Consequence
Low	Ideal for drinking/swimming
Relatively high	Supports fish
Excessive	Rapid algal growth; ↓ DO during decomp. of algae = Indicator of ***eutrophication***

15

Eutrophication is a process whereby lakes or slow-moving streams receive excess nutrients that stimulate excessive plant growth - http://toxics.usgs.gov/definitions/eutrophication.html

A Eutrophic lake has increased algal blooming due to high amounts of nutrients. Image available at http://salem.rutgers.edu/nre_homeowner/homeowner.html

16

Water Quality Parameters – Cont.

7. **Nutrient levels**

- Nutrients (nitrates, phosphates), carbon (from CO_2), and trace elements affect <u>productivity</u>
  - Excessive levels can lead to eutrophication

8. **Salinity**

- Determines the *kind of life forms* present
- Irrigation water may pick up harmful levels of <u>salt</u>

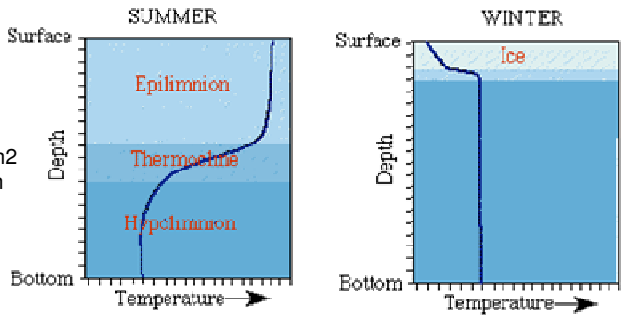
Harmful to freshwater organisms

17

Stratification of Lakes

Thermal stratification = separation of a body of water into layers differing in temperature (and properties)

Source of diagram: http://users.aber.ac.uk/ejh2/lake%20stratification.htm



Epilimnion = surface layer; heats up in the summer

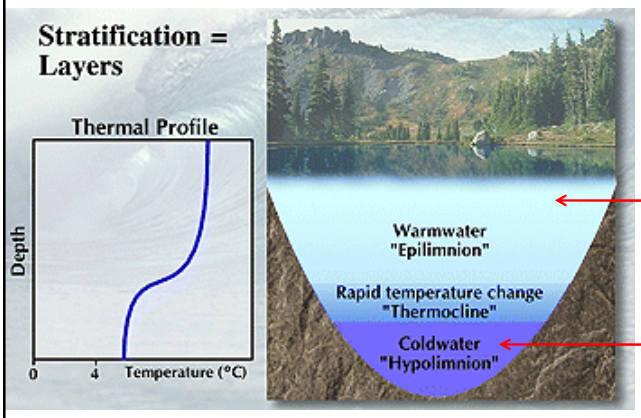
Hypolimnion = bottom layer

Thermocline = layer between the epilimnion and hypolimnion

18

Thermal Stratification: Summer

Image available at http://www.aquatic.uoguelph.ca/lakes/season/page1.htm



Supports growth of algae (more sunlight); **High DO**
Chemical species in **oxidized form** (Ex. CO_2, SO_4^{2-})

Low DO; Chemical species usually in **reduced form** (Ex. CH_4, H_2S)

Spring and Fall

- Thermal stratification usually disappears => entire body of water behaves as one hydrologic unit

19

Stratification of Lakes

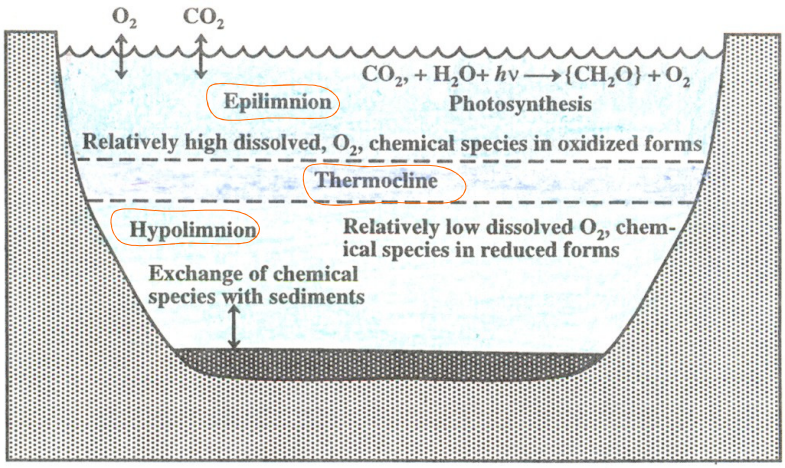
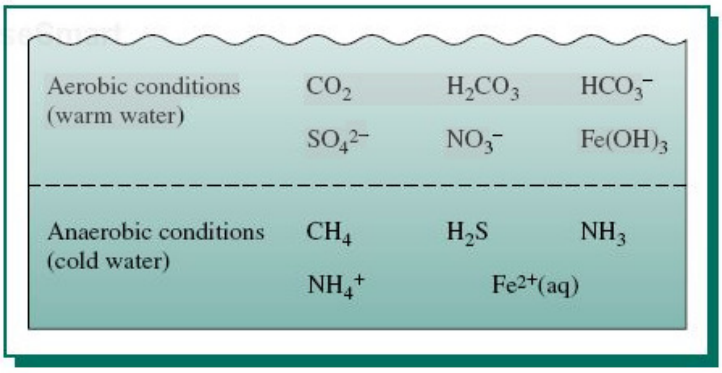


Figure 3.6. Stratification of a lake.

Source: Manahan, 2001.

20

FIGURE 13- 3 **The stratification of a lake in the summer,** showing the typical forms of the major elements it contains at different levels.



Oxidized form of species predominate

Reduced form predominate

21

Aquatic Chemistry

Note: **{CH_2O}** represents organic matter or **biomass**, such as carbohydrates (from simple sugars to polysaccharides like starch and cellulose)

Major aquatic chemical processes - Manahan, p. 64

Note: Double arrows ⇌ or ⟺ indicate ***reversible reactions***

Example: Gas exchange – formation of DO and dissolved carbon dioxide

$$O_{2\ (atm)} \Longleftrightarrow O_{2\ (aq)}$$
$$CO_{2\ (atm)} \Longleftrightarrow CO_{2\ (aq)}$$

22

Chemical Processes in Aquatic Systems

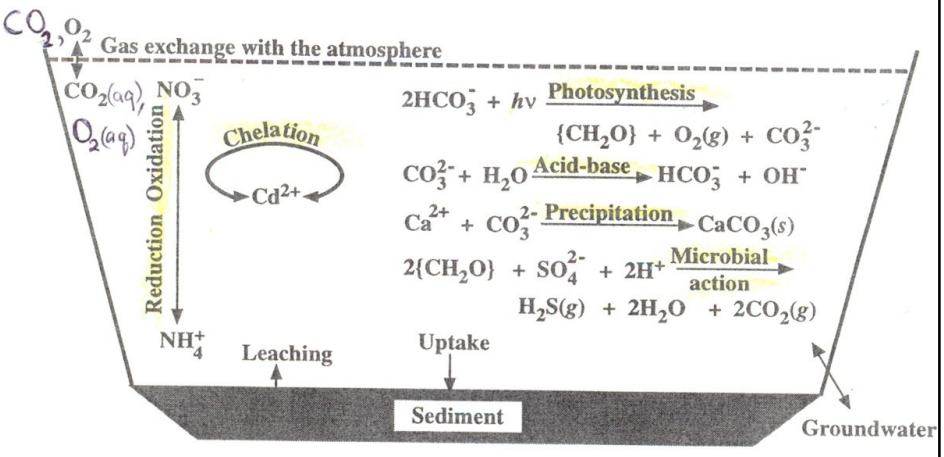


Figure 3.7. Major aquatic chemical processes.

Source: Manahan, 2001.

Chemical Processes in Aquatic Systems – Cont.

1. ***Gas exchange*** with the atmosphere
   - Supplies dissolved O_2 (DO) to support life and dissolved CO_2 (for photosynthesis)
   - Temperature-dependent (↓ solubility of gases as T ↑)

Dissolved oxygen, DO

Dissolution process: $O_{2\,(g)} \overset{K_H}{\Longleftrightarrow} O_{2\,(aq)}$

- Equilibrium constant for dissolution process is the ***Henry's law constant***, K_H

$K_H = [O_{2\,(aq)}]/P_{O2}$ = 1.3 x 10^{-3} mol/L atm at 25 ^{0}C

Gas exchange – Cont.

- *Note*: In dry air at sea level, the partial pressure, P_{O2}, of oxygen is 0.21 atm.
- ***Solubility of O_2*** is 8.7 mg/L H_2O --- Problem 13-1, p. 562

PROBLEM 13-1

Confirm by calculation the value of 8.7 mg/L for the solubility of oxygen in water at 25°C.

Question: Will there be more dissolved O_2 in the summer or in the winter?

25

Gas exchange (Cont.)

Dissolved CO_2: $CO_{2\,(g)} \Longleftrightarrow CO_{2\,(aq)}$

- To be discussed under acid-base chemistry (pp. 578 -)
- Controls pH and principal ion concentrations in freshwater systems

2. ***Photosynthesis*** by algae – uses C in the form of bicarbonate ion, HCO_3^-

$$HCO_{3\,(aq)}^- + h\nu \longrightarrow \{CH_2O\} + O_{2\,(g)} + CO_{3\,(aq)}^{2-}$$

Bicarbonate ion — Carbonate ion

26

Photosynthesis – Cont.

- Photosynthesis can raise water pH (= alkaline) - HOW?
  - Due to removal of dissolved CO_2 (forms HCO_3^-, which is used up in photosynthesis).
  - Since dissolved CO_2 forms acidic solution, its removal raises the pH of water.

27

Chemical Processes in Aquatic Systems – Cont.

3. ***Acid-base equilibria*** - involves loss/gain of H^+
   - Natural waters contain significant quantities of:
     - Dissolved CO_2 and the anions it produces
     - Cations Ca^{2+} and Mg^{2+}
   - The **carbonate-carbonic acid system** *dominates the acid-base chemistry* in natural water.
   - Carbonic acid in natural waters results from the dissolution of **CO_2 gas** in water
     - From the air
     - From decomposition of OM

$$\mathbf{CO_{2\,(g)} + H_2O \Longleftrightarrow H_2CO_{3\,(aq)}}$$

Carbonic acid

28

Acid-base equilibria (Cont.)

$$CO_{2\,(g)} + H_2O \overset{K_{eq} = K_H}{\Longleftrightarrow} H_2CO_{3\,(aq)}$$

Carbonic acid

- Reaction above shows that CO_2 gas in the air and the acid in water are in equilibrium with each other
- The relevant equilibrium constant for this reaction is the Henrys law constant, K_H, for CO_2
- $K_H = 3.2 \times 10^{-2}$; Small K means ***most of the CO_2 exists as dissolved CO_2*** rather than as carbonic acid, $H_2CO_{3\,(aq)}$

Acid-base equilibria involving **dissolved CO_2**

- First and second dissociations of carbonic acid, H_2CO_3, a ***diprotic*** acid :

$$H_2CO_3 \overset{K_{a1}}{\Longleftrightarrow} HCO_3^- + H^+$$

Carbonic acid — **Bicarbonate ion**

$$K_{a1} = \frac{[HCO_3^-]x[H^+]}{[H_2CO_3]}$$

$$K_{a1} = 4.5 \times 10^{-7}$$

- $K_{a1} >> K_{a2}$, meaning carbonate formation (from 2nd dissociation), is less likely to take place in natural waters

$$HCO_3^- \overset{K_{a2}}{\Longleftrightarrow} CO_3^{2-} + H^+$$

Bicarbonate — **Carbonate ion**

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

$$K_{a2} = 4.7 \times 10^{-11}$$

The CO_2-Carbonate System

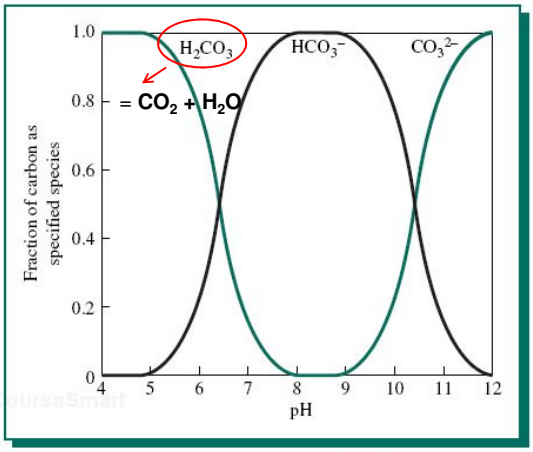


FIGURE 13- 6 **Species diagram for the aqueous carbon dioxide bicarbonate ion carbonate system.** [Source: S. E. Manahan, Environmental Chemistry, 6th ed. (Boca Raton, FL: Lewis Publishers, 2000), Figure 3.3, p. 54.]

- **CO_2** (aq) predominates in **acidic (low) pH < 6**
- **HCO_3^-**(aq) predominates in **neutral to slightly basic pH**
- **CO_3^{2-}**(aq) predominates in **basic (high) pH > 11**

31

The CO_2-Carbonate System

- The **pH** of pure water in equilibrium with the current level of atmospheric CO_2 is **5.6**.
- The sequestration of CO_2, as such, into oceans would result in an increase in the acidity of the surrounding waters --- Why?
  - Due to formation of carbonic acid, H_2CO_3, which gives rise to further dissociation
- The acidity (decrease in pH) could affect biological life.

Indeed, the increase in the atmospheric level of CO_2 that has already occurred has resulted to a **drop of about 0.1 pH unit in surface ocean water** worldwide.

32

Q. Where do most of the CO_3^{2-} in natural waters come from?

- Not from $CO_{2\ (aq)}$
- ***Limestone rocks***, which are mostly calcium carbonate, **$CaCO_3$**

$$CaCO_{3\ (s)} \Longleftrightarrow Ca^{2+} + CO_3^{2-}$$

Other species that contribute to acidity:

- **Metal ions** = naturally-occurring or from waste
  - Hydrated ***multivalent metal ions*** are acidic

Ex. Fe^{3+} ; Al^{3+} in water exist as $Fe(H_2O)_6^{3+}$; $Al(H_2O)_6^{3+}$

33

Other species that contribute to acidity:

- Dissociation of hydrated ions:

$$Fe(H_2O)_6^{3+} \Longleftrightarrow Fe(H_2O)_5(OH)^{2+} + H^+$$

Acidic

- **Mineral acids** - e.g. from acid mine [such as HCl, H_2SO_4]

34

Water in Equilibrium with Solid Calcium Carbonate

Natural waters exposed to limestone are called **calcareous** [kal-kair-ee-uhs] **waters**. The dissolved CO_3^{2-} ion acts as a base, producing its bicarbonate and hydroxide ions in the water. These reactions that occur in the natural three-phase (air, water, rock) system are summarized below:

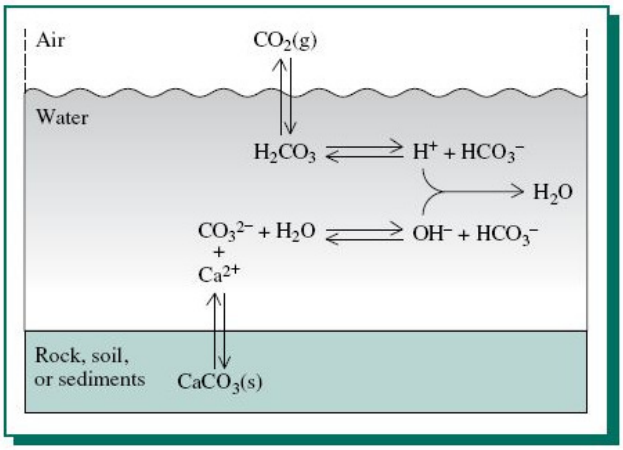


FIGURE 13- 7 Reactions among the three phases (air, water, rocks) of the carbon dioxide carbonate system.

35

The **reactions of the carbon dioxide - carbonate system** are summarized for convenience in Table 13- 3.

TABLE 13-3 Reactions in the CO_2–Bicarbonate–Carbonate System

Reaction Number	Reaction	Equilibrium Constant	K Value at 25°C
1	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	K_{a1} (H_2CO_3)	4.5×10^{-7}
2	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	K_{a2} (H_2CO_3)	4.7×10^{-11}
3	$CO_2(g) + H_2O(aq) \rightleftharpoons H_2CO_3(aq)$	K_H	3.4×10^{-2}
4	$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$	K_{sp}	4.6×10^{-9}
5	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	K_b (CO_3^{2-})	2.1×10^{-4}
6	$CaCO_3(s) + H_2O(aq) \rightleftharpoons Ca^{2+} + HCO_3^- + OH^-$		
7	$H^+ + OH^- \rightleftharpoons H_2O(aq)$	$1/K_w$	1.0×10^{14}
8	$CaCO_3(s) + CO_2(g) + H_2O(aq) \rightleftharpoons Ca^{2+} + 2\,HCO_3^-$		

36

Acid-base equilibria (Cont.)

Alkalinity of natural water and wastewater

- Capacity to accept (*neutralize*) H^+ ions
  - Can be determined by titration with sulfuric acid
  - Usually:

High alkalinity = high pH + high levels of dissolved solids

Undesirable in municipal water

  - Used in *calculating the amount of chemical* to be added during treatment of water

37

Alkalinity – Cont.

Species generally responsible for **alkalinity, [Alk]**

Species	Reaction (Neutralization of H^+):
HCO_3^-, bicarbonate	$HCO_3^- + H^+ \leftrightarrow CO_{2\,(aq)} + H_2O$
CO_3^{2-}, carbonate	$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$
OH^-, hydroxide	$OH^- + H^+ \leftrightarrow H_2O$

38

Basicity versus ***Alkalinity***

- High basicity = high pH
- High alkalinity = excellent capacity to neutralize H^+

Example: Compare 1 L each of 1.00 x 10^{-3} M NaOH and 0.100 M $NaHCO_3$.

Solution	pH	Alkalinity
1.00 x 10^{-3} M NaOH	11	1.00 x 10^{-3} M H^+
0.100 M $NaHCO_3$	8.34	0.100 M H^+

- The NaOH solution is more basic but has a lower alkalinity than the $NaHCO_3$ solution

  Requires less acid (H^+) to neutralize

39

Other importance of alkalinity:

- Biologists use alkalinity as a ***measure of water fertility***. WHY?

Assuming no input of additional $CO_2(aq)$:

- At ***higher alkalinity***, ***more biomass*** is produced from photosynthesis

  = higher levels of HCO_3^-, CO_3^{2-}

Photosynthesis: $HCO_{3\,(aq)}^- + h\nu \longrightarrow \{CH_2O\} + O_{2\,(g)} + CO_{3\,(aq)}^{2-}$

40

Chemical Processes in Aquatic Systems – Cont.

4. ***Precipitation*** = removes soluble ions from the water

$$Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow CaCO_{3\,(s)}$$

= Soluble ions naturally present in bodies of water

- Precipitated compounds either <u>settle</u> to the bottom or <u>redissolve</u>
- The reaction above is related to acid-base chemistry of natural water (as affected by the CO_2-carbonate system) --- *discussed earlier*

41

Chemical Processes in Aquatic Systems – Cont.

5. ***Microbial action***

Example : Bacterial degradation of biomass:

$$\{CH_2O\}_{(s)} + O_{2\,(g)} \xrightarrow{\text{Bacteria}} CO_{2\,(g)} + H_2O_{(l)}$$

- Favored under oxidizing conditions (plenty of O_2)

Or

$$2\,\{CH_2O\}_{(s)} + SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} \xrightarrow{\text{Bacteria}} H_2S_{(g)} + 2\,H_2O_{(l)} + 2CO_{2\,(g)}$$

- Biomass is oxidized to CO_2; Sulfate (SO_4^{2-}) is reduced to hydrogen sulfide gas, H_2S
- Formation of H_2S can cause pollution problems

42

Chemical Processes in Aquatic Systems – Cont.

6. ***Reduction-oxidation* (REDOX) *reactions***

Recall from Chem Principles : LEO the lion says GER

Loss of electrons (or increase in the number of O) = **Oxidation**

Gain of electrons (or decrease in the number of O) = **Reduction**

Oxidizing agent = gains electrons; becomes reduced

Reducing agent loses electrons; becomes oxidized

43

6. **REDOX *reactions*** – *Cont.*

Example: Oxidation of soluble iron

$$Fe^{2+} \Longleftrightarrow Fe^{3+} + e^-$$

Soluble iron

Insoluble iron (precipitates as $Fe(OH)_3$ or Fe_2S_3

- ***Dissolved oxygen*** = most important oxidizing agent in natural waters

44

REDOX *reactions* (Cont.)

Oxidation States of Various Forms of Nitrogen

TABLE 13-2 Common Oxidation Numbers for Nitrogen

	Increasing Levels of Nitrogen Oxidation →						
Oxidation Number of N	−3	0	+1	+2	+3	+4	+5
Aqueous solution and salts	NH_4^+ NH_3				NO_2^-		NO_3^-
Gas phase	NH_3	N_2	N_2O	NO		NO_2	

Reduced form **Oxidized form** →

Interconversions of forms of N

Reduction: NO_3^- ⟺ NH_4^+

Nitrate ion Ammonium ion

Oxidation: NH_4^+ ⟺ NO_3^- (or NO_2^-)

45

REDOX *reactions* (Cont.)

Reduction of nitrate by microbial action *(reduction half-reaction only):*

$$NO_3^- + 10H^+ + 8e^- \Longleftrightarrow NH_4^+ + 3H_2O$$

- pH dependent (favored in acidic medium)
- NO_3^- ions occur in aerobic environments (e.g. surface of lakes)

Oxidation of ammonia or ammonium ion by microbial action:

$$NH_4^+ + 2O_2 \xLeftrightarrow{\text{Bacteria}} NO_3^- + 2H^+ + H_2O$$

46

REDOX *reactions* (Cont.)

Oxidation States of Various Forms of Sulfur

TABLE 13-1 Common Oxidation Numbers for Sulfur

	Increasing Levels of Sulfur Oxidation →				
Oxidation Number of S	−2	−1	0	+4	+6
Aqueous solution and salts	H_2S			H_2SO_3	H_2SO_4
	HS^-			HSO_3^-	HSO_4^-
	S^{2-}	S_2^{2-}		SO_3^{2-}	SO_4^{2-}
Gas phase	H_2S			SO_2	SO_3
Molecular solids			S_8		

Reduced form **Oxidized form**

Example of redox reaction involving sulfur:

- Conversion of OM to CO_2 by anaerobic bacteria

$$3\{CH_2O\} + 2SO_4^{2-} + 4H^+ \Longleftrightarrow 3CO_2 + 2S + 5H_2O$$

47

Significance of redox reactions in natural waters

1. Oxidation of biomass by O_2 ***lowers DO***, which can be fatal to fish
2. The rate of oxidation of sewage is crucial to the operation of waste treatment plants
   - Reduction of insoluble Fe^{3+} to soluble Fe^{2+} in a reservoir makes the removal of iron more difficult
   - Oxidation of NH_4^+ to NO_3^-, a form more absorbable by algae in water, can result to eutrophication

48

Aerial view of Lake 227 in 1994. Note the bright green color caused by algae stimulated by the experimental addition of phosphorus for the 26th consecutive year. Lake 305 in the background is unfertilized. (photo by Karen Scott)

Image available at http://www.umanitoba.ca/institutes/fisheries/eutro.html

49

Chemical Processes in Aquatic Systems – Cont.

7. ***Complexation reactions***

or ***chelation*** = formation of soluble/insoluble metal-*ligand* bond

Can be organic (like humic acid)
or inorganic (like CN^-)

Example: Complexation between CN^- ion and soluble iron (II)

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

Hydrated Fe^{2+} (**metal ion**)	Cyanide (**ligand**)	**Metal-ligand complex**	Displaced water

- Common metal ions (natural waters): Ca^{2+}, Mg^{2+}, $Fe^{2+}/Fe^{3+} \equiv \mathbf{M^{n+}}$
- Metal ions exist as ***hydrated ions***, $\mathbf{M(H_2O)_x^{n+}}$, or complexed to other species

Example: $\mathbf{Fe^{3+}}$ exists in water as $\mathbf{Fe(H_2O)_6^{3+}}$

50

Complexation reactions – Cont.

- Highly-charged hydrated metal ions are *usually acidic*

Example: $Fe(H_2O)_6^{3+} \Longleftrightarrow Fe(H_2O)_5OH^{2+} + H^+$

(proton-donor = acid); Ka <<< 1, weak acid

Implication: ***Water rich in Fe^{3+}*** (also Al^{3+}, Cr^{3+}) tend to be slightly acidic

51

Importance of Complexation Reactions

1. ***Affects solubility of metals*** – i.e. Complexation may result in:

   (a) A metal becoming solubilized from an insoluble compound, or

   (b) Formation of insoluble complex, thus removing metal ions from the water

Example: **Removal of Ca^{2+}** by precipitation with orthophosphate

$$Ca^{2+} + 3\ PO_4^{3-} + OH^- \Longleftrightarrow Ca_5OH(PO_4)_{3\ (s)}$$

Dissolved calcium

Insoluble calcium complex

52

Importance of Complexation Reactions (Cont.):

2. Complexation can influence the **transport** properties of metals = related to solubility

3. Complexation can influence the **biological effects** of metal ions

Not covered in this course

The next slides show the nature and concentration of *common ions in natural waters* versus those in *sea water*

53

The **abundant ions in fresh water** and maximum concentration of ions recommended for drinking water in the U.S. and Canada

TABLE 13-5 River Water Concentrations and Drinking Water Standards for Ions

Ion	River Water Molar Concentration: Average for World	River Water Molar Concentration: Average for U.S.	Drinking Water Concentration in ppm: Average U.S.	Drinking Water Concentration in ppm: Maximum Recommended Concentration: U.S.	Drinking Water Concentration in ppm: Maximum Recommended Concentration: Canada
*HCO_3^-	9.2×10^{-4}	9.6×10^{-4}	60		
Ca^{2+}	3.8×10^{-4}	3.8×10^{-4}	15		
Mg^{2+}	1.6×10^{-4}	3.4×10^{-4}	8		
Na^+	3.0×10^{-4}	2.7×10^{-4}	6		200
Cl^-	2.3×10^{-4}	2.2×10^{-4}	8	250	250
SO_4^{2-}	1.1×10^{-4}	1.2×10^{-4}	12	250	500
K^+	5.4×10^{-5}	5.9×10^{-5}	2		
F^-	—	5.3×10^{-6}	0.1	0.8–2.4	1.5
NO_3^-	1.4×10^{-5}	—			
Fe^{3+}	7.3×10^{-6}	—			

*** Note: The value for bicarbonate is actually the total alkalinity.** Sources: World data from R. A. Larson and E. J. Weber, Reaction Mechanisms in Environmental Organic Chemistry (Boca Raton, FL: Lewis Publishers).

54

Ions in sea water

Species	mg/kg or ppm	Species	mg/kg or ppm
Cl^-	19,350	HCO_3^-	142
Na^+	10,760	Br^-	67
SO_4^{2-}	2,710	BO_4^{3-}	4.5
Mg^{2+}	1,290	F^-	1.3
Ca^{2+}	411	H_4SiO_4	0.5-10
K^+	399	H^+	$10^{-8.35}$ M

http://www.science.uwaterloo.ca/~cchieh/cact/applychem/waternatural.html

55

Other Important Ions in Aquatic Systems

1. **Calcium and Magnesium Ions, Ca^{2+} & Mg^{2+}**

Importance:

- High levels cause water "hardness," which is measured in terms of hardness index

Definition:

Hardness index is a measure of the total concentration of Ca^{2+} and Mg^{2+} in water, or

Hardness = $[Ca^{2+}] + [Mg^{2+}]$

Experimental determination:

- Complexometric **titration** with a chelating agent, **EDTA** (a hexadentate ligand)

56

Major sources:

- Dissolution of limestone (mostly $CaCO_3$) or $CaSO_4$ minerals in natural water

The photographs below show crystals of typical **calcite**, the major mineral in limestones, marbles, and sea shells.

- $CaCO_3$ is the ingredient for both calcite and **aragonite**. These minerals differ in crystal structures and appearance.
- $CaCO_3$ minerals dissolve in water, with a solubility product as shown below.

$$CaCO_3 \Longleftrightarrow Ca^{2+} + CO_3^{2-} \qquad Ksp = 5 \times 10^{-9}$$

Typical calcite crystals

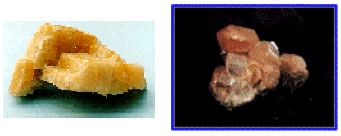


Image available at http://www.science.uwaterloo.ca/~cchieh/cact/applychem/waternatural.html

57

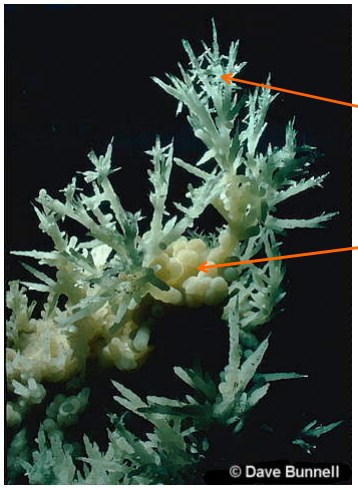


Image available at http://www.science.uwaterloo.ca/~cchieh/cact/applychem/waternatural.html

58

- **Mg^{2+} ions** come from the dissolution of **dolomitic limestone**, $CaMg(CO_3)_2$

Effects of hard water:

- Ca^{2+} and Mg^{2+} ions form insoluble salts with anions in soap, forming a ***scum*** in wash water
- Ca^{2+} and Mg^{2+} ions cause ***mineral buildup*** in sinks, tubs
  - Water is "**hard**" if its **hardness index > 150 mg/L**
  - **Calcareous waters** are water exposed to limestone. They are considered "hard" water

59

Other Important Ions in Aquatic Systems – Cont.

2. **Aluminum, Al^{3+}**
   - Usually in small amounts, ~ 10^{-6} M. WHY?
     - Solubility of Al in rocks and soil is very small in the typical pH range of natural waters (pH 6-9)

Major Sources:

- Al^{3+} comes from the dissolution of Al-containing soil and rocks

  e.g. due to acid rain
  - Solubility increases with increasing acidity of water

Recall that in acidic lakes where high levels of Al^{3+} ions are present, aluminum hydroxide, **$Al(OH)_3$** precipitates as a **gel** upon contact with the less acidic gills of fish

Suffocates and kills fish

60

References (aside from the ones cited with the slides)

1. Manahan, Stanley E. "Environmental Chemistry," (7th ed.) Boca Raton: Lewis, 1999.

2. C. Baird and M. Cann, *Environmental Chemistry*, Freeman and Co.: New York, 2005 (3rd ed.)

61