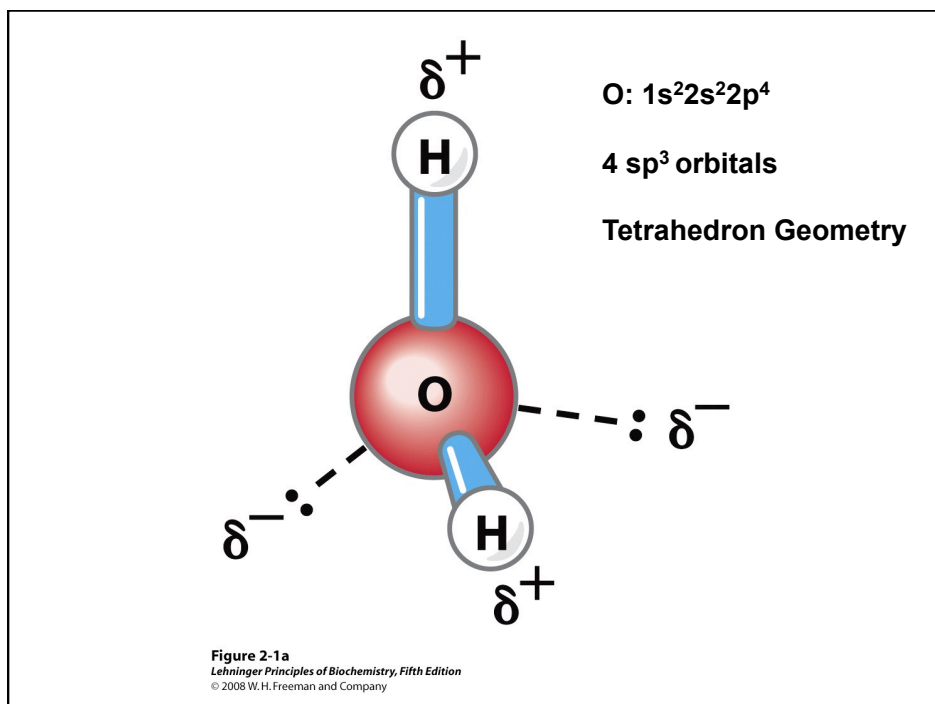# Water

- **Introduction**
- **Unusual Properties of Water**
- **Hydrogen Bond**
  HB in water
  HB in other molecules
- **Interaction between water and charged molecules**
- **Interaction between water and polar molecules**
- **Interaction between water and non-polar molecules**
- **Structure and function of biomolecules depended on weak interaction**
- **Solute's effect on colligative properties of aqueous solution**
  colligative properties
  hypertonic solution, isotonic solution, hypotonic solution
- **Ionization of water**

Figure 2-1a
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Properties of Alkanes

Alkanes show regular increases in both boiling point and melting point as molecular weight increases

- Due to the presence of weak dispersion forces between molecules
  - Dispersion forces increase as molecular size increases
  - A sufficient amount of energy is needed to overcome the dispersion forces and melt a solid or boil a liquid
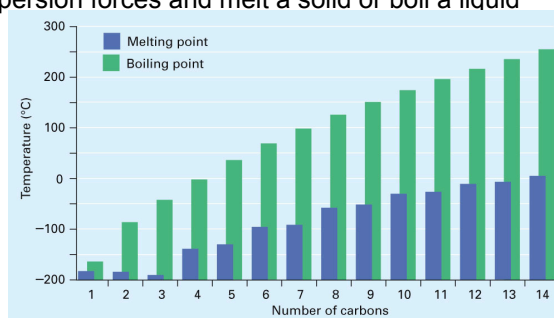
TABLE 2–1	Melting Point, Boiling Point, and Heat of Vaporization of Some Common Solvents		
	Melting point (°C)	Boiling point (°C)	Heat of vaporization (J/g)*
Water	0	100	2,260
Methanol (CH_3OH)	−98	65	1,100
Ethanol (CH_3CH_2OH)	−117	78	854
Propanol ($CH_3CH_2CH_2OH$)	−127	97	687
Butanol ($CH_3(CH_2)_2CH_2OH$)	−90	117	590
Acetone (CH_3COCH_3)	−95	56	523
Hexane ($CH_3(CH_2)_4CH_3$)	−98	69	423
Benzene (C_6H_6)	6	80	394
Butane ($CH_3(CH_2)_2CH_3$)	−135	−0.5	381
Chloroform ($CHCl_3$)	−63	61	247

*The heat energy required to convert 1.0 g of a liquid at its boiling point and at atmospheric pressure into its gaseous state at the same temperature. It is a direct measure of the energy required to overcome attractive forces between molecules in the liquid phase.

Table 2-1
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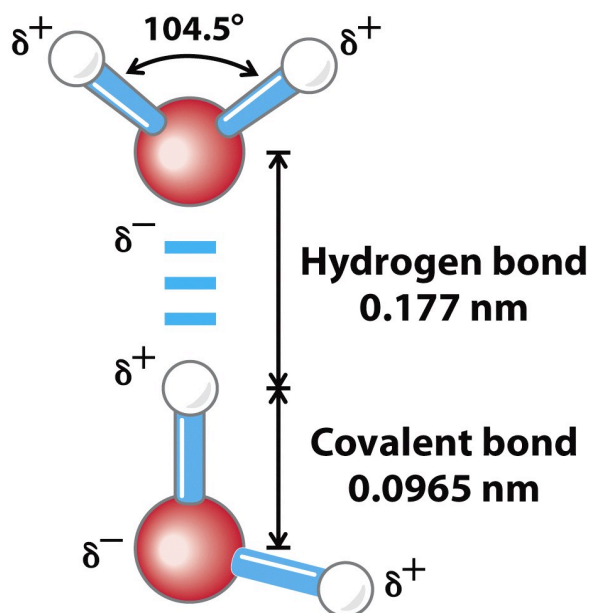© 2008 W. H. Freeman and Company

Figure 2-1b
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Figure 2-2
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Atom Dependent
Directional
Dynamic
Number Limited

Strong hydrogen bond

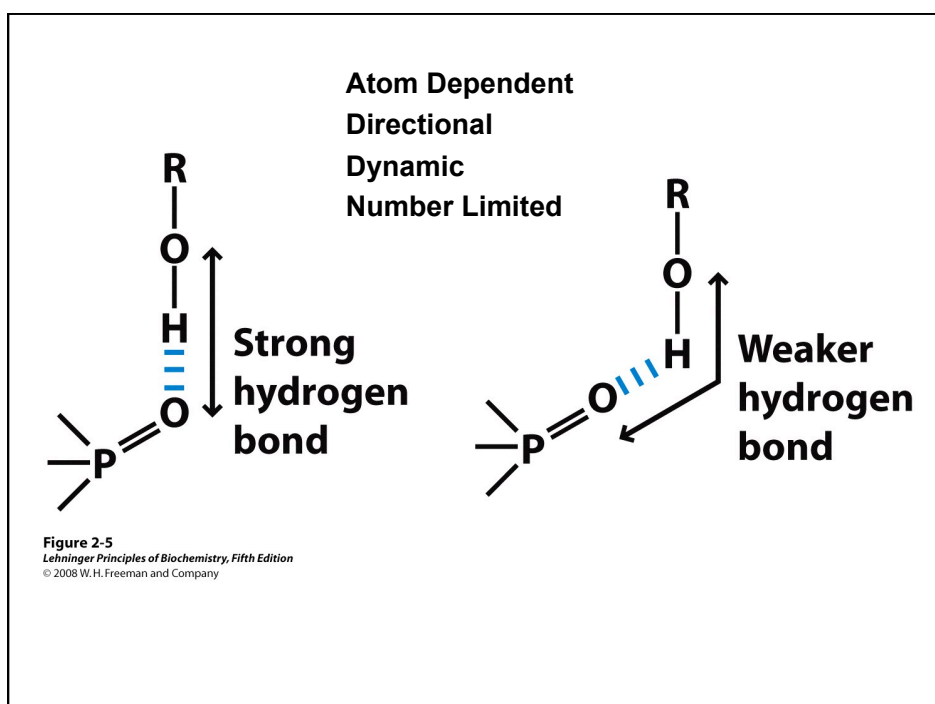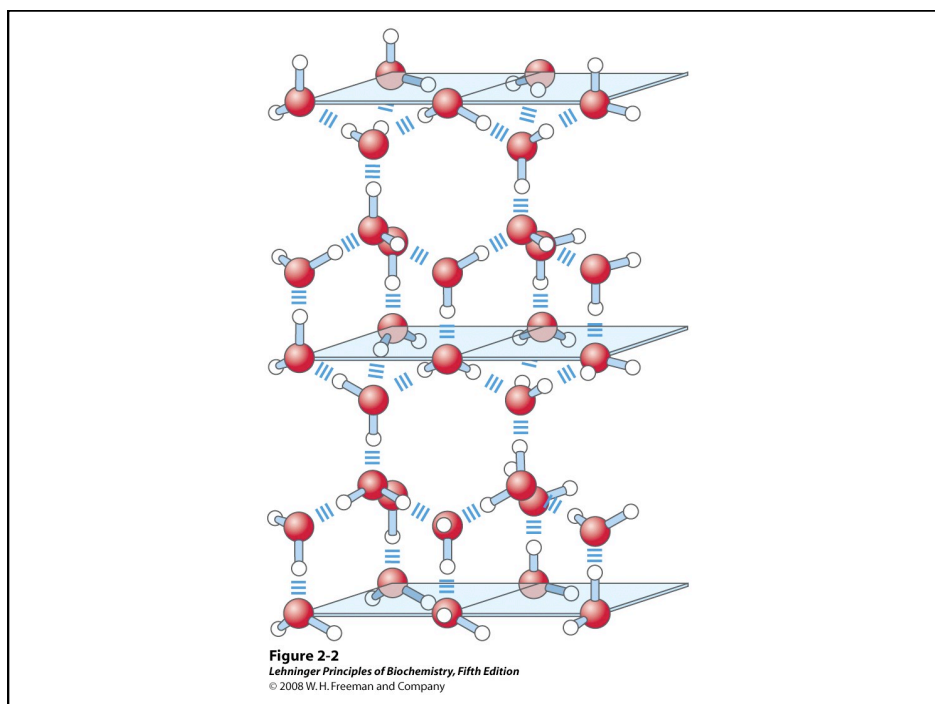**Weaker hydrogen bond**

Figure 2-5
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Periodic Table of Elements: Electronegativity

Period	Group																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.1																	He 0
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne 0
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.9	P 2.19	S 2.58	Cl 3.16	Ar 0
4	K 0.82	Ca 1	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.9	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 0
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.2	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	La 1.1	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.2	Pt 2.28	Au 2.54	Hg 2	Tl 2.04	Pb 2.33	Bi 2.02	Po 2	At 2.2	Rn 0
7	Fr 0.7	Ra 0.89	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						

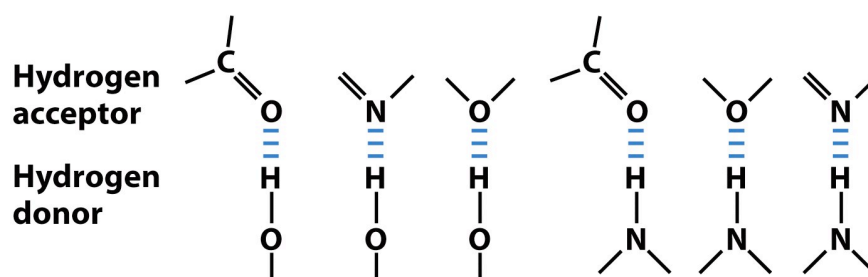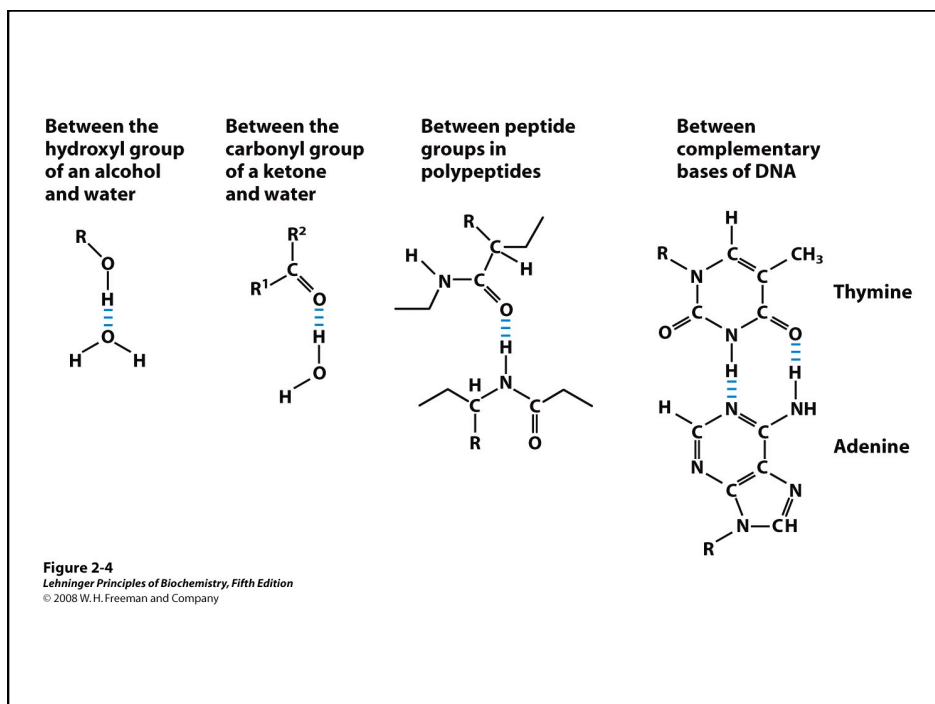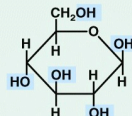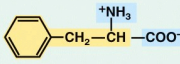| Lanthanides	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
Actinides	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr
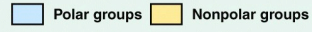
Figure 2-3
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Between the hydroxyl group of an alcohol and water

Between the carbonyl group of a ketone and water

Between peptide groups in polypeptides

Between complementary bases of DNA

Thymine

Adenine

Figure 2-4
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TABLE 2–2	Some Examples of Polar, Nonpolar, and Amphipathic Biomolecules (Shown as Ionic Forms at pH 7)

Polar — Glucose, Glycine, Aspartate, Lactate, Glycerol

Nonpolar — Typical wax

Amphipatic — Phenylalanine, Phosphatidylcholine

Polar groups / Nonpolar groups

Table 2-2
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TABLE 2–3	Solubilities of Some Gases in Water		
Gas	**Structure***	**Polarity**	**Solubility in water (g/L)†**
Nitrogen	$N\equiv N$	**Nonpolar**	**0.018 (40 °C)**
Oxygen	$O=O$	**Nonpolar**	**0.035 (50 °C)**
Carbon dioxide	$\delta^- \quad \delta^-$ $O=C=O$	**Nonpolar**	**0.97 (45 °C)**
Ammonia	$H \underset{N}{\diagdown} \overset{H}{} H \quad \downarrow \delta^-$	**Polar**	**900 (10 °C)**
Hydrogen sulfide	$H \underset{S}{\diagdown} H \quad \downarrow \delta^-$	**Polar**	**1,860 (40 °C)**

*The arrows represent electric dipoles; there is a partial negative charge (δ^-) at the head of the arrow, a partial positive charge (δ^+; not shown here) at the tail.

†Note that polar molecules dissolve far better even at low temperatures than do nonpolar molecules at relatively high temperatures.

Table 2-3
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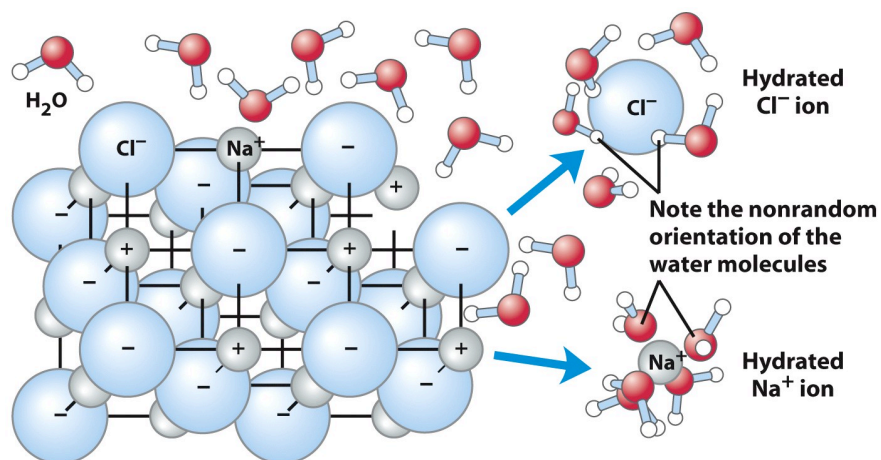
Figure 2-6
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Hydrophilic "head group"

Hydrophobic alkyl group

"Flickering clusters" of H_2O molecules in bulk phase

Highly ordered H_2O molecules form "cages" around the hydrophobic alkyl chains

Figure 2-7a
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Dispersion of lipids in H_2O

Each lipid molecule forces surrounding H_2O molecules to become highly ordered.

Figure 2-7b part 1
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Clusters of lipid molecules

Only lipid portions at the edge of the cluster force the ordering of water. Fewer H_2O molecules are ordered, and entropy is increased.

Figure 2-7b part 2
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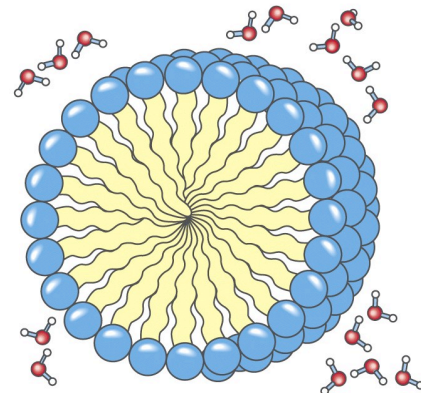
Micelles

All hydrophobic groups are sequestered from water; ordered shell of H_2O molecules is minimized, and entropy is further increased.

Figure 2-7b part 3
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Figure 2-8
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© 2008 W. H. Freeman and Company
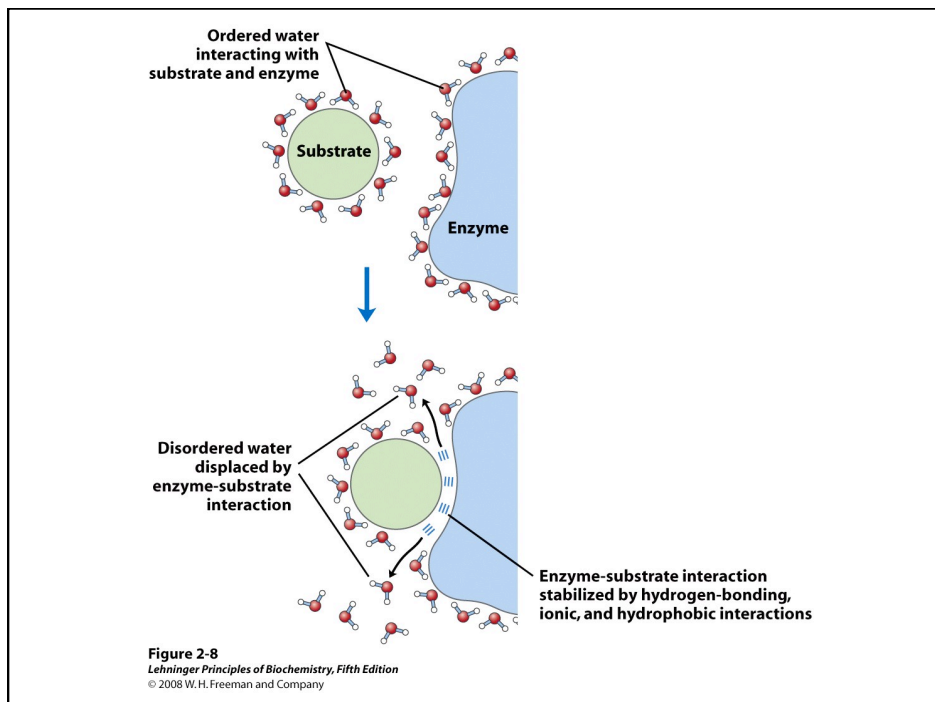
TABLE 2–4	van der Waals Radii and Covalent (Single-Bond) Radii of Some Elements	
Element	van der Waals radius (nm)	Covalent radius for single bond (nm)
H	0.11	0.030
O	0.15	0.066
N	0.15	0.070
C	0.17	0.077
S	0.18	0.104
P	0.19	0.110
I	0.21	0.133

Sources: For van der Waals radii, Chauvin, R. (1992) Explicit periodic trend of van der Waals radii. *J. Phys. Chem.* 96, 9194–9197. For covalent radii, Pauling, L. (1960) *Nature of the Chemical Bond,* 3rd edn, Cornell University Press, Ithaca, NY.

Note: van der Waals radii describe the space-filling dimensions of atoms. When two atoms are joined covalently, the atomic radii at the point of bonding are less than the van der Waals radii, because the joined atoms are pulled together by the shared electron pair. The distance between nuclei in a van der Waals interaction or a covalent bond is about equal to the sum of the van der Waals or covalent radii, respectively, for the two atoms. Thus the length of a carbon-carbon single bond is about 0.077 nm + 0.077 nm = 0.154 nm.

Table 2-4
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TABLE 2–5 | **Four Types of Noncovalent ("Weak") Interactions among Biomolecules in Aqueous Solvent**

Table 2-5
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COLLIGATIVE PROPERTIES

## Melting Point

Boiling Point

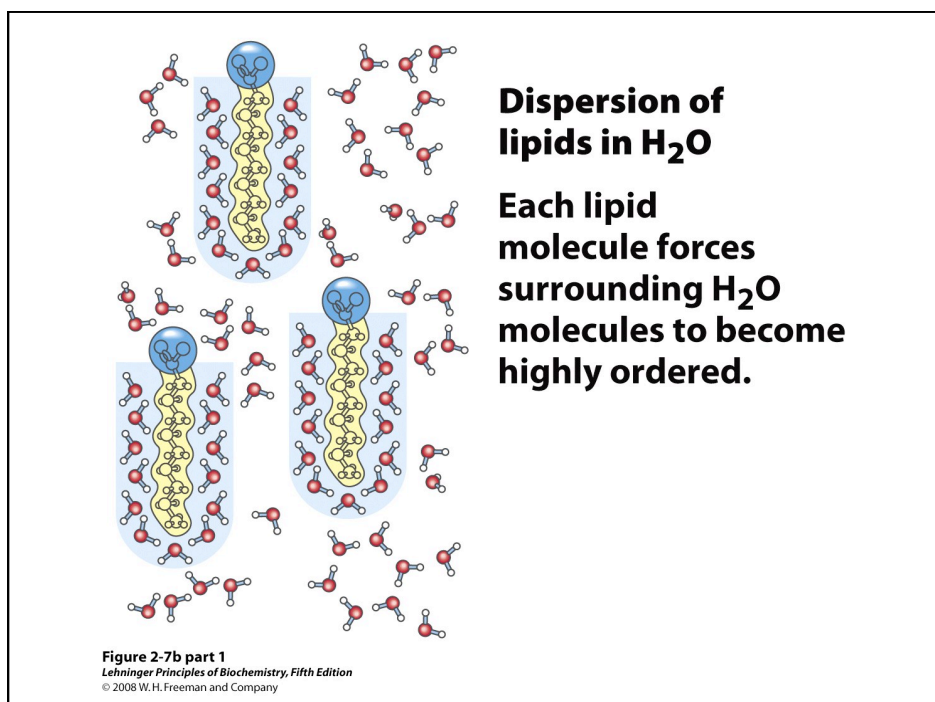## Vapor Pressure

Osmotic Pressure

Figure 2-11
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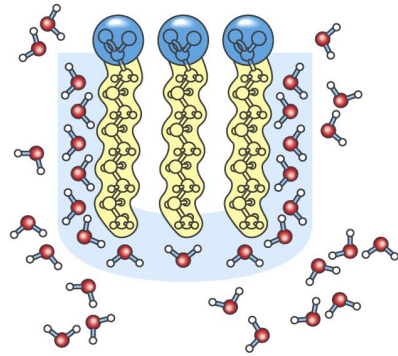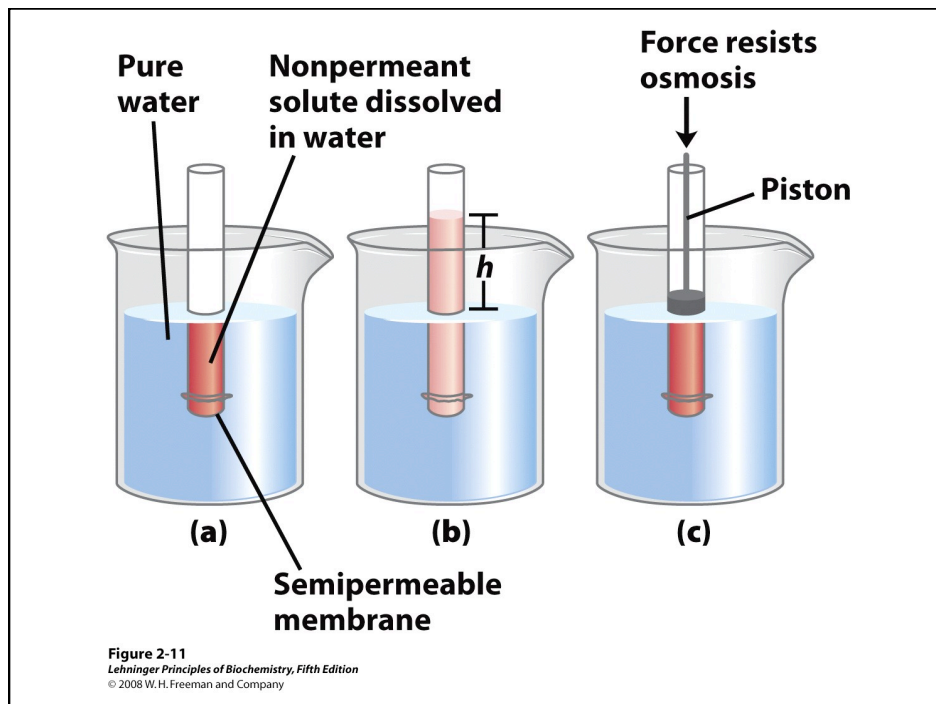
Hypertonic solutions are those in which more solute (and hence lower water potential) is present.
Isotonic solutions have equal (iso-) concentrations of substances. Water potentials are thus equal, although there will still be equal amounts of water movement in and out of the cell, the net flow is zero.
Hypotonic solutions are those with less solute (again read as higher water potential).

Cells placed in distilled water

Cells placed in concentrated salt solution

H_2O H_2O

Cells swell and burst

Cells shrink and shrivel

Cell wall

Nucleus

Plasma membrane
Cytoplasm

Vacuole

Plant cell placed in distilled water

Plant cell placed in concentrated salt solution

Cell stiffens but generally retains shape

Cell body shrinks and pulls away from cell wall

Extracellular solutes
Intracellular solutes

(a) Cell in **isotonic** solution; no net water movement.

(b) Cell in **hypertonic** solution; water moves out and cell shrinks.

(c) Cell in **hypotonic** solution; water moves in, creating outward pressure; cell swells, may eventually burst.

Figure 2-12
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IONIZATION OF WATER

Concentration Definition

Molarity
Nomality
Molality
Percentage Concentration

Unit Conversion

CONCENTRATION

- Concentration: amount of substance present in a given volume of solution.

- Concentrated Solution: solution with a high concentration.

- Dilute Solution: solution with low concentration.

- Mole: amount of substance.

- Molar Concentration: the number of moles of the substance contained in 1L of solution, i.e., moles of solute/L of a solution.

- Percentage Concentration.

- Very Low Concentration.

- Normality

- To find the Molarity of a solution, one has to use the following formula:

$$c = \frac{n}{V}$$

c = molar concentration (mol/L)

n = number of moles (mol)

V = volume (L)

- **For example: What is the [NaCl] in a solution containing 6.25 g of NaCl in 0.250 L of solution?**
- ***1 mole of NaCl = 58.5 g**

- ***since mass and volume are given, all we need to do now is to first convert the mass into moles and then use the moles and volume to find Molarity of the solution.**

$$\text{moles of NaCl} = \frac{6.25 \text{ g}}{58.5 \text{ g/mol}} = 0.107 \text{ mol}$$

$$[NaCl] = \frac{0.107 \text{ mol}}{0.250 \text{ L}} = 0.428 \text{ M}$$

$$MW = \frac{Weight}{Moles}$$

- Molarity can be determined if the amount of solution and solvent is given. For example:
- If a 2.0 L of solution contains 8.0 mol of NaCl,

$$[NaCl] = \frac{8.0 \; mol}{2.0 \; L} = 2.0 \; M$$

- **When expressed in words, the unit symbol "M" is written as "molar".**

- **The easier way of writing "molar concentration of…" is using a set of brackets: […].**

- **For example: If a 2.0 L of solution contains 5.0 mol of NaCl, the molar concentration can be written as:**

- **molar concentration of NaCl= 2.5 M**

- **[NaCl]= 2.5 M**

- **The Molarity of the sodium chloride is 2.50 molar.**

Percentage Concentration

1) % concentration can be in V/V, W/W, or W/V
- Like most %s, V/V and W/W need to have the same units on top and bottom.
- W/V is sort of in the same units; V is mostly water and water's density is 1 g/mL or 1 kg/L
- 3 g H_2O_2/100 mL solution ≈ 3 g H_2O_2/100 g solution

Very Low Concentration

2) Expressing concentrations in parts per million (ppm) requires the unit on top to be 1,000,000 times smaller than the unit on the bottom

    E.g. 1 mg/kg or μg/g
- Multiples of 1000 are expressed in this order

    μ_, m_, _, k_ ("_" is the base unit)
- For parts per billion (ppb), the top unit would have to be 1,000,000,000 times smaller

3) Molar concentration is the most commonly used in chemistry. Ensure that units are mol/L.

Nomality

- The number of "equivalent weights" of solute per liter of solution
  - Another way to express concentration
  - Used when it's important to know how many "reactive groups" are present in a solution rather than how many molecules

---

- *Reactive groups and equivalent weight*
  - Used in reference to acids and bases
    - Acids dissociate in solution to release H^+ ions
    - Bases dissociate to release OH^- ions
  - For an acid:
    - 1 equivalent weight is equal to the number of grams of that acid that reacts to yield 1 mole of H^+ ions, that is, 1 mole of reactive groups
  - For a base:
    - 1 equivalent weight is equal to the number of grams of that base that supplies 1 mole of OH^-, that is , 1 mole of reactive groups

○ NaOH $\rightarrow$ Na$^+$ OH$^-$

○ 1 mole of NaOH dissociates to produce 1 mole of Na$^+$ and 1 mole of OH$^-$

● Because 1 equivalent weight of NaOH is the number of grams that will produce 1 mole of OH$^-$ ions, the equivalent weight of NaOH is the same as its molecular weight.
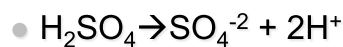
● H$_2$SO$_4$$\rightarrow$SO$_4^{-2}$ + 2H$^+$

○ 1 mole of sulfuric acid dissociates to form 2 moles of H$^+$ ions.

● It only requires 0.5 mole of H$_2$SO$_4$ to produce 1 mole of H$^+$ ions.

● Therefore, the FW of H$_2$SO$_4$ = 98.1, but its equivalent weight is 98.1 x 0.5 = 49.1

I M = 2 N

For H$_3$PO$_4$, 1 M = 3 N

Concentration after Dilution

$$C_1V_1 = C_2V_2$$

For Example: 20 mL 0.5 M NaCl is diluted to 200 mL, to find the final NaCl concentration, we do the following calculation:

$$0.02 \text{ L} \times 0.5 \text{ M} = C_2 \times 0.20 \text{ L} \implies$$

$$C_2 = \frac{0.02 \text{ L} \times 0.5 \text{ M}}{0.20 \text{ L}} = 0.05 \text{ M}$$

Unit Conversion

Weight: $1 \text{ g} = 1000 \text{ mg} = 10^6 \text{ } \mu\text{g}$

Length: $1 \text{ m} = 10 \text{ dm} = 100 \text{ cm} = 1000 \text{ mm}$

Area: $1 \text{ m}^2 = 100 \text{ dm}^2$

Volume: $1 \text{ dm}^3 = 1 \text{ L} = 1000 \text{ cm}^3 = 1000$ c.c.

$$= 1000 \text{ mL} = 10^6 \text{ } \mu\text{L}$$

Concentration Conversion

$M \Longrightarrow N$

$M \Longrightarrow \%$

1 M NaCl: $1\ M = \dfrac{1\ mol}{1\ L} = \dfrac{1\ mol \times 58.5\ g/mol}{1\ L \times 1000\ mL/L}$

$= \dfrac{58.5\ g}{10 \times 100\ mL} = \dfrac{5.85\ g}{100\ mL} = 5.85\%$

$\% \Longrightarrow M$

5 % NaOH: $5\ \% = \dfrac{5.0\ g}{100\ mL} = \dfrac{5.0\ g \times 1\ mol/40\ g}{100\ mL \times 1\ L/1000\ mL}$

$= \dfrac{1.25\ mol}{1\ L} = 1.25\ M$

Brønsted-Lowry Acids & Bases

- A BrØnsted-Lowry acid is a proton donor.
- A BrØnsted-Lowry base is a proton acceptor.
- H^+ = proton

Figure 2.1 Examples of Brønsted–Lowry acids and bases

Brønsted–Lowry acids [H–A]		Brønsted–Lowry bases [B:]	
Inorganic	Organic	Inorganic	Organic
HCl	CH_3CO_2H		$CH_3\ddot{N}H_2$ $CH_3\ddot{O}:^-$
H_2SO_4	acetic acid	$H_2\ddot{O}:$ $:NH_3$	methylamine methoxide
HSO_4^-			CH_3
H_2O	OH		
H_3O^+	$HO_2CCH_2-C-CH_2CO_2H$	$:\ddot{O}H$ $:\ddot{N}H_2$	$C=\ddot{O}$ $CH_2=CH_2$
	COOH		CH_3 ethylene
	citric acid		acetone

- All Brønsted–Lowry acids contain a proton.
- The net charge may be zero, (+), or (–).

- All Brønsted–Lowry bases contain a lone pair of electrons or a π bond.
- The net charge may be zero or (–).

Reactions of Brønsted-Lowry Acids and Bases

- **Loss of a proton from an acid forms its conjugate base.**
- **Gain of a proton by a base forms its conjugate acid.**
- **A double reaction arrow is used between starting materials and products to indicate that the reaction can proceed in the forward and reverse directions. These are equilibrium arrows.**

Examples:

Lewis Acids and Bases

- **A <u>Lewis acid</u> is an electron pair acceptor.**
- **A <u>Lewis base</u> is an electron pair donor.**
- Lewis bases & Brønsted-Lowry bases - both have an available electron pair—a lone pair or an electron pair in a π bond.
- A Brønsted -Lowry base always donates this electron pair to a proton, but a Lewis base donates this electron pair to anything that is electron deficient.
- A Lewis acid must be able to accept an electron pair, but there are many ways for this to occur.
- All Brønsted-Lowry acids are also Lewis acids, but the reverse is not necessarily true.
- o **Any species that is electron deficient and capable of accepting an electron pair is also a Lewis acid.**

Lewis Acids

- A Lewis acid is also called an electrophile.
- When a Lewis base reacts with an electrophile other than a proton, the Lewis base is also called a nucleophile. In this example, BF_3 is the electrophile and H_2O is the nucleophile.
- Lewis acid-base reactions illustrate a general pattern in organic chemistry. Electron-rich species react with electron-poor species.
- In the simplest Lewis acid-base reaction one bond is formed and no bonds are broken..

Lewis acid   Lewis base

electrophile   **nucleophile**

new bond

Lewis Acids & Bases

Other good examples involve metal ions.

ACID   BASE

Such bonds as the H_2O ---> Co bond are often called COORDINATE COVALENT BONDS because both electrons are supplied by one of the atoms of the bond.

Acid Strength and pK_a

- Acid strength is the tendency of an acid to donate a proton.
- The more readily a compound donates a proton, the stronger an acid it is.
- Acidity is measured by an equilibrium constant
- When a Brønsted-Lowry acid H—A is dissolved in water, an acid-base reaction occurs, and an equilibrium constant can be written for the reaction.

$$K_{eq} = \frac{[products]}{[starting\ materials]} = \frac{[H_3O^+][A\!:^-]}{[H\!-\!A][H_2O]}$$

Acid Strength and pK_a

Because the concentration of the solvent H_2O is essentially constant, the equation can be rearranged and a new equilibrium constant, called the acidity constant, K_a, can be defined.

$$\text{Acidity constant} = K_a = [H_2O]K_{eq} = \frac{[H_3O^+][A\!:^-]}{[H\!-\!A]}$$

It is generally more convenient when describing acid strength to use "pK_a" values than K_a values.

Definition: pK_a = −log K_a

K_a	pK_a = −log K_a
K_a values of typical organic acids	pK_a values of typical organic acids
10^{-5} to 10^{-50}	+5 to +50
larger number smaller number	smaller number larger number
stronger acid weaker acid	stronger acid weaker acid

Factors that Determine Acid Strength

q **Anything that stabilizes a conjugate base A:¯ makes the starting acid H—A more acidic.**

q **Four factors affect the acidity of H—A. These are:**

1. **Element effects**

2. **Inductive effects**

3. **Resonance effects**

4. **Hybridization effects**

q **No matter which factor is discussed, the same procedure is always followed. To compare the acidity of any two acids:**

o **Always draw the conjugate bases.**

o **Determine which conjugate base is more stable.**

o **The more stable the conjugate base, the more acidic the acid.**

---

1. Element Effects—Trends in the Periodic Table.

Across a row of the periodic table, the acidity of H—A increases as the electronegativity of A increases.

$pK_a \approx 50$	$pK_a \approx 38$	$pK_a \approx 16$	$pK_a = 3.2$
—C—H	—N—H	—O—H	H—F

Increasing electronegativity

Increasing acidity

Positive or negative charge is stabilized when it is spread over a larger volume.

F⁻ smaller anion — less stable conjugate base

H—F $pK_a = 3.2$ less acidic

Br⁻ larger anion — more stable conjugate base

H—Br $pK_a = -9$ more acidic

$pK_a = 3.2$	$pK_a = -7$	$pK_a = -9$	$pK_a = -10$
H—F	H—Cl	H—Br	H—I

Increasing size

Increasing acidity

2. Inductive Effects

- An **inductive effect** is the **pull of electron density** through σ bonds caused by **electronegativity differences in atoms**.

$$CH_3CH_2O{-}H$$
ethanol
$pK_a = 16$

$$CF_3CH_2O{-}H$$
2,2,2-trifluoroethanol
$pK_a = 12.4$ ← **stronger acid**

$$CH_3CH_2O^-$$

No additional electronegative atoms stabilize the conjugate base.

CF$_3$ withdraws electron density, stabilizing the conjugate base.

3. Resonance Effects

- **Resonance is a third factor that influences acidity.**
- **In the example below, when we compare the acidities of ethanol and acetic acid, we note that the latter is more acidic than the former.**

$$CH_3CH_2O{-}H$$
ethanol
$pK_a = 16$

acetic acid
$pK_a = 4.8$ ← **stronger acid**

- **When the conjugate bases of the two species are compared, it is evident that the conjugate base of acetic acid enjoys resonance stabilization, whereas that of ethanol does not.**

$$CH_3CH_2O{-}H \longrightarrow CH_3CH_2\ddot{O}{:}^-$$
ethanol acid

ethoxide conjugate base

The negative charge is localized on O.

only one Lewis structure

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3. Resonance Effects

- **Resonance delocalization makes CH$_3$COO⁻ more stable than CH$_3$CH$_2$O⁻, so CH$_3$COOH is a stronger acid than CH$_3$CH$_2$OH.**

The negative charge is delocalized on two O atoms.

acetic acid   acetate conjugate base   hybrid

two resonance structures

resonance-stabilized conjugate base

- **The acidity of H—A increases when the conjugate base A:⁻ is resonance stabilized.**

4. Hybridization Effects

- **The final factor affecting the acidity of H—A is the hybridization of A.**

Let us consider the relative acidities of three different compounds containing C—H bonds.

	CH$_3$CH$_3$ ethane	CH$_2$=CH$_2$ ethylene	H−C≡C−H acetylene	
weakest acid →	pK_a = 50	pK_a = 44	pK_a = 25	← strongest acid

Increasing acidity

- **The higher the percent of *s*-character of the hybrid orbital, the closer the lone pair is held to the nucleus, and the more stable the conjugate base.**

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4. Hybridization Effects

$CH_3\ddot{C}H_2$ $CH_2=\ddot{C}H$ $H-C\equiv\ddot{C}:$

sp^3 hybridized C 25% s-character	sp^2 hybridized C 33% s-character	sp hybridized C 50% s-character

→ **Increasing percent s-character**
Increasing stability

→ **Increasing percent s-character**
Increasing carbanion stability

• As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.

Summary of Factors that Determine Acidity

Figure 2.5 Summary of the factors that determine acidity

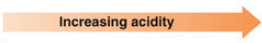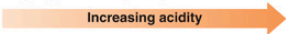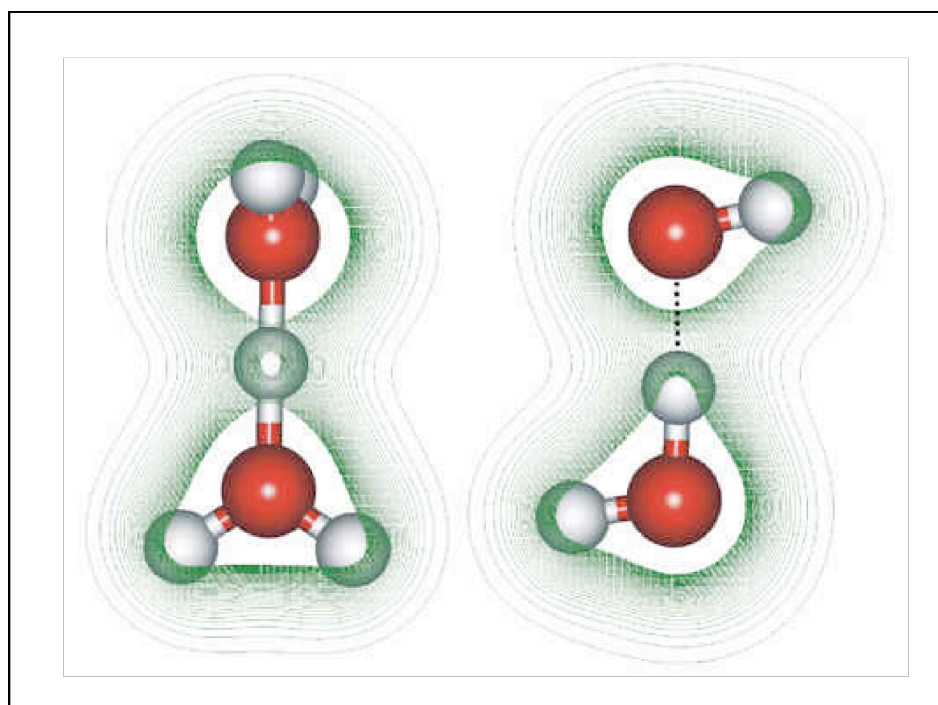| Factor	Example
1. **Element effect:** The acidity of H−A increases both left-to-right across a row and down a column of the periodic table.	Increasing acidity → $-\overset{\|}{\underset{\|}{C}}-H$ $-N-H$ $-O-H$ $H-F$ $-S-H$ $H-Cl$ $H-Br$ $H-I$ ↓ Increasing acidity
2. **Inductive effects:** The acidity of H−A increases with the presence of electron-withdrawing groups in A.	CH_3CH_2O-H CF_3CH_2O-H **more acidic**
3. **Resonance effects:** The acidity of H−A increases when the conjugate base A:⁻ is resonance stabilized.	CH_3CH_2O-H CH_3COO-H **more acidic**
4. **Hybridization effects:** The acidity of H−A increases as the percent s-character of A:⁻ increases.	CH_3CH_3 $CH_2=CH_2$ $H-C\equiv C-H$ Increasing acidity →

$$H_2O \xrightleftharpoons[\quad]{K_w} H^+ \quad + \quad OH^-$$

Hydronium ion gives up a proton

Proton hop

**Water accepts proton and
becomes a hydronium ion**

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pH of pure Water

$$H_2O \;\overset{K_W}{\rightleftharpoons}\; H^+ \;+\; OH^-$$

$$K_W = \frac{[H^+][OH^-]}{[H_2O]}$$

$$[H^+][OH^-] = K_W[H_2O]$$

$$n = \frac{Weight}{MW} = \frac{d \times V}{MW}$$

$$[H_2O] = \frac{n}{V} = \frac{1000\ mL \times 1\ g\ /\ mL\ /\ 18\ g\ /\ mL}{1\ L} = 55.5\ M$$

$$K_W = 1.8 \times 10^{-16}\ M$$

$$[H^+]\,[OH^-] = K_W\,[H_2O] = 1.8 \times 10^{-16}\ M \times 55.5\ M$$

$$= 1.0 \times 10^{-14}\ M^2$$

$$[H^+] = [OH^-]$$

$$[H^+]^2 = 1.0 \times 10^{-14}\ M^2$$

$$[H^+] = 1.0 \times 10^{-7}\ M$$

$$p = -\log\ (\ )$$

$$pH = -\log[H^+] = -\log\left(1.0 \times 10^{-7}\right) = 7.0$$

$$pH + pOH = 14$$

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Temperature	Kw
-35°C	$1.0 \times 10^{-17}\ mol^2L^{-2}$
0°C	$1.12 \times 10^{-15}\ mol^2L^{-2}$
25°C	$9.91 \times 10^{-15}\ mol^2L^{-2}$
60°C	$9.311 \times 10^{-14}\ mol^2L^{-2}$
300°C (~ 50 MPa)	$9.311 \times 10^{-12}\ mol^2L^{-2}$

$pK_w = -\log_{10}(K_w)$ [IAPWS]

TABLE 2–6	The pH Scale		
$[H^+]$ (M)	pH	$[OH^-]$ (M)	pOH*
10^0 (1)	0	10^{-14}	14
10^{-1}	1	10^{-13}	13
10^{-2}	2	10^{-12}	12
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-10}	10
10^{-5}	5	10^{-9}	9
10^{-6}	6	10^{-8}	8
10^{-7}	7	10^{-7}	7
10^{-8}	8	10^{-6}	6
10^{-9}	9	10^{-5}	5
10^{-10}	10	10^{-4}	4
10^{-11}	11	10^{-3}	3
10^{-12}	12	10^{-2}	2
10^{-13}	13	10^{-1}	1
10^{-14}	14	10^0 (1)	0

*The expression pOH is sometimes used to describe the basicity, or OH^- concentration, of a solution; pOH is defined by the expression pOH = $-\log [OH^-]$, which is analogous to the expression for pH. Note that in all cases, pH + pOH = 14.

Table 2-6
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Figure 2-14
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How to Find pH of A Solution?

- A Strong Acid or Strong Base Solution
- A Weak Acid or A Weak Base Solution
- A Solution with Both Weak Acid and Weak Base (Buffer)

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pH of Strong Acid/Base

- Strong Acids: HCl, HBr, HI, $HClO_4$, H_2SO_4, HNO_3, etc. (Leveling Effect: which one is the strongest acid?)
- Strong Bases: NaOH, KOH, RbOH, CsOH
- For HCl, $[H^+]$ = [HCl], so pH = $-\log[H^+]$ = $-\log$ [HCl]
- For NaOH, $[OH^-]$ = [NaOH], pOH = $-\log[OH^-]$ = $-\log$[NaOH], pH = 14 - pOH

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Conjugate Acid-Base Pairs

- Chemical entities that differ only by H^+ in the equation are considered conjugate acid-base pairs:
- e.g. $CH_3COOH_{(aq)}$ and $CH_3COO^-_{(aq)}$
-         $H_3O^+_{(aq)}$ and $H_2O_{(aq)}$

$$H^+ \qquad\qquad H^+$$

- e.g. $CH_3COOH_{(aq)}$ + $H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)}$ + $CH_3COO^-_{(aq)}$
-     B-L acid   B-L base $\rightleftharpoons$ B-L acid   B-L base

- **conj. acid-base pair**

- **conj. acid-base pair**

Strengths of Conjugate Acid – Base pairs

- In chemical equilibrium, we have a competition between forward and reverse reactions. For acid and base reactions, this means we have a competition between two sets of acids and bases
- i.e.   acid 1 + base 1 $\rightleftharpoons$ acid 2 + base 2
- If acid 1 and base 1 are stronger than acid 2 and base 2, then the forward reaction will dominate
- If acid 2 and base 2 are stronger than acid 1 and base 1, then the reverse reaction will dominate
- **The stronger the acid, the weaker it's conjugate base and the weaker the acid, the stronger it's conjugate base.**

pH of Weak Acid

$$CH_3COOH \;\overset{K_a}{\rightleftharpoons}\; CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
Initial Conc.	c	0	0
Change	-x	x	x
Final Conc.	c - x	x	x

$$K_a = \frac{[AcO^-][H^+]}{[AcOH]}$$

$$K_a = \frac{x \times x}{c - x} = \frac{x^2}{c - x}$$

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$$x^2 = K_a (c - x) = K_a c - K_a x$$

$$x^2 + K_a x - K_a c = 0$$

For $ax^2 + bx + c = 0$

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-K_a + \sqrt{K_a^2 - 4 \times 1 \times (-K_a c)}}{2} = \frac{-K_a + \sqrt{K_a^2 + 4 K_a c}}{2}$$

If $C_a / K_a > 100$, you can simplify K_a expression to just $K_a = (x^2 / C_a)$

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For acetic acid, if $c = 0.25\,M$, $K_a = 1.74 \times 10^{-5}\,M$
$x = 0.00208\,M$, $pH = -\log(0.00208) = 2.68$
$x / c = 0.00208 / 0.25 = 0.0083 = 0.83\%$

$K_a = X^2/C$, $X = 0.00209\,M$, almost no error.

For acetic acid, if $c = 0.00025\,M$, $x = 0.0000578$,
$pH = -\log(0.0000578) = 4.24$
$x / c = 0.0000578 / 0.00025 = 0.231 = 23.1\%$

$K_a = X^2/C$, $X = 0.0000660\,M$, $(0.0000660-0.0000578)/0.0000578$
$\times 100\% = 14.2\%$.
$pH = -\log(0.0000660) = 4.18$.

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Buffers

- Buffer Solutions resist a change in pH

- Buffers contain relatively large concentrations of either
    - An acid, HA and its conjugate base A⁻
    - A base, B, and its conjugate acid (BH⁺)

Conjugate Acid-Base Pairs

- Chemical entities that differ only by H^+ in the equation are considered conjugate acid-base pairs:
- e.g. $CH_3COOH_{(aq)}$ and $CH_3COO^-_{(aq)}$

e.g. $CH_3COOH_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

$$K_a = \frac{[AcO^-][H^+]}{[AcOH]}$$

$$[H^+] = \frac{K_a[AcOH]}{[AcO^-]}$$

$$pH = -\log[H^+] = -\log\left(\frac{K_a[AcOH]}{[AcO^-]}\right) = -\log K_a + \left(-\log\frac{[AcOH]}{[AcO^-]}\right)$$

$$= pK_a + \log\frac{[AcO^-]}{[AcOH]}$$

For a general equation:

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

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Titration Terminology

Titrant - solution of known concentration used in titration

Analyte - substance being analyzed

Standard Solution - A solution whose concentration is known accurately.

Primary Standard Solution -Prepared by dissolving carefully weighed solid sample in enough water to give an accurately known volume of solution.

Equivalent Point - point at which stoichiometrically equivalent amounts of reactants have reacted.

End Point - the point at which the indicator changes color

Monoprotic acids
Acetic acid
($K_a = 1.74 \times 10^{-5}$ M)

Ammonium ion
($K_a = 5.62 \times 10^{-10}$ M)

Diprotic acids
Carbonic acid
($K_a = 1.70 \times 10^{-4}$ M);
Bicarbonate
($K_a = 6.31 \times 10^{-11}$ M)

Glycine, carboxyl
($K_a = 4.57 \times 10^{-3}$ M);
Glycine, amino
($K_a = 2.51 \times 10^{-10}$ M)

Triprotic acids
Phosphoric acid
($K_a = 7.25 \times 10^{-3}$ M);
Dihydrogen phosphate
($K_a = 1.38 \times 10^{-7}$ M);
Monohydrogen phosphate
($K_a = 3.98 \times 10^{-13}$ M)

$CH_3C \rightleftharpoons CH_3C + H^+$ $pK_a = 4.76$

$NH_4^+ \rightleftharpoons NH_3 + H^+$ $pK_a = 9.25$

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ $pK_a = 3.77^*$

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ $pK_a = 10.2$

$pK_a = 2.34$ $pK_a = 9.60$

$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$ $pK_a = 2.14$

$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ $pK_a = 6.86$

$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$ $pK_a = 12.4$

pH

Figure 2-15
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Figure 2-16
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Figure 2-17
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$$K_w = [H^+][OH^-]$$

OH$^-$ H$_2$O

Acetic acid   HAc   Ac$^-$ Acetate
(CH$_3$COOH)   (CH$_3$COO$^-$)

H$^+$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$

Figure 2-18
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pKa of molecules for buffers in biochemistry studies

Name	PKa	Name	pKa
MES	6.15	Bicine	8.35
Boric acid	9.24	CHES	9.50
Phosphoric acid	6.91 (pK$_a$2)	Citric acid	3.06 (pK$_a$1)
Citric acid	5.40 (pK$_a$3)	Citric acid	4.74 (pK$_a$2)
ADA	6.60	Glycylglycine	8.40
Succinic acid	3.06 (pK$_a$1)	HEPES	7.55
Imidazole	7.00	HEPPS	8.00
Phosphoric acid	2.12 (pK$_a$1)	MOPS	7.20
Bis-Tris Propane	6.80	Phosphoric acid	12.32 (pK$_a$3)
Glycine amide (HCl)	8.20	PIPES	6.80
Formic acid	3.75	TES	7.50
Acetic acid	4.76	Tricine	8.15
Succinic acid	5.57 (pK$_a$2)	Tris	8.30

Figure 2-20
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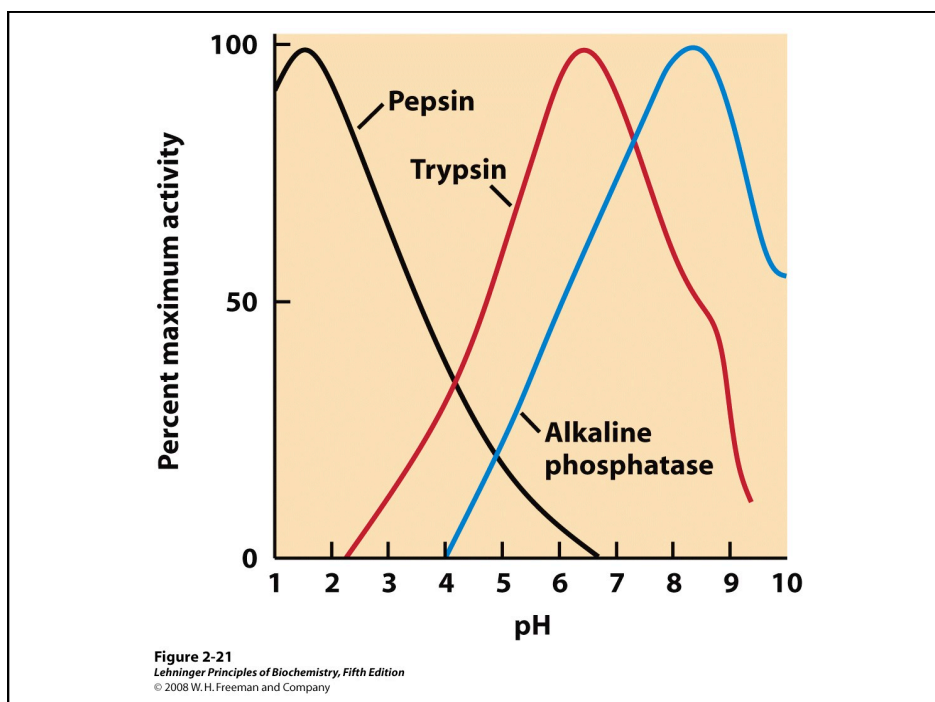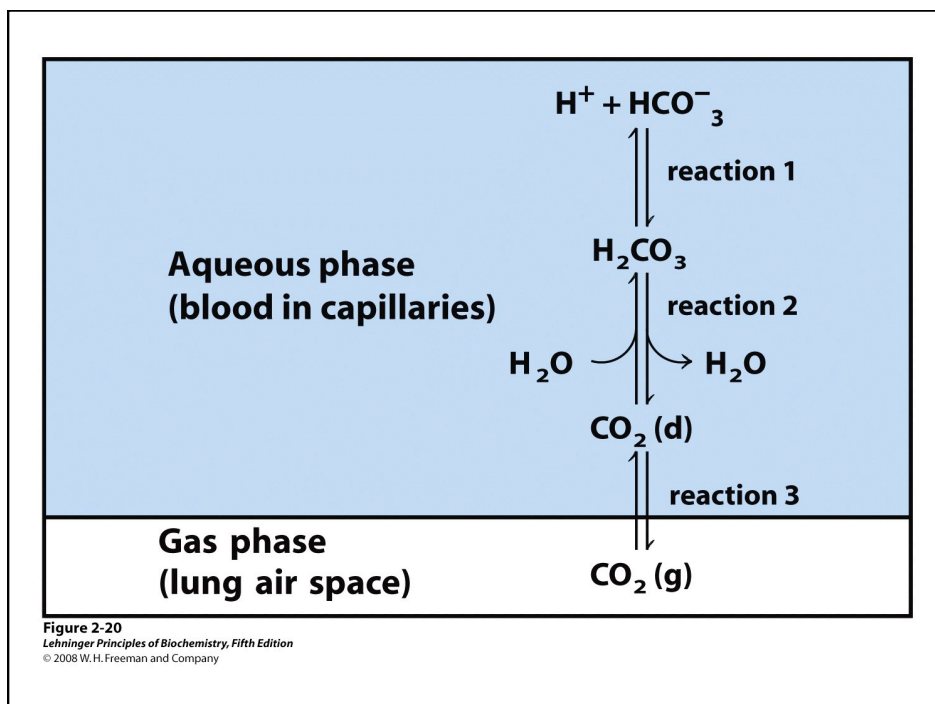
1. Find out the pH of 0.01 M HCl and 1.0 M NaOH solution

- Calculate the pH of 0.2 M AcOH with a Ka of 1.74×10^{-5} M

- Calculate the pH of sodium acetate and acetic acid buffer at the following concentration: [NaAc] = 0.17 M, [AcOH] = 0.35 M

- Prepare the 4 L of PBS buffer by given the condition that [NaCl] = 0.15 M, $[PO_4^{3-}]$ = 0.01 M, pKa = 6.91.