BIOCH 755: Biochemistry I   Fall 2015

2. Water; Acid-base reactions

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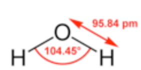
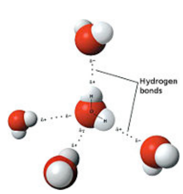
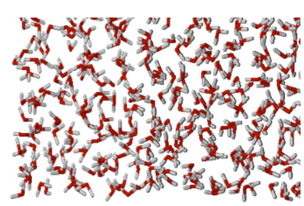
2.1 Physical Properties of Water

- **Key Concepts 2.1**
  - Water molecules, which are polar, can form hydrogen bonds with other molecules.
  - In ice, water molecules are hydrogen bonded in a crystalline array, but in liquid water, hydrogen bonds rapidly break and re-form in irregular networks.
  - The attractive forces acting on biological molecules include ionic interactions, hydrogen bonds, and van der Waals interactions.
  - Polar and ionic substances can dissolve in water.







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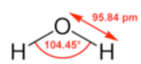
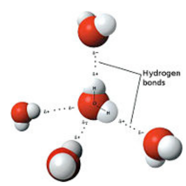
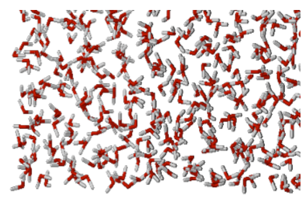
2.1 Physical Properties of Water

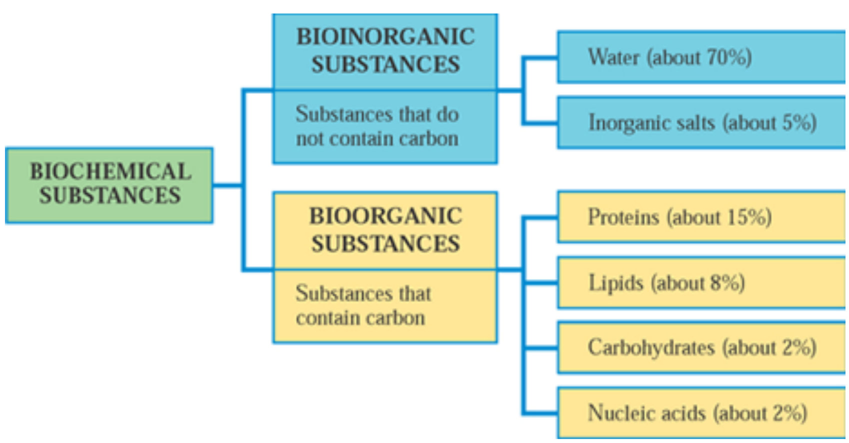
- **Key Concepts 2.1**
  - The hydrophobic effect explains the exclusion of nonpolar groups as a way to maximize the entropy of water molecules.
  - Amphiphilic substances form micelles or bilayers that hide their hydrophobic groups while exposing their hydrophilic groups to water.
  - Molecules diffuse across membranes which are permeable to them from regions of higher concentration to regions of lower concentration.
  - In dialysis, solutes diffuse across a semipermeable membrane from regions of higher concentration to regions of lower concentration.







Human Body Mass Composition



Structure of Water

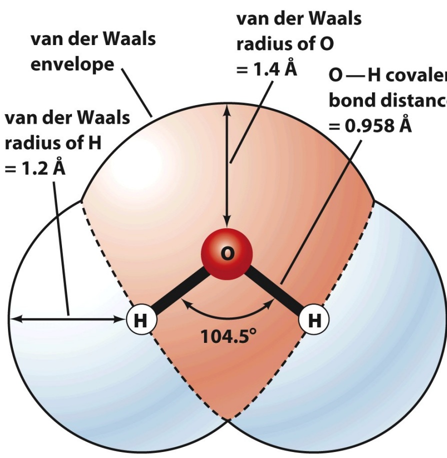
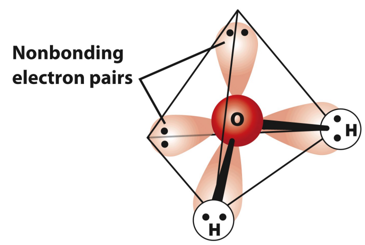


Figure 2-1a



Water Hydrogen Bonding

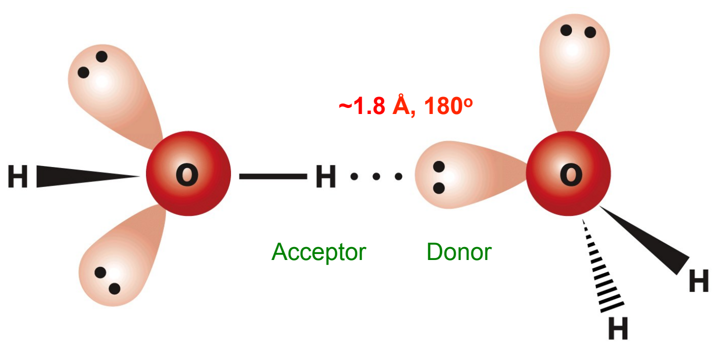


Figure 2-2

Typical Bond Energies

TABLE 2-1 Bond Energies in Biomolecules

Type of Bond	Example	Bond Strength ($kJ \cdot mol^{-1}$)
Covalent	O—H	460
	C—H	414
	C—C	348
Noncovalent		
Ionic interaction	$—COO^{-} \cdots {}^{+}H_3N—$	86
van der Waals forces		
Hydrogen bond	$—O—H \cdots O<$	20
Dipole–dipole interaction	$>C=O \cdots >C=O$	9.3
London dispersion forces	$—CH_2—H \cdots H—CH_2—$	0.3

Table 2-1

Hydrogen bond networks of water/ice

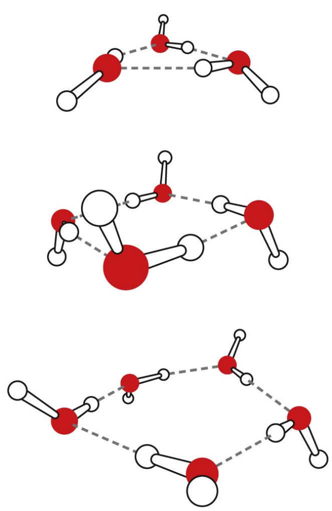


Figure 2-4
 After Liu, K., Cruzan, J.D., and Saykally, R.J., *Science* 271, 929 (1996).

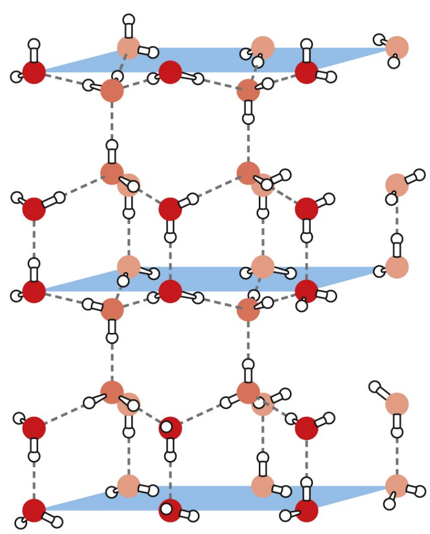
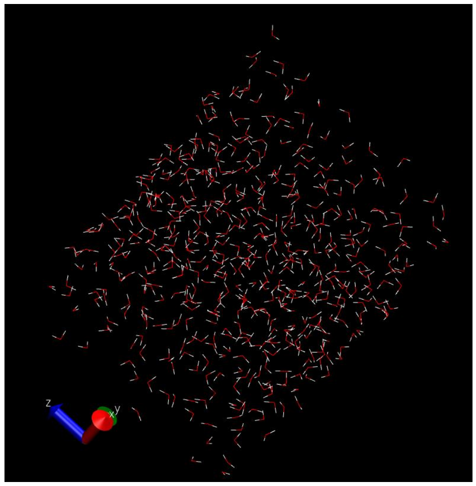


Figure 2-3
 After Pauling, L., *The Nature of the Chemical Bond* (3rd ed.), p. 465, Cornell University Press (1960).

Dynamics of water hydrogen bonding network



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(512 waters, 200 ps simulation @ 300K, 1 ps per frame)

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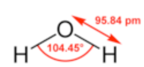
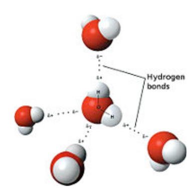
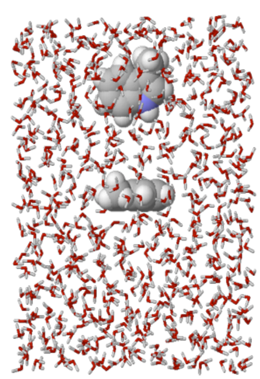
Water



- Solvent of life
- Many unique properties
  - Maximum density at 4 ^{o}C
    - Ice is lighter than liquid water
  - Polar molecule
    - hydrogen bonding network
    - High specific heat capacity
- Hydrophobicity and hydrophilicity
  - Solute polarity (carry partial charges or not)
  - Salts (e.g. NaCl) dissolve in water readily
  - Hydrocarbons (oil) do not mix with water
- Amphipathic molecules
  - Self-assembly to micelles, biological membranes





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Hydrophilic Solutes

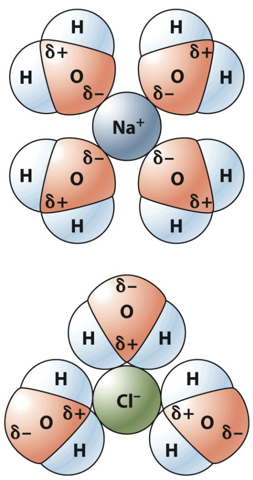

Figure 2-6

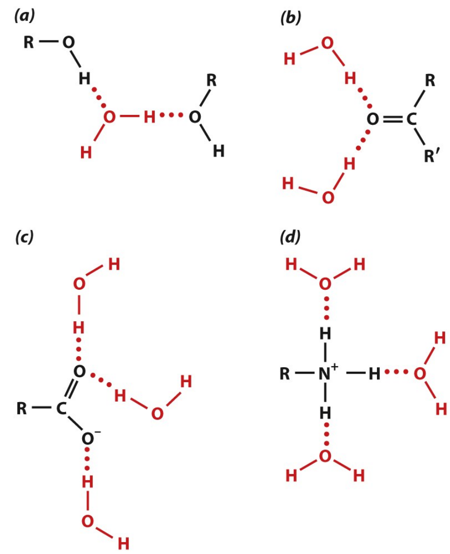

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Figure 2-7

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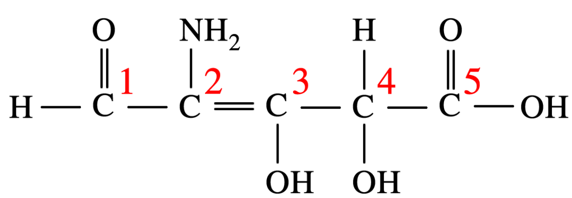
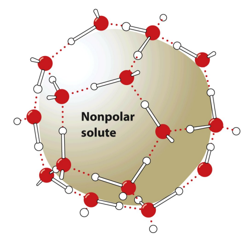
Is this compound hydrophilic?

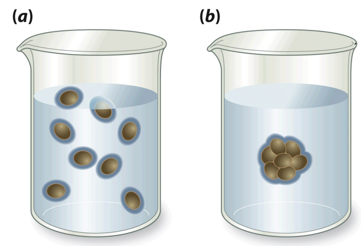


A. Yes.
B. No.
C. What does "hydrophilic" mean?

Hydrophobic Effects: Aggregation and Phase Separation

- Hydrophobic disrupt water HB network
- Minimize expose hydrophobic surface leads to aggregation/phase separation



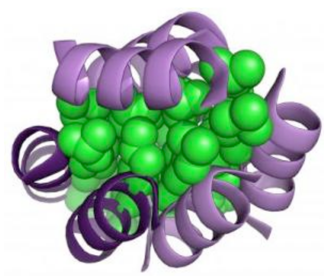


Which of the following is true regarding the hydrophobic effect?

A. Hydrophobic bonds are the association of nonpolar molecules or groups with other nonpolar molecules
B. Nonpolar molecules interrupt the hydrogen-bonding pattern of water
C. Water molecules that surround a less polar molecule are more restricted in their interactions with other water molecules
D. B and C
E. All of the above

Amphiphiles and Self-Assembly

- Hydrophobic + hydrophilic tails



Protein folding is also largely a self-assembly process!

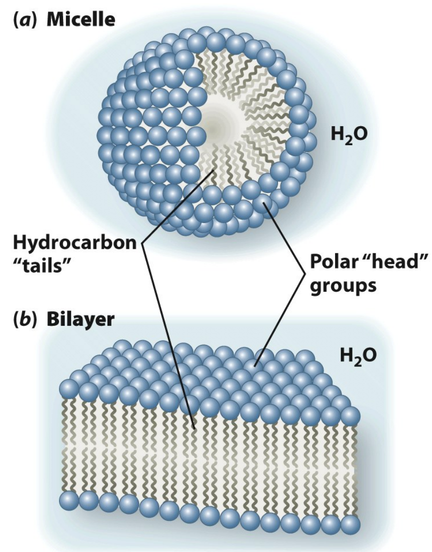


Figure 2-11

Osmosis and Osmotic Pressure

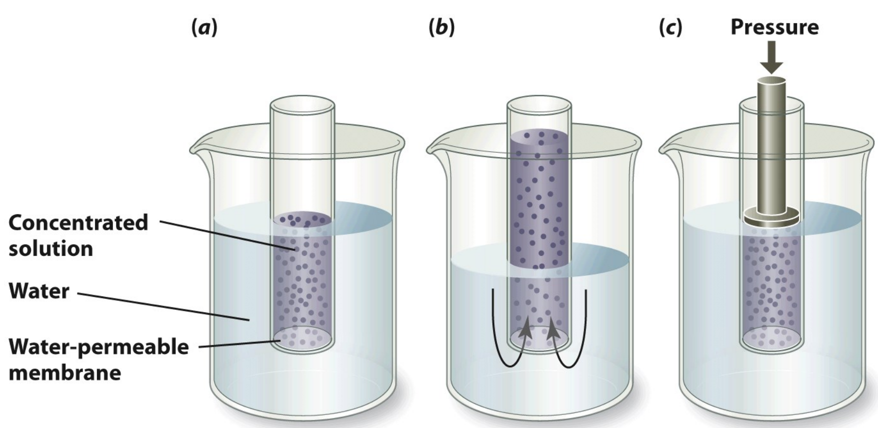


Figure 2-13

Dialysis: (Selective) Diffusion of Solutes

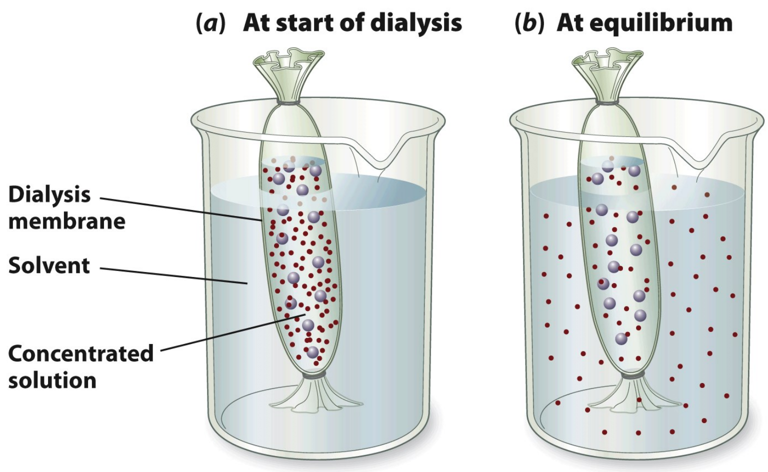


Figure 2-14

2.2 Chemical Properties of Water

- **Key Concepts 2.2**
  - Water dissociates to form H^+ and OH^- ions, with a dissociation constant of 10^{-14}.
  - The acidity of a solution is expressed as a pH value: pH = - log [H^+]
  - An acid is a compound that can donate a proton, and a base is a compound that can accept a proton.
  - A dissociation constant varies with the strength of an acid.
  - The Henderson–Hasselbalch equation relates the pH of a solution of a weak acid to the pK and the concentrations of the acid and its conjugate base.
  - A titration curve demonstrates that if the concentrations of an acid and its conjugate base are close, the solution is buffered against changes in pH when acid or base is added.
  - Many biological molecules contain ionizable groups so that they are sensitive to changes in pH

Water Disassociation (Ionization)

$$K_w = K_{eq}\,[H_2O] = [HO^-][H^+] = 1 \times 10^{-14}$$

- No actual free proton: H_3O^+ (hydronium ion), and other larger water clusters

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Proton Transfer Between Waters

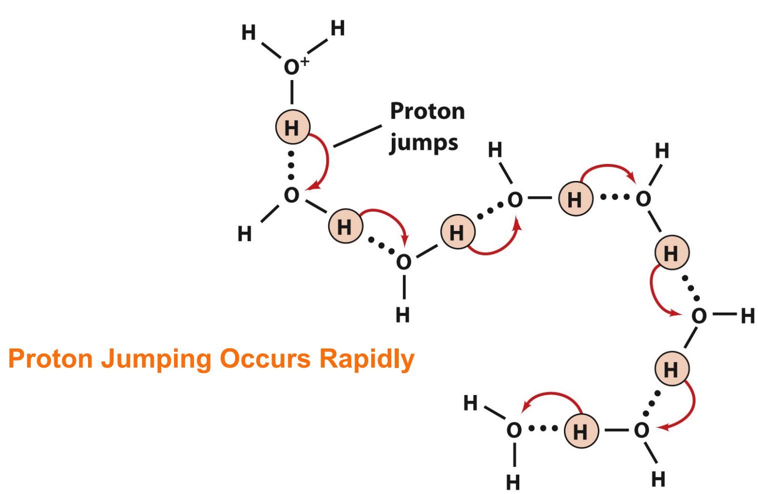

Figure 2-15

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Water Disassociation

$$K_w = K_{eq}\,[H_2O] = [HO^-][H^+] = 1 \times 10^{-14}$$

- No actual free proton: H_3O^+ (hydronium ion), and other larger water clusters
- Ionization constant: $K_w = 10^{-14}$ (under standard conditions)
- Pure water: $[H^+] = [OH-] = 10^{-7}$
- Definition of pH: pH = - log $[H^+]$ (= 7 for pure water @ 25°C)
  - One pH unit corresponds to 10 x change in $[H^+]$
- Acidic: higher $[H^+]$ (lower pH)
- Basic: lower $[H^+]$ (higher pH)

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Relationship of pH, $[H^+]$, and $[OH^-]$

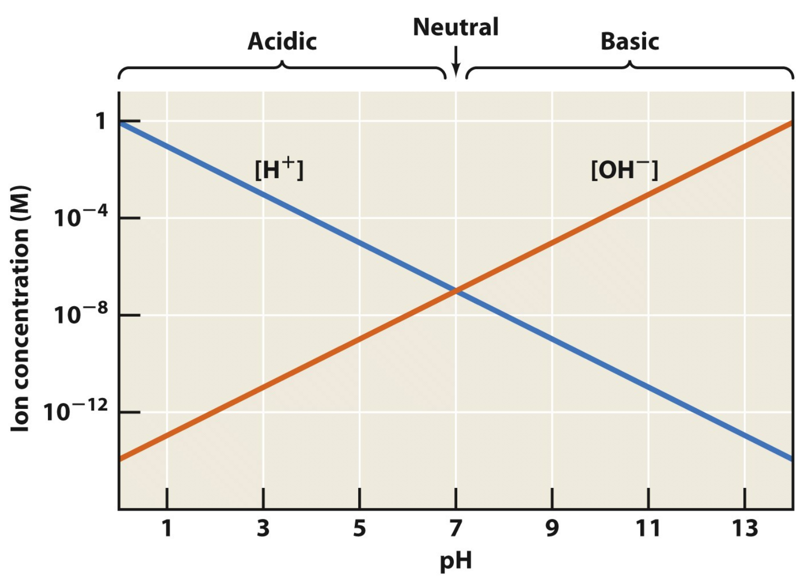

Figure 2-16

What is the pH of a 0.01 M NaOH solution?

A. 10
B. 11
C. 12
D. 13
E. 14

Acids and Bases

- Acid: donate protons (lower pH)
- Base: accept/sequester proton (higher pH)
- Acid-base reaction: $HA + H_2O \longleftrightarrow A^- + H_3O^+$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- pKa = -log Ka
- Lower pKa means stronger acid: stronger tendency to donate proton

TABLE 2-4 Dissociation Constants and p*K* Values at 25°C of Some Acids

Acid	*K*	p*K*
Oxalic acid	5.37×10^{-2}	1.27 (pK_1)
H_3PO_4	7.08×10^{-3}	2.15 (pK_1)
Formic acid	1.78×10^{-4}	3.75
Succinic acid	6.17×10^{-5}	4.21 (pK_1)
Oxalate⁻	5.37×10^{-5}	4.27 (pK_2)
Acetic acid	1.74×10^{-5}	4.76
Succinate⁻	2.29×10^{-6}	5.64 (pK_2)
2-(*N*-Morpholino)ethanesulfonic acid (MES)	8.13×10^{-7}	6.09
H_2CO_3	4.47×10^{-7}	6.35 (pK_1)[a]
Piperazine-*N,N'*-bis(2-ethanesulfonic acid) (PIPES)	1.74×10^{-7}	6.76
$H_2PO_4^-$	1.51×10^{-7}	6.82 (pK_2)
3-(*N*-Morpholino)propanesulfonic acid (MOPS)	7.08×10^{-8}	7.15
N-2-Hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES)	3.39×10^{-8}	7.47
Tris(hydroxymethyl)aminomethane (Tris)	8.32×10^{-9}	8.08
Boric acid	5.75×10^{-10}	9.24
NH_4^+	5.62×10^{-10}	9.25
Glycine (amino group)	1.66×10^{-10}	9.78
HCO_3^-	4.68×10^{-11}	10.33 (pK_2)
Piperidine	7.58×10^{-12}	11.12
HPO_4^{2-}	4.17×10^{-13}	12.38 (pK_3)

[a] The p*K* for the overall reaction $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$; see Box 2-2.

Source: Dawson, R.M.C., Elliott, D.C., Elliott, W.H., and Jones, K.M., *Data for Biochemical Research* (3rd ed.), pp. 424–425, Oxford Science Publications (1986); *and* Good, N.E., Winget, G.D., Winter, W., Connolly, T.N., Izawa, S., and Singh, R.M.M., *Biochemistry* 5, 467 (1966).

Table 2-4

Acids and Bases

- Acid: donate protons (lower pH)
- Base: accept/sequester proton (higher pH)
- Acid-base reaction:

$$HA + H_2O \longleftrightarrow A^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- pKa = - log Ka
  - Lower pKa means stronger acid: stronger tendency to donate proton
- The relative concentrations of acid and base determines the solution pH: Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

TABLE 2-3 pH Values of Some Common Substances

Substance	pH
1 M NaOH	14
Household ammonia	12
Seawater	8
Blood	7.4
Milk	7
Saliva	6.6
Tomato juice	4.4
Vinegar	3
Gastric juice	1.5
1 M HCl	0

Table 2-3

Buffers: Titration Curves of Weak Acids

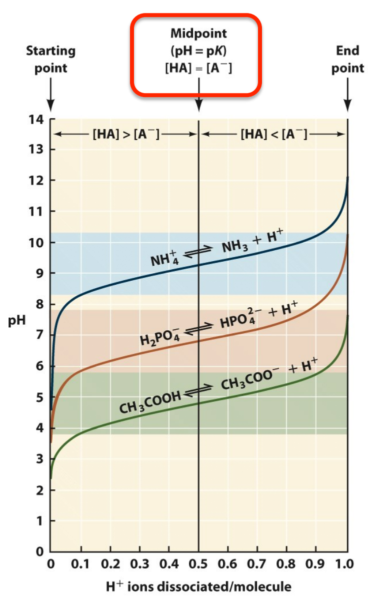

Figure 2-17

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

"Buffering" capability: slow change in solution pH with addition or removal of proton

Buffering capacity is maximal near the pKa value of the weak acid/base

Buffers: Titration of a Polyprotic Acid

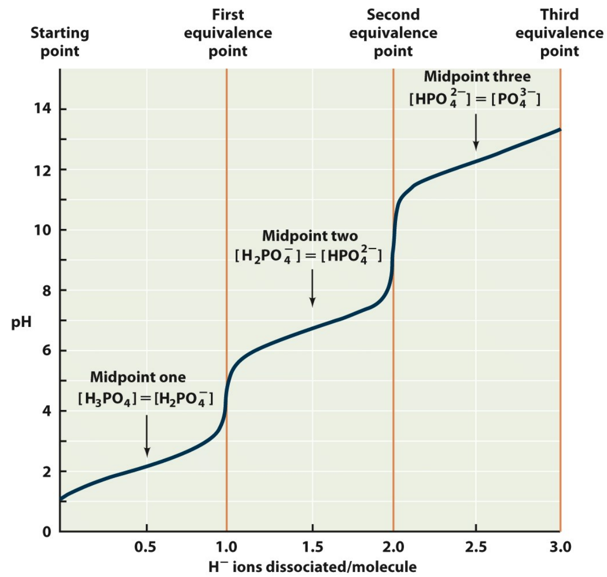

Figure 2-18

Summary

- Unique physical properties of water
- Hydrophilicity, hydrophobicity
- Water ionization: pH
- Acid-base reactions: buffers

- Coming up: Amino acids and proteins