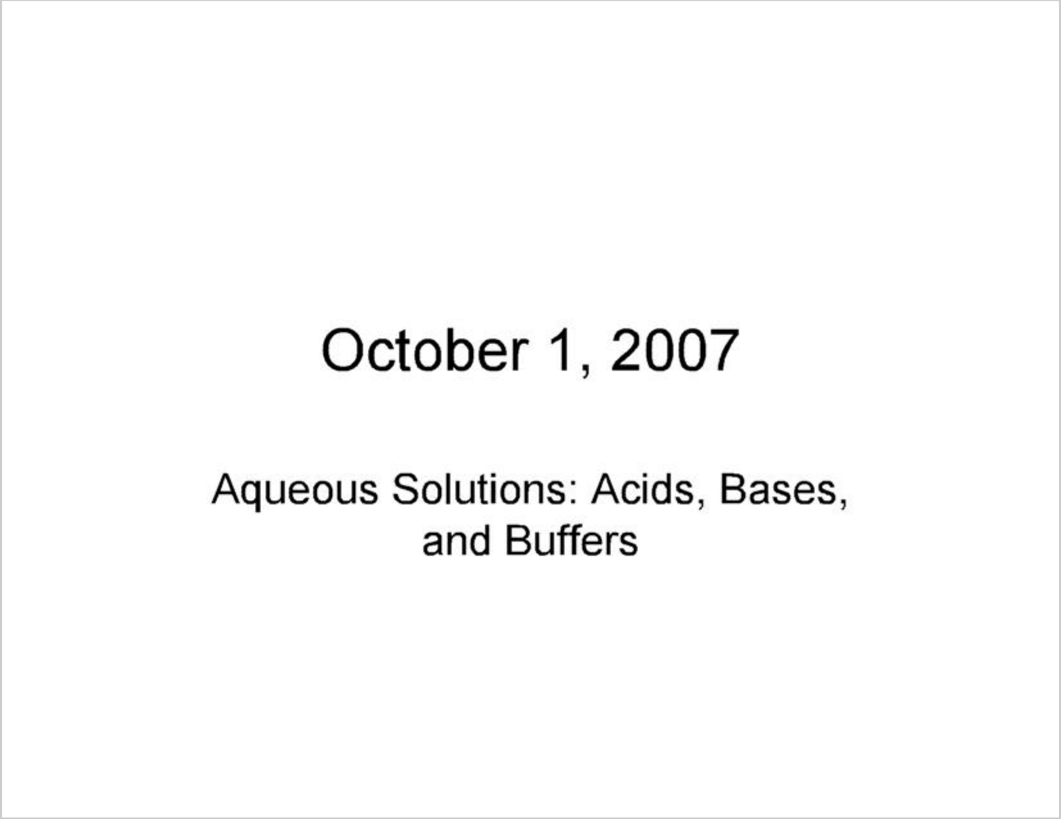
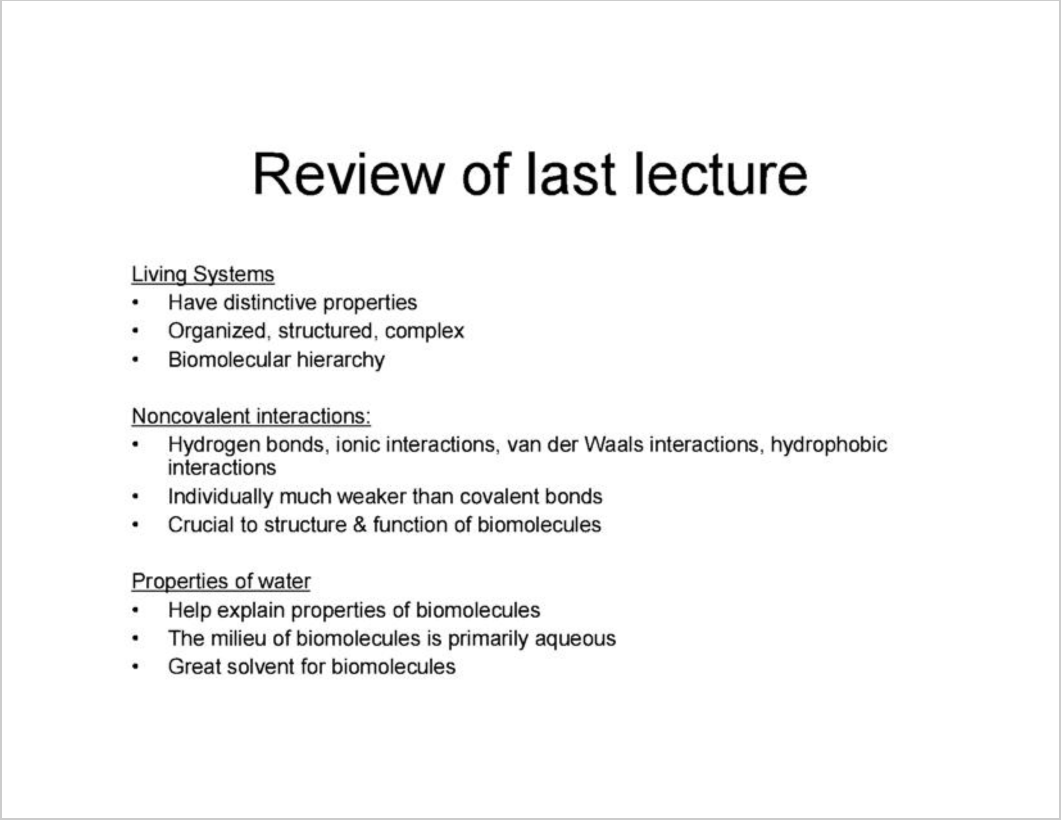
Notes 10/1

Monday, October 01, 2007
10:00 AM



October 1, 2007

Aqueous Solutions: Acids, Bases, and Buffers



Review of last lecture

Living Systems
- Have distinctive properties
- Organized, structured, complex
- Biomolecular hierarchy

Noncovalent interactions:
- Hydrogen bonds, ionic interactions, van der Waals interactions, hydrophobic interactions
- Individually much weaker than covalent bonds
- Crucial to structure & function of biomolecules

Properties of water
- Help explain properties of biomolecules
- The milieu of biomolecules is primarily aqueous
- Great solvent for biomolecules

Today's Outline

- More on water
- Acids, Bases
- Buffers
- Titration Curves

Relative strengths of interactions/bonds (in general)

- Covalent bond>>ionic interactions>hydrogen bonds>hydrophobic interactions
- There are exceptions sometimes.

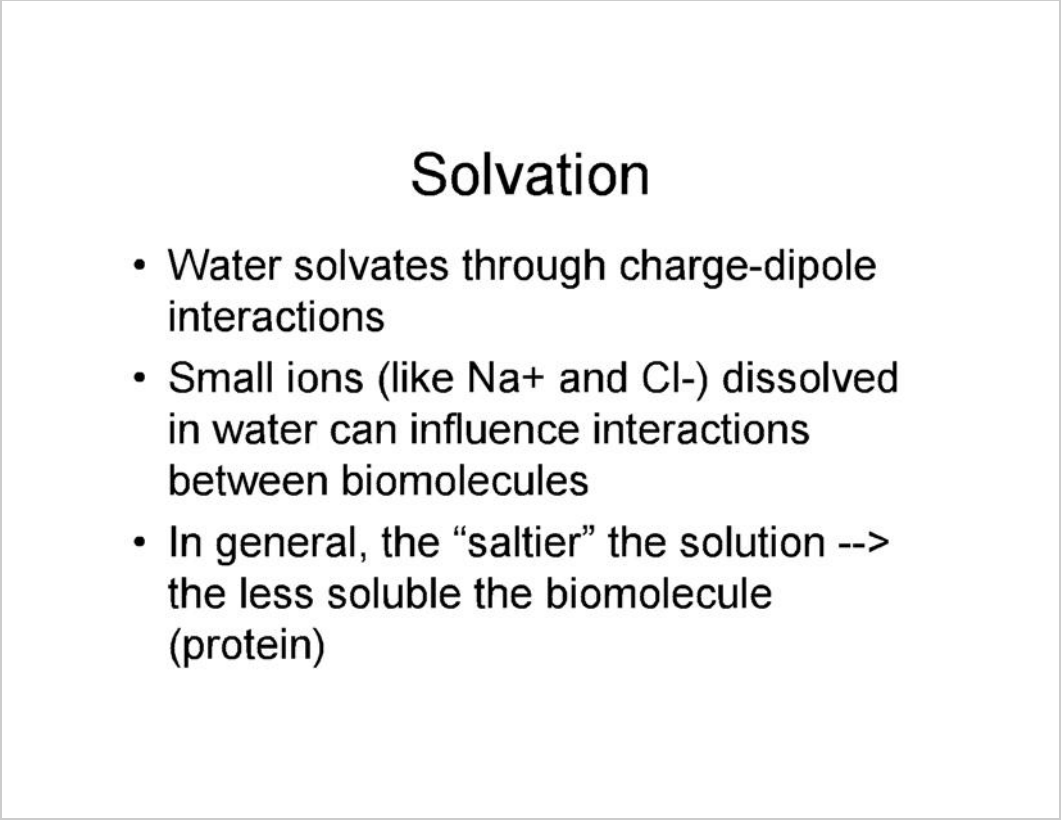
Ice vs. liquid water

In the transition of pure liquid water to ice, the enthalpy change is favorable because heat is released in the process but the entropy change is unfavorable because the transition is to the more ordered, crystalline state. Below a temperature of 32°F (273K) the enthalpy term, ΔH, predominates and the process is spontaneous, but at higher temperatures the entropy term, $T\Delta S$, predominates, and the transition does not occur.

Main point: temperature dictates structure of pure water

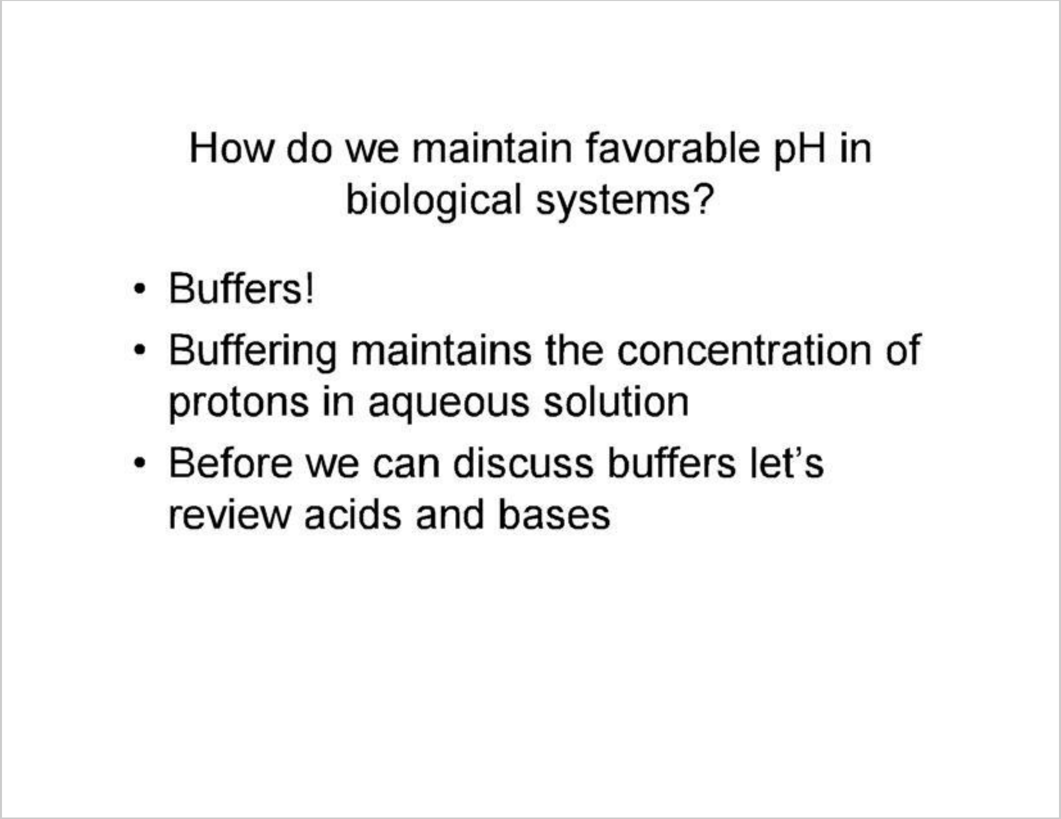
Ionic interactions in water are much weaker than in other solvents.

- High dielectric constant
- Coulomb's Law: $F = k\dfrac{Q_1Q_2}{\varepsilon \bullet r^2}$
  - F = strength (force) of interactions between charged particles
  - = dielectric constant of medium
  - r = distance between charged groups
  - k = proportionality constant
  - Q = electrical charge



Solvation

- Water solvates through charge-dipole interactions
- Small ions (like Na+ and Cl-) dissolved in water can influence interactions between biomolecules
- In general, the “saltier” the solution --> the less soluble the biomolecule (protein)

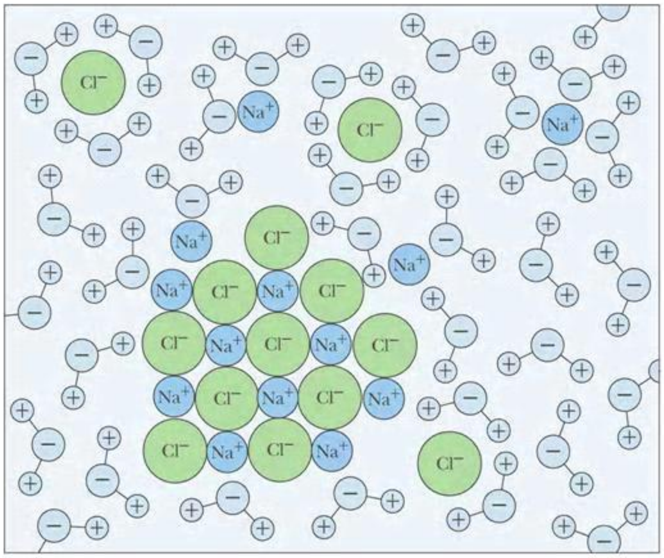


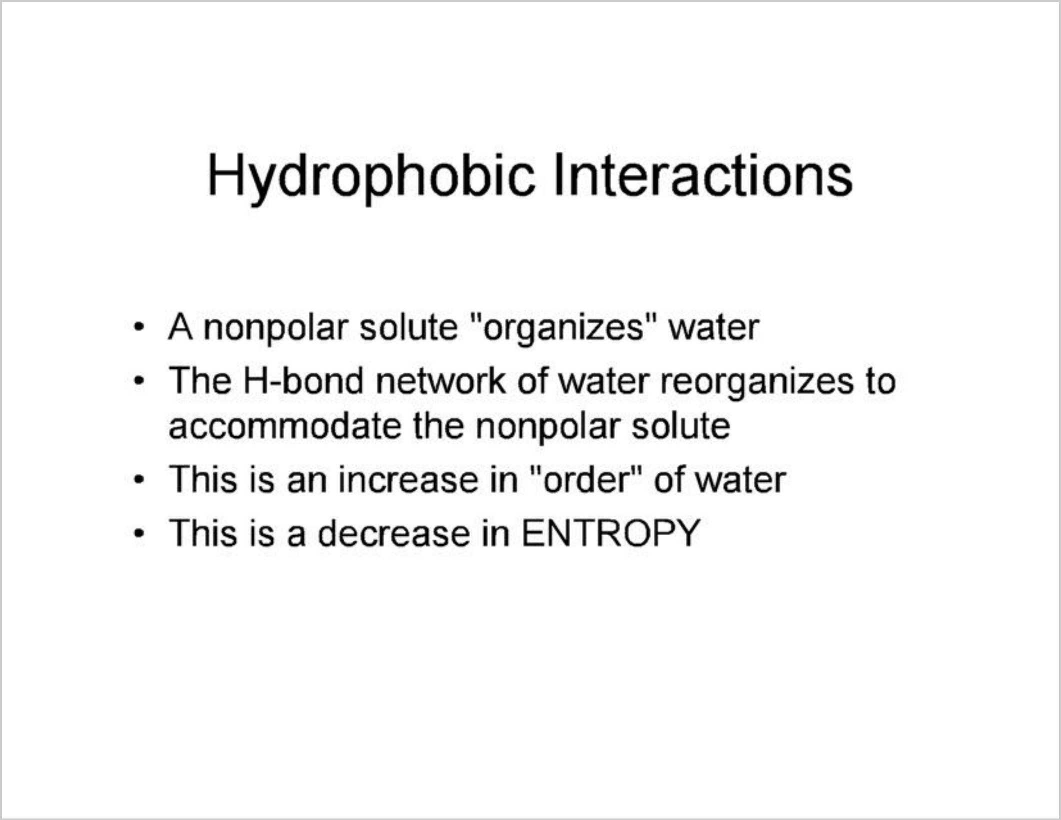
How do we maintain favorable pH in biological systems?

- Buffers!
- Buffering maintains the concentration of protons in aqueous solution
- Before we can discuss buffers let’s review acids and bases

The Solvent Properties of Water Derive from Its Polar Nature

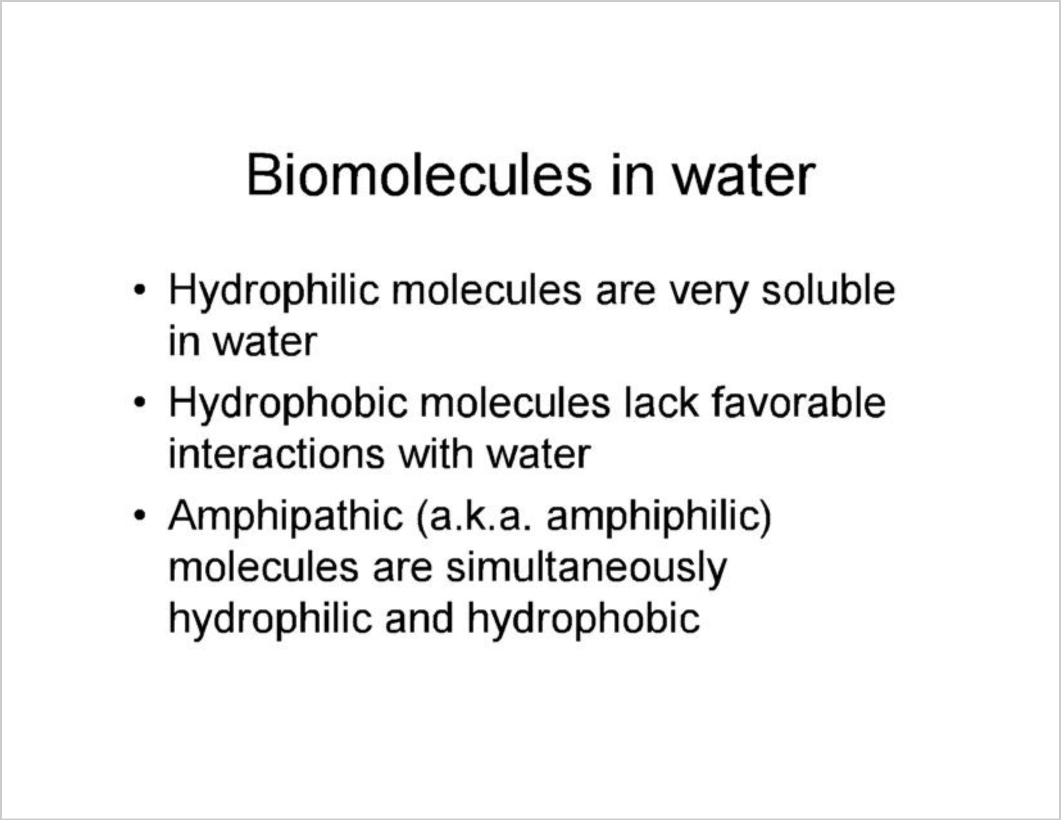
- Ions are always hydrated in water and carry around a "hydration shell"
- Water forms H-bonds with polar solutes
- Hydrophobic interactions - a "secret of life"





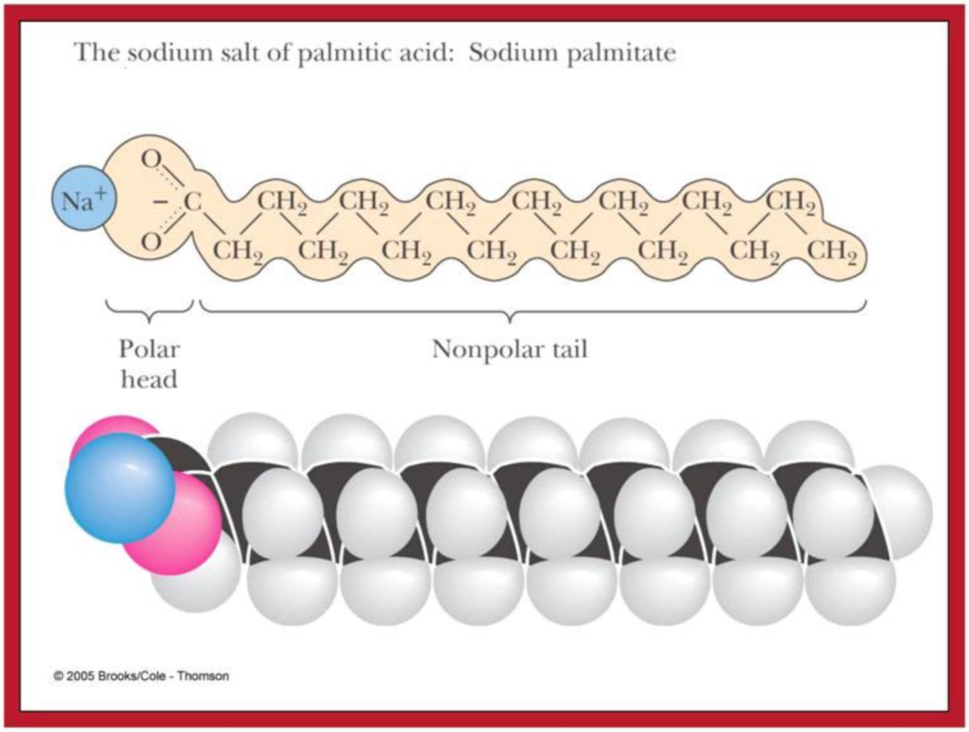
Hydrophobic Interactions

- A nonpolar solute "organizes" water
- The H-bond network of water reorganizes to accommodate the nonpolar solute
- This is an increase in "order" of water
- This is a decrease in ENTROPY



Biomolecules in water

- Hydrophilic molecules are very soluble in water
- Hydrophobic molecules lack favorable interactions with water
- Amphipathic (a.k.a. amphiphilic) molecules are simultaneously hydrophilic and hydrophobic



The sodium salt of palmitic acid: Sodium palmitate

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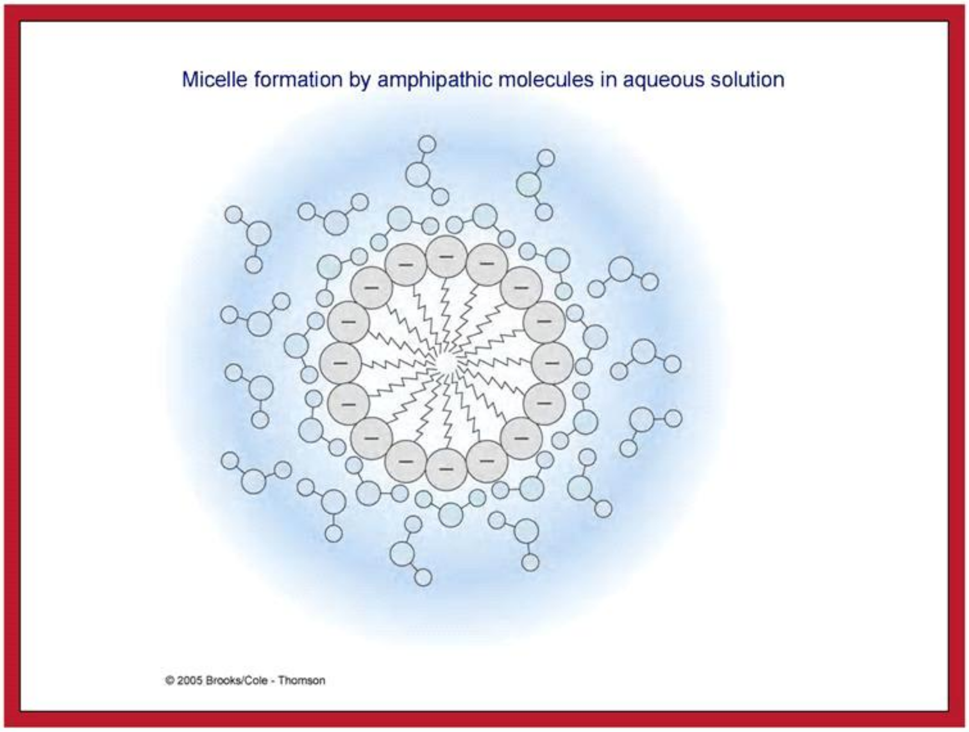

Micelle formation by amphipathic molecules in aqueous solution

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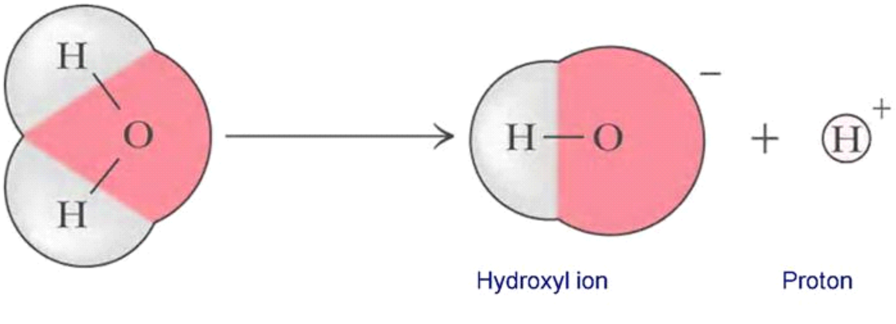
Biomolecules in water

- Most biomolecules have functional groups that are weak acids (e^- pair acceptor) or bases (e^- pair donor)
- Ionization of functional groups affect structure and function

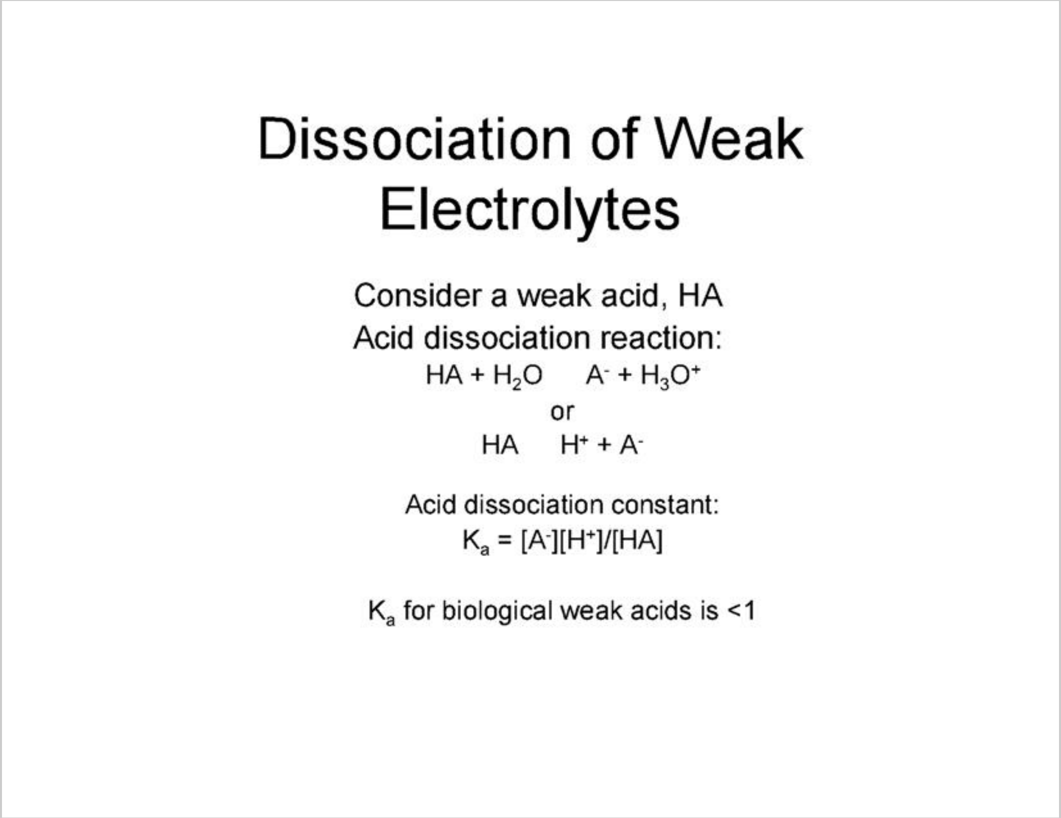
Water can ionize to form H^+ and OH^-



Free protons are immediately hydrated

$H^+ + H_2O$ H_3O^+

Hydronium ion



Dissociation of Weak Electrolytes

Consider a weak acid, HA

Acid dissociation reaction:

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

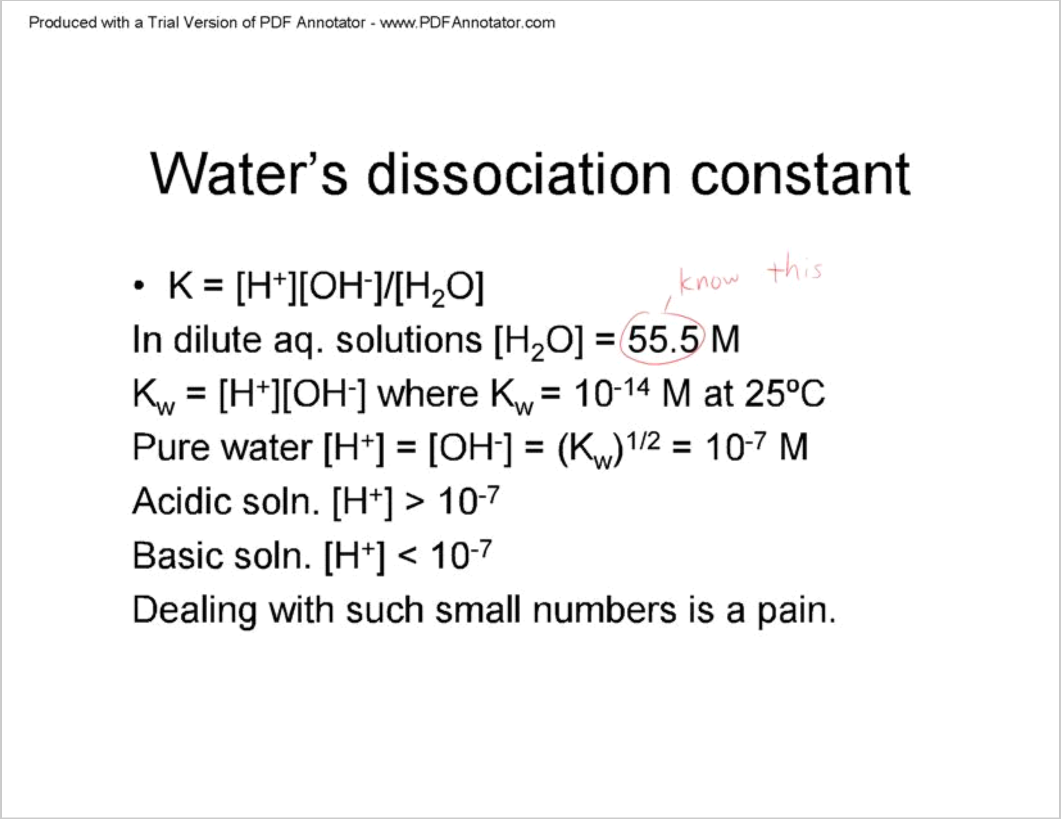
or

$HA \quad H^+ + A^-$

Acid dissociation constant:

$K_a = [A^-][H^+]/[HA]$

K_a for biological weak acids is <1



Water's dissociation constant

- $K = [H^+][OH^-]/[H_2O]$

know this

In dilute aq. solutions $[H_2O] =$ 55.5 M

$K_w = [H^+][OH^-]$ where $K_w = 10^{-14}$ M at 25ºC

Pure water $[H^+] = [OH^-] = (K_w)^{1/2} = 10^{-7}$ M

Acidic soln. $[H^+] > 10^{-7}$

Basic soln. $[H^+] < 10^{-7}$

Dealing with such small numbers is a pain.

The pH Scale for convenience

- $pH = -\log_{10} [H^+]$
- If $[H^+] = 1 \times 10^{-7}$ *M*
- Then *pH* = 7 (neutral)
- Acids: $pH < 7.0$
- Bases: $pH > 7.0$
- pH meter

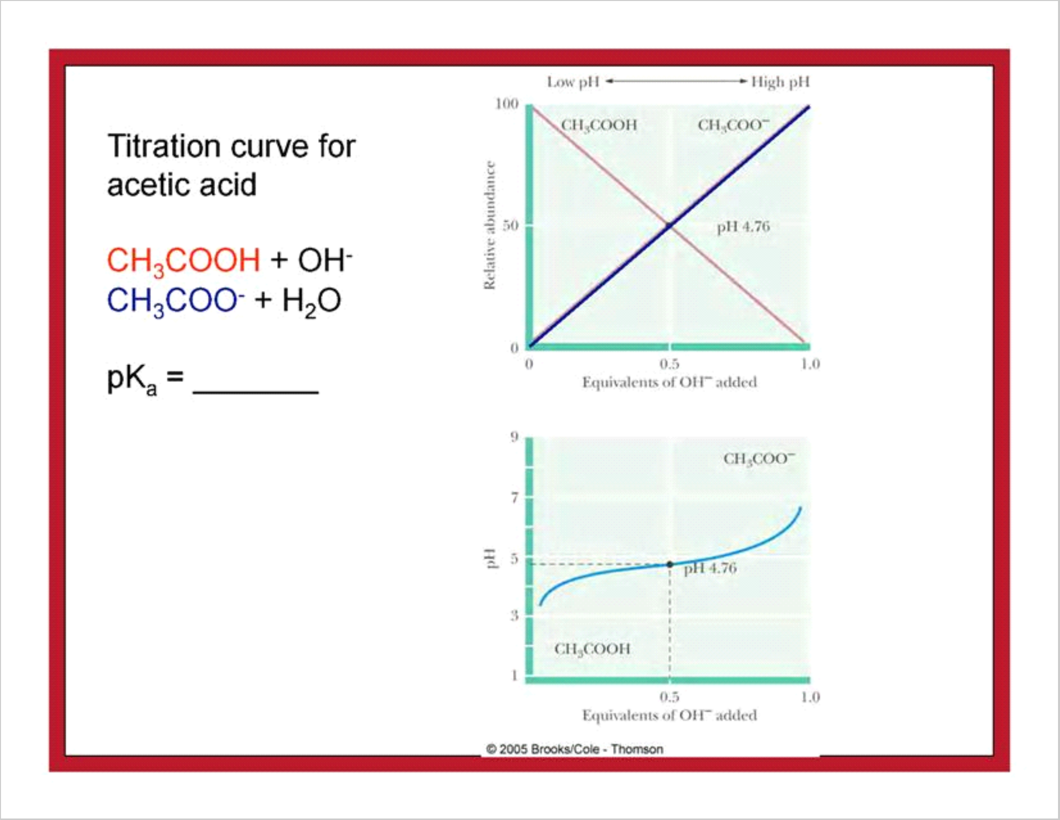
The Henderson-Hasselbalch Equation

Know this! You'll use it constantly

- For any acid HA, the relationship between the pK_a (the concentrations existing at equilibrium) and the solution pH is given by:

$$pH = pK_a + \log ([A^-]/[HA])$$

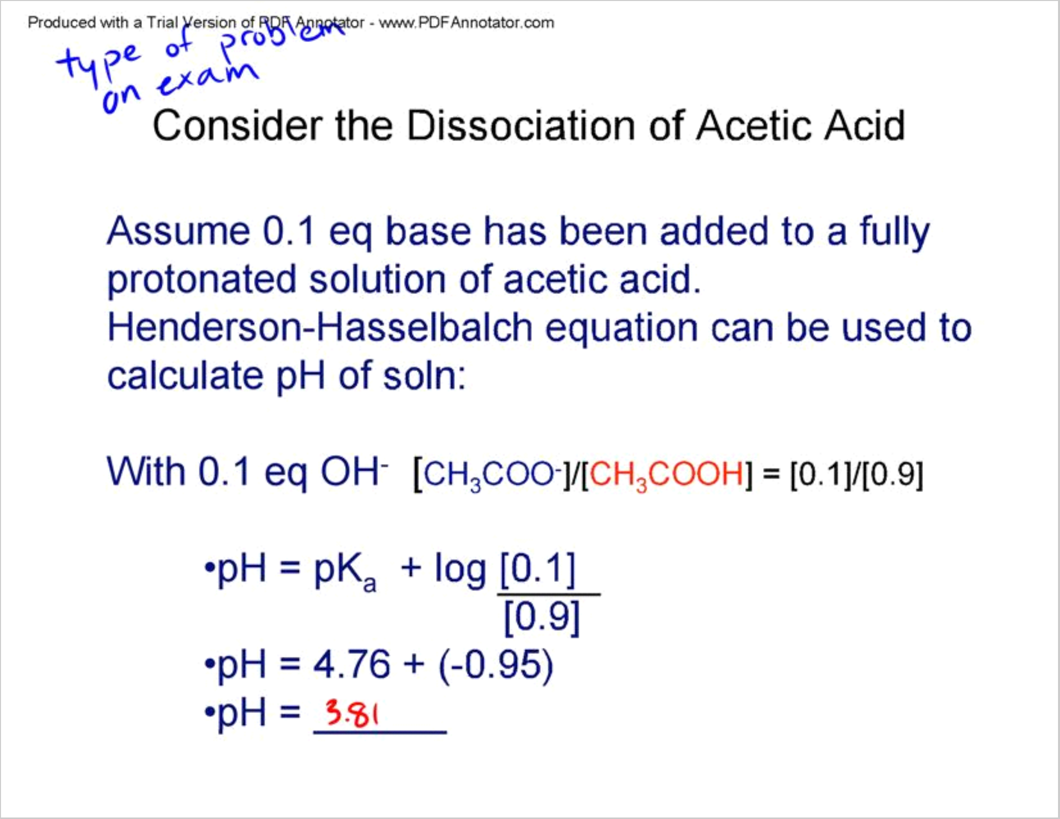
- $[A^-] = [HA] = 1$
- $\log 1 = 0$
- Then $pH = pK_a$



Titration curve for acetic acid

$CH_3COOH + OH^-$
$CH_3COO^- + H_2O$

pK_a = ________



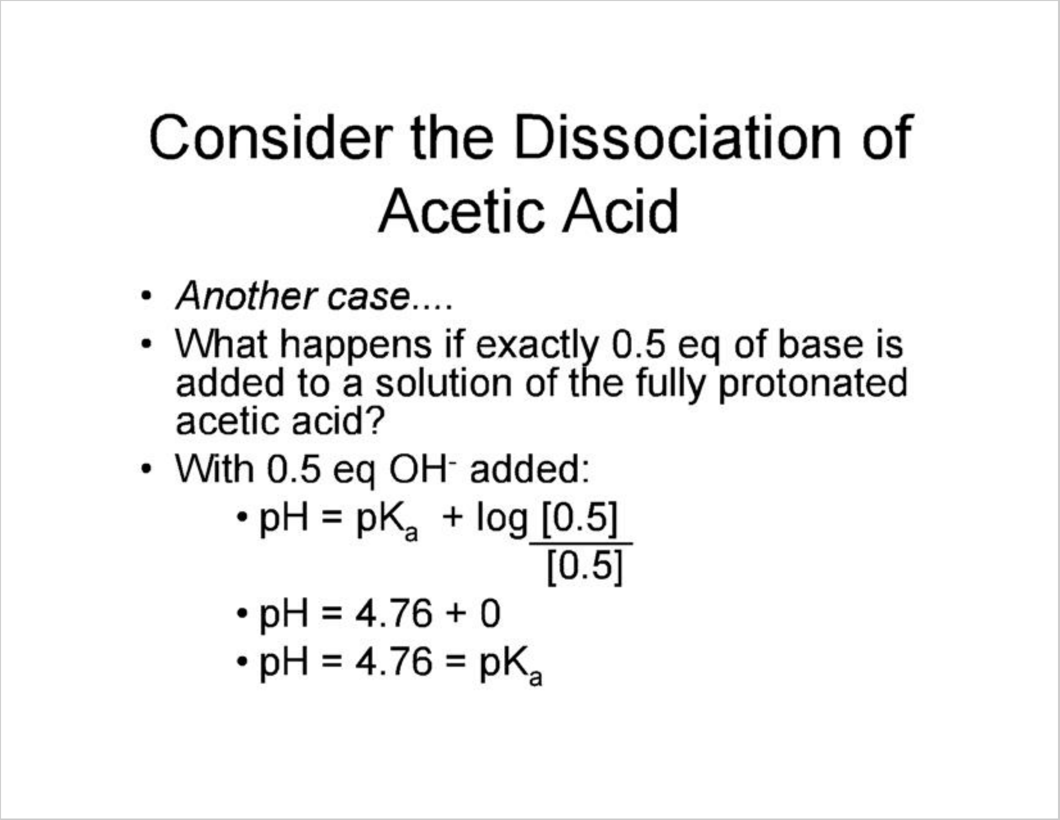
type of problem on exam

Consider the Dissociation of Acetic Acid

Assume 0.1 eq base has been added to a fully protonated solution of acetic acid. Henderson-Hasselbalch equation can be used to calculate pH of soln:

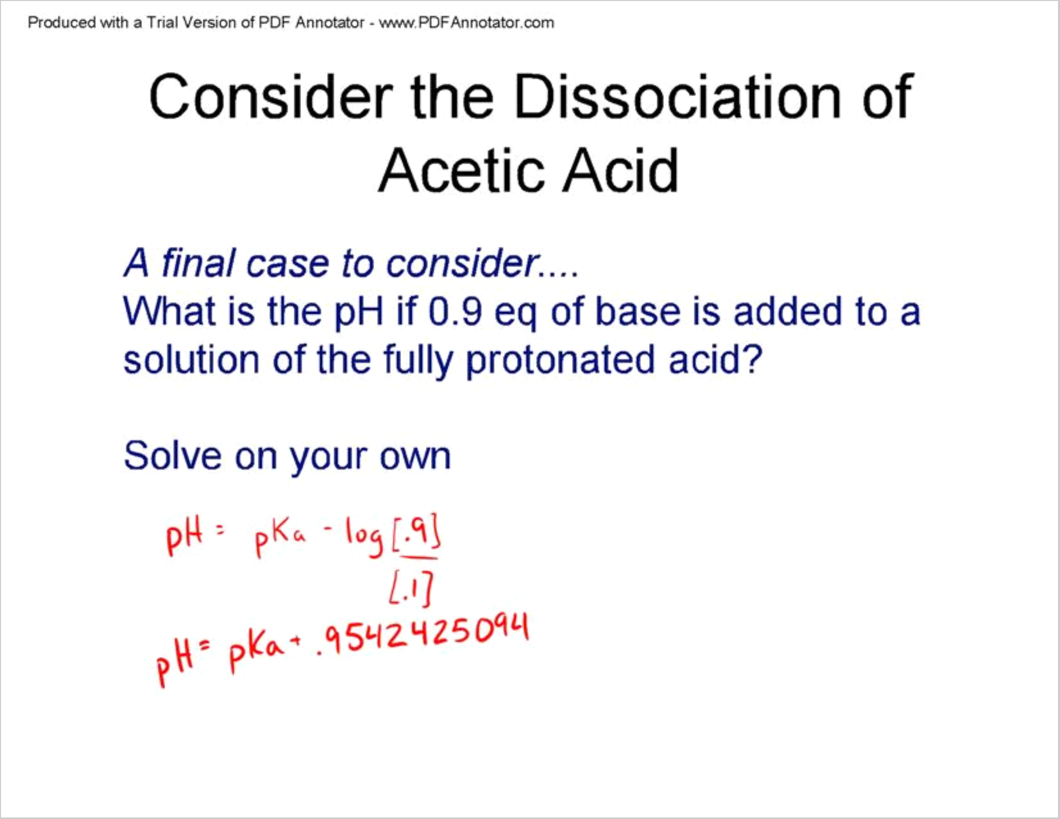
With 0.1 eq OH^- $[CH_3COO^-]/[CH_3COOH] = [0.1]/[0.9]$

- $pH = pK_a + \log \frac{[0.1]}{[0.9]}$
- $pH = 4.76 + (-0.95)$
- pH = 3.81



Consider the Dissociation of Acetic Acid

- *Another case....*
- What happens if exactly 0.5 eq of base is added to a solution of the fully protonated acetic acid?
- With 0.5 eq OH^- added:
  - $pH = pK_a + \log \frac{[0.5]}{[0.5]}$
  - $pH = 4.76 + 0$
  - $pH = 4.76 = pK_a$



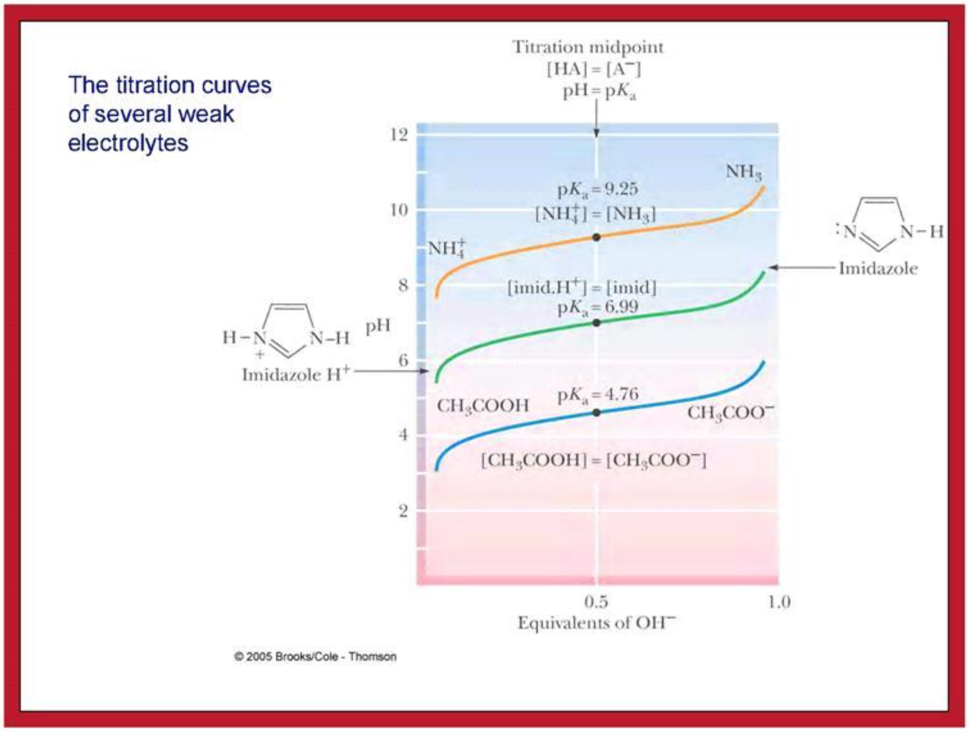
Consider the Dissociation of Acetic Acid

A final case to consider....
What is the pH if 0.9 eq of base is added to a solution of the fully protonated acid?

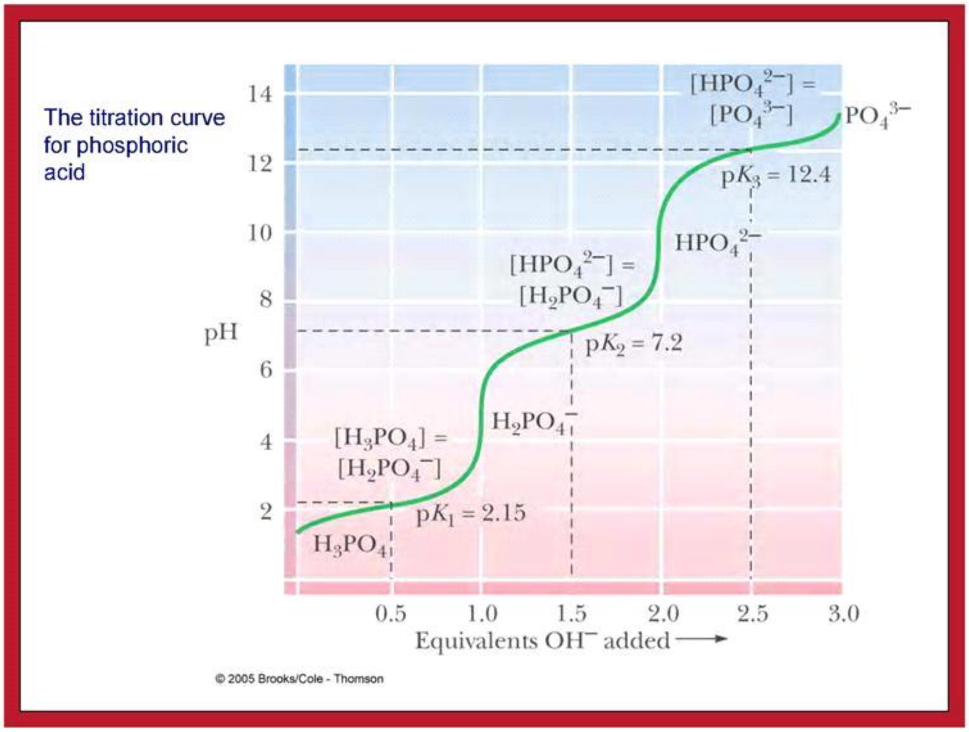
Solve on your own

$pH = pKa - \log \frac{[.9]}{[.1]}$

$pH = pKa + .9542425094$



The titration curves of several weak electrolytes

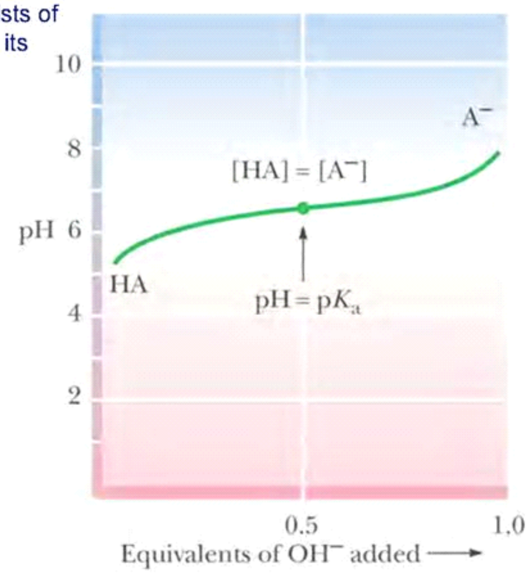


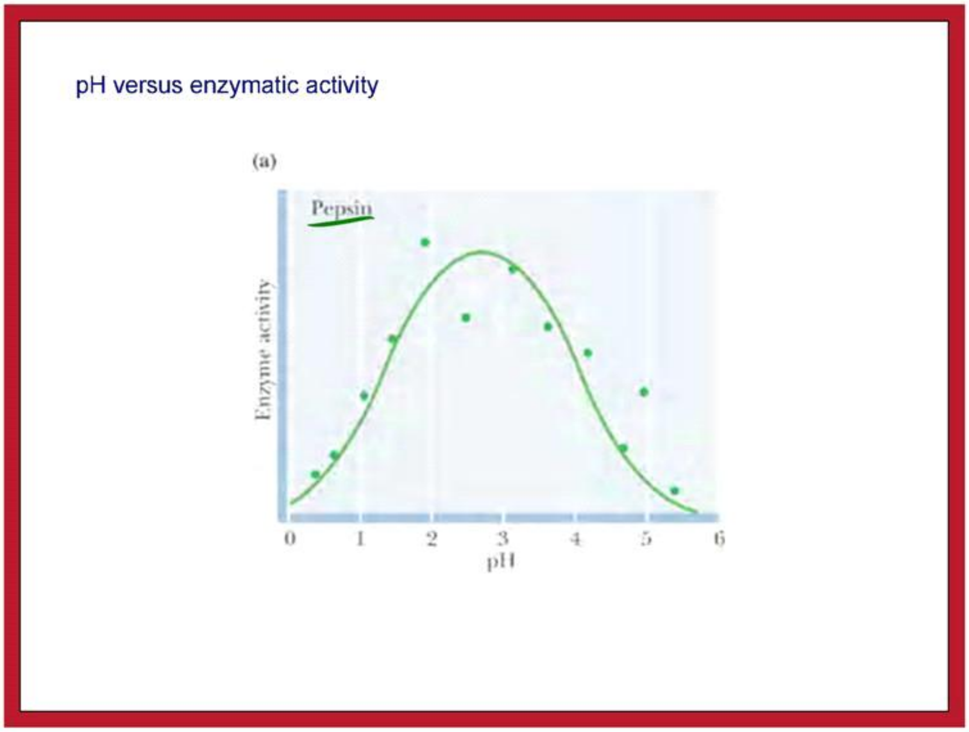
The titration curve for phosphoric acid

What Are Buffers, and What Do They Do?

- Buffers are solutions that resist changes in pH as acid and base are added
- Most buffers consist of a weak acid and its conjugate base
- Note how plot of pH versus base added is flat near the pK_a
- Buffers can only be used reliably within a pH unit of their pK_a

A buffer system consists of a weak acid, HA, and its conjugate base, A^-





pH versus enzymatic activity