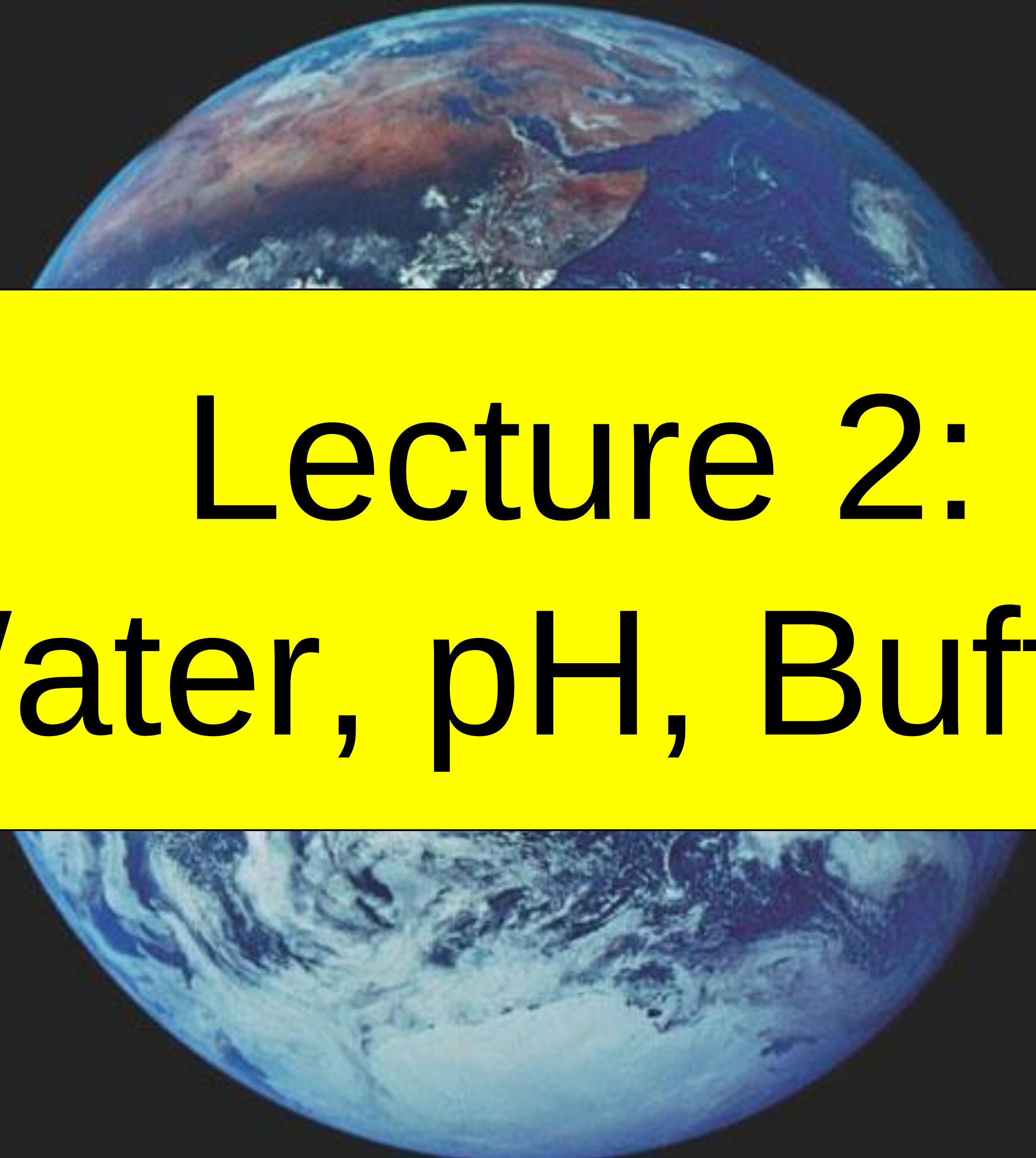
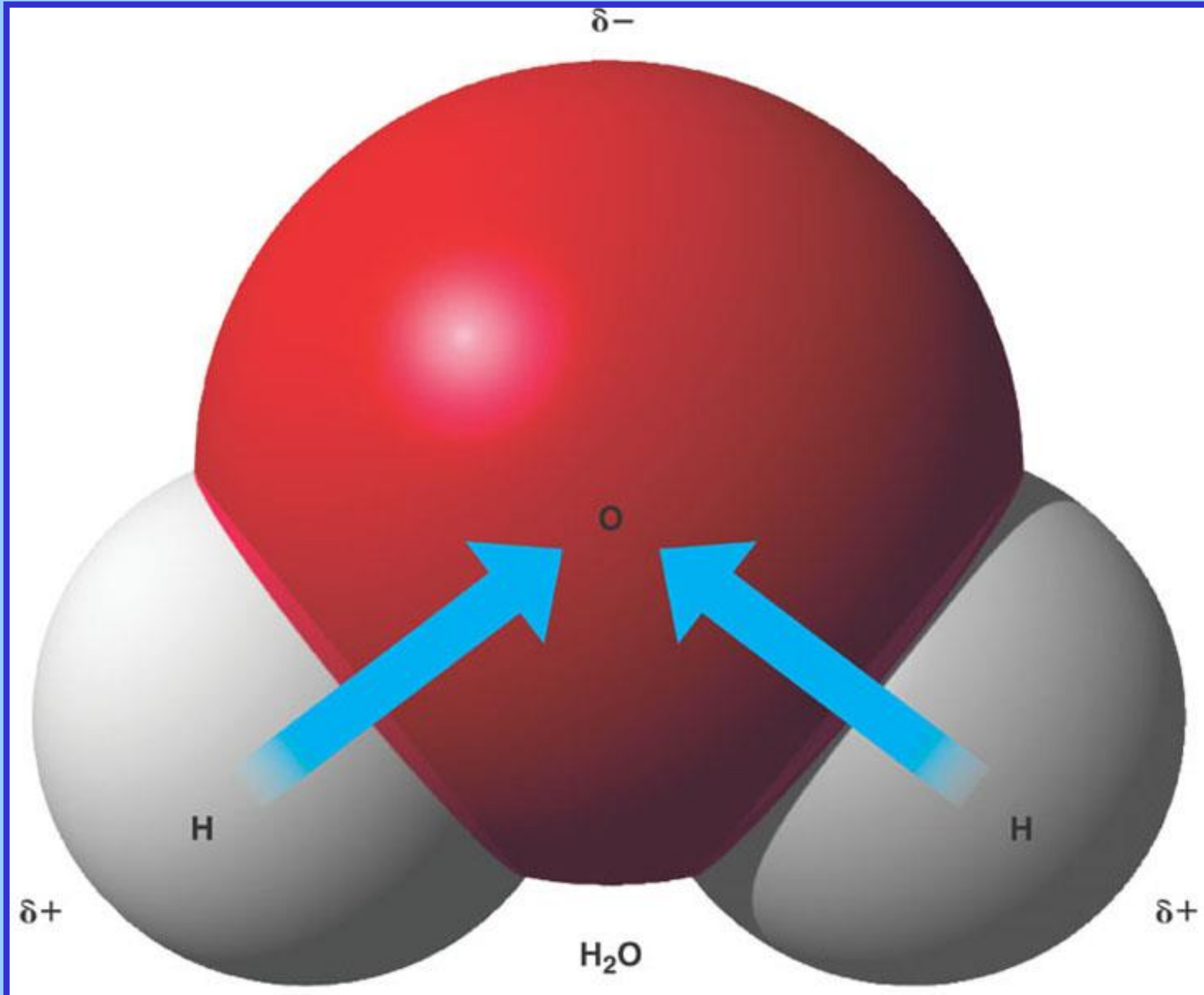
Lecture 2:
Water, pH, Buffers



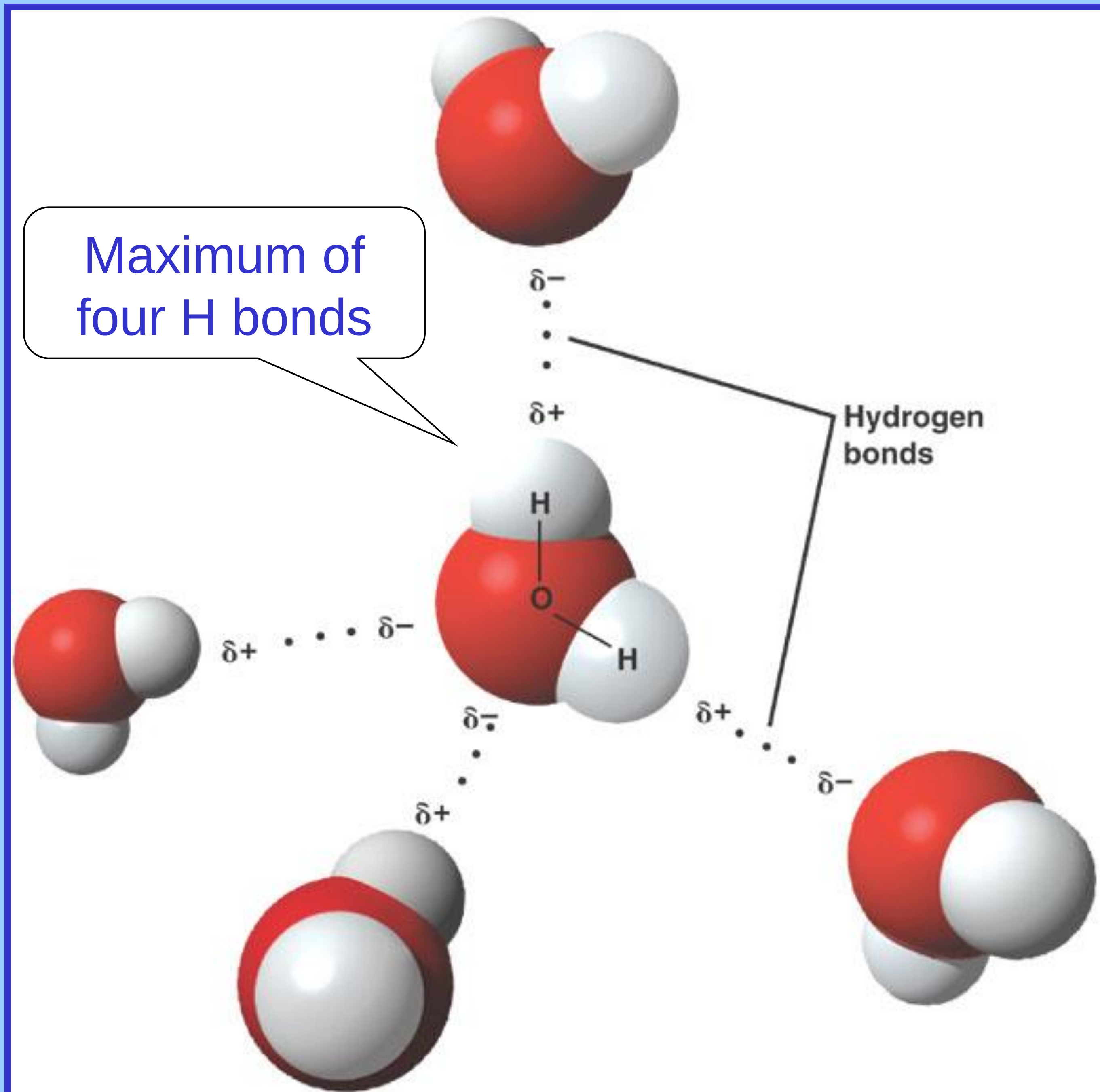
Outline

- Properties of Water
- pH
- Buffers
- Water's Unique Role in the Fitness of the Environment

H_2O & Polar Covalence



H_2O & Hydrogen Bonds



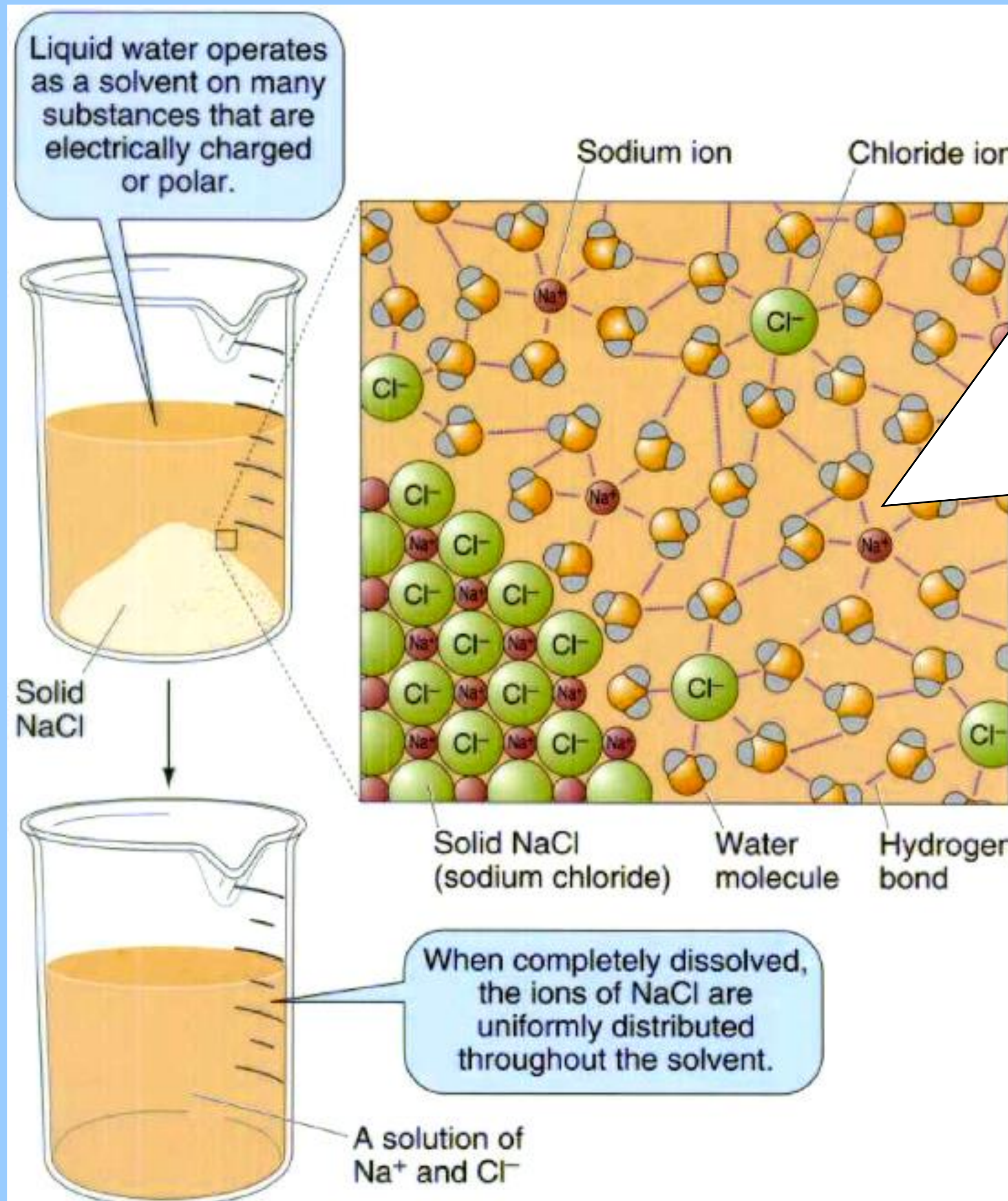
H_2O Properties from H Bonds

- Water molecules adhere to other molecules (adhesion)
- Liquid water effects hydrophobic exclusion
- Liquid water has high specific heat
- Liquid water has high heat of vaporization
- Water molecules adhere to each other (cohesion)
- Water is a liquid rather than gas at room temperature
- Ice floats
- Liquid water Is a powerful polar solvent

Hydrophilic/Hydrophobic

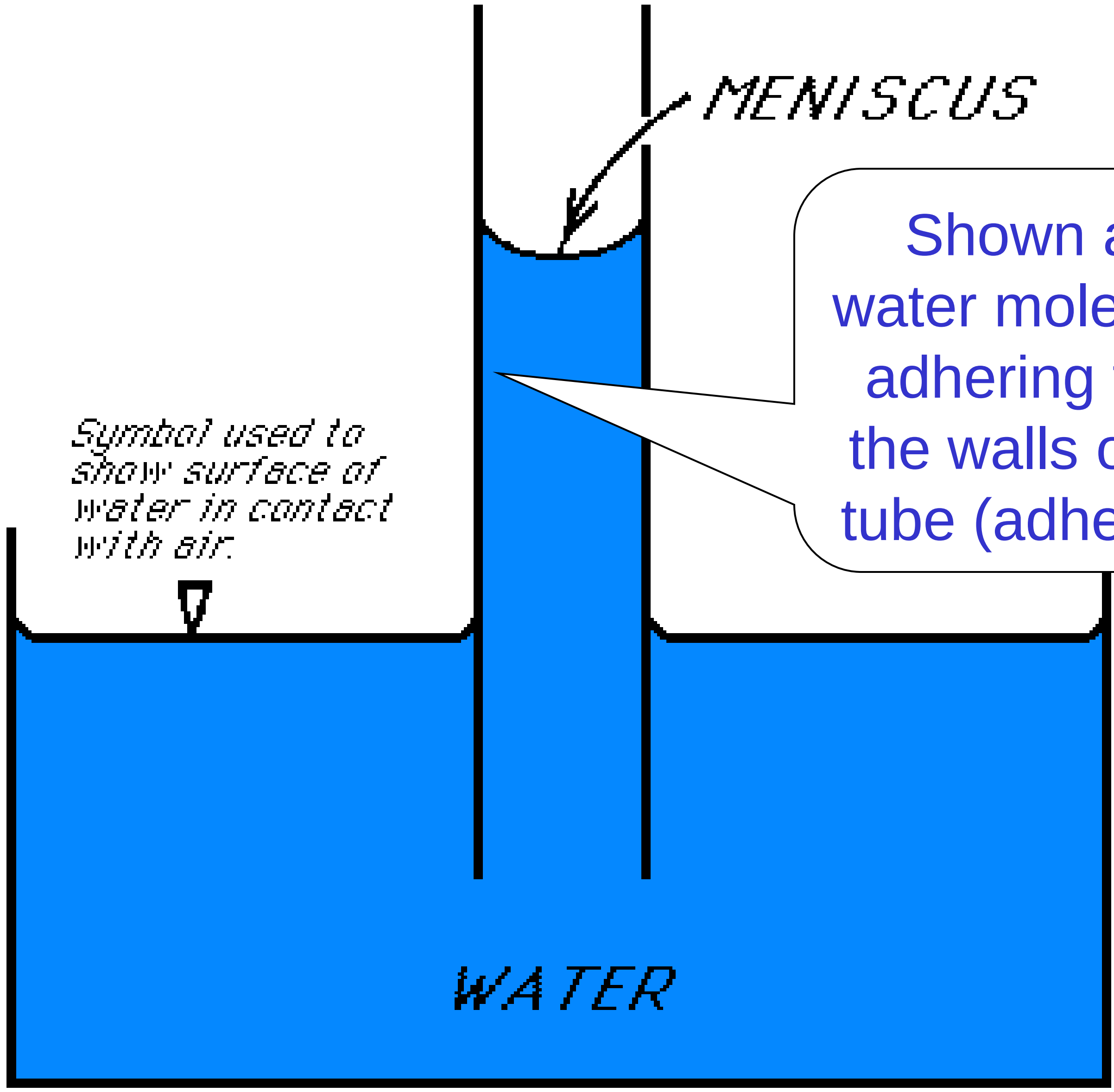
- Hydrophilic = Water Loving
  - These are things that like to dissolve in or be wet by water
  - Typically these things have polar bonds or full charges
- Hydrophobic = Water Hating
  - Things that do <u>not</u> like to dissolve in or be wet by water
  - Typically these things lack polar bonds or full charges
  - For example, hydrocarbons are hydrophobic, e.g., oils

Adhesion—Hydration Shells



Shown are water molecules adhering to various ions (adhesion), forming hydration shells around them

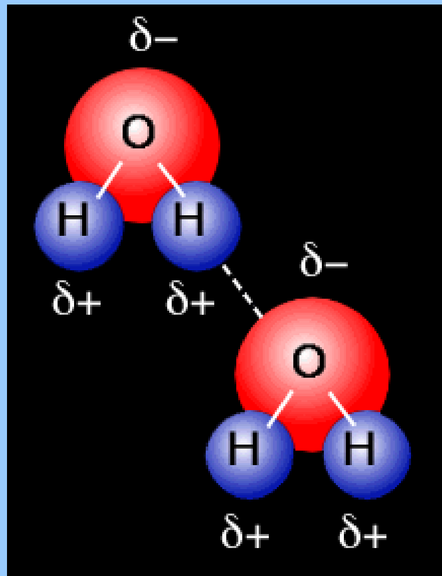
Adhesion—Capillary Action



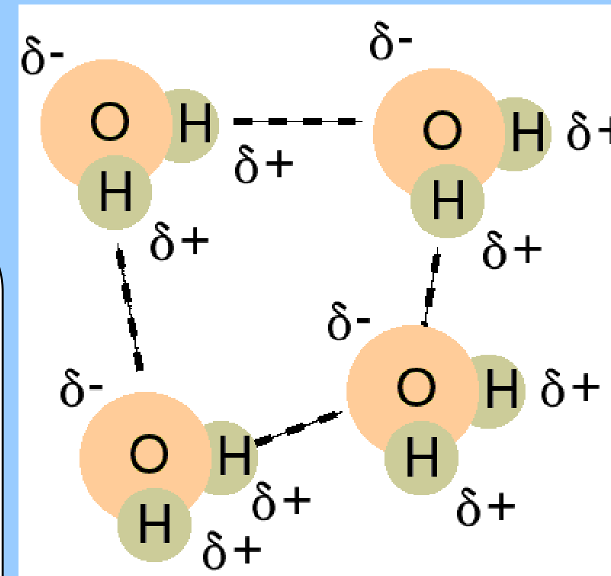
Water rising in a small glass tube by capillary action.

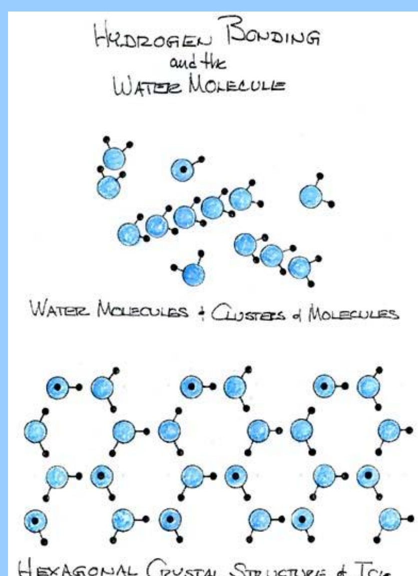
Shown are water molecules adhering to to the walls of the tube (adhesion)

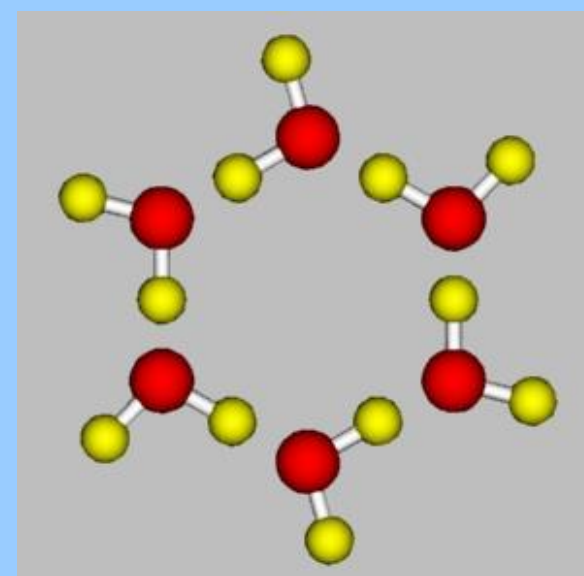
Cohesion



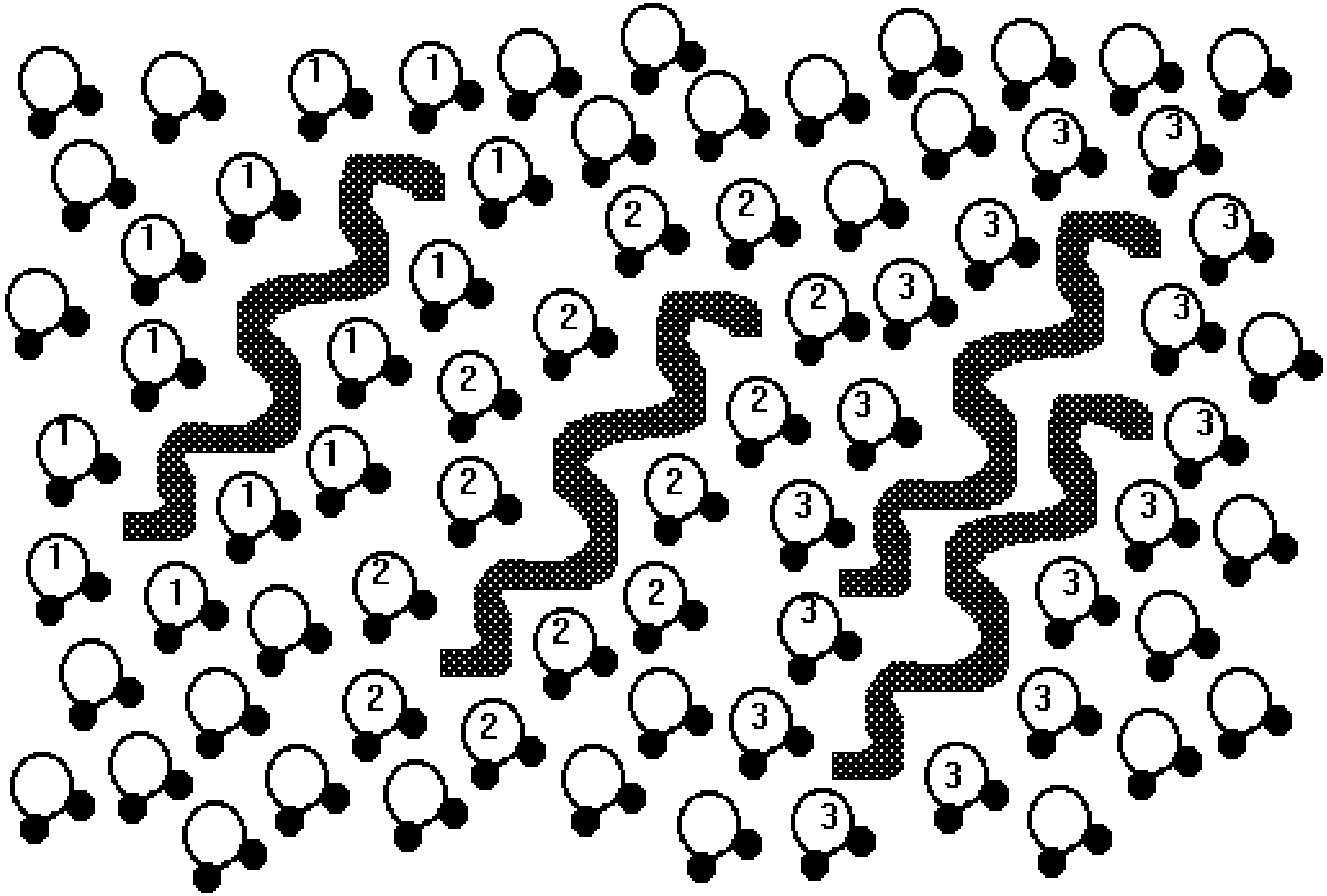
“Cohesion” refers to the high potential for water molecules to hydrogen bond to each other





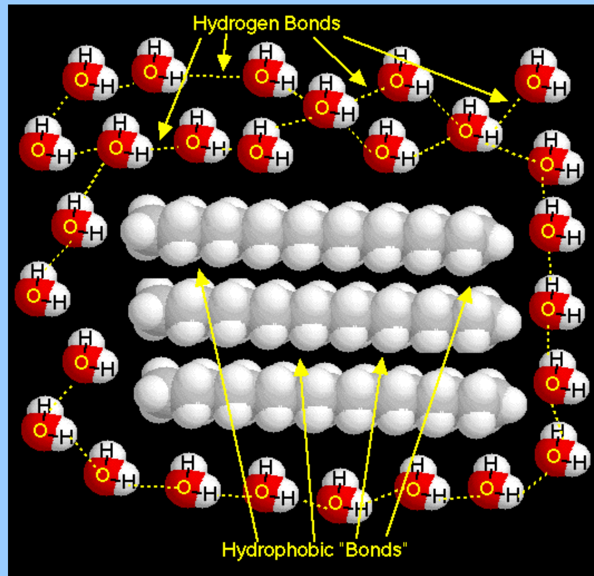


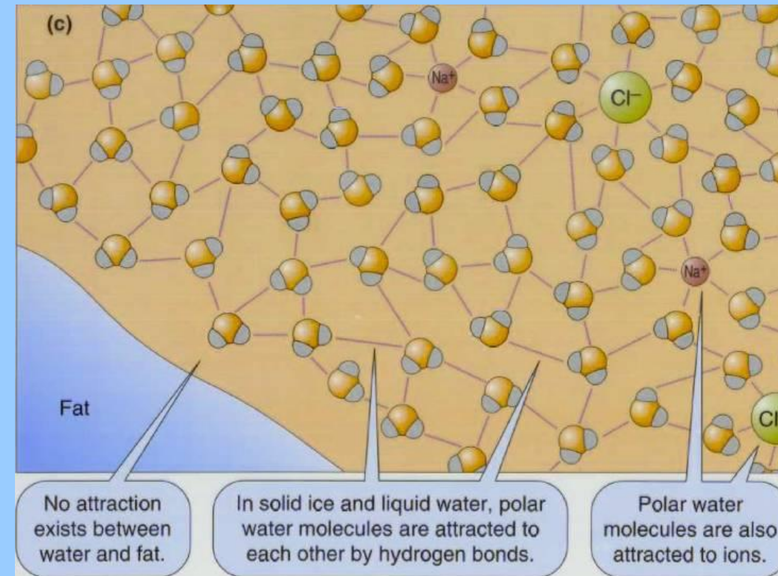
Hydrophobic Exclusion

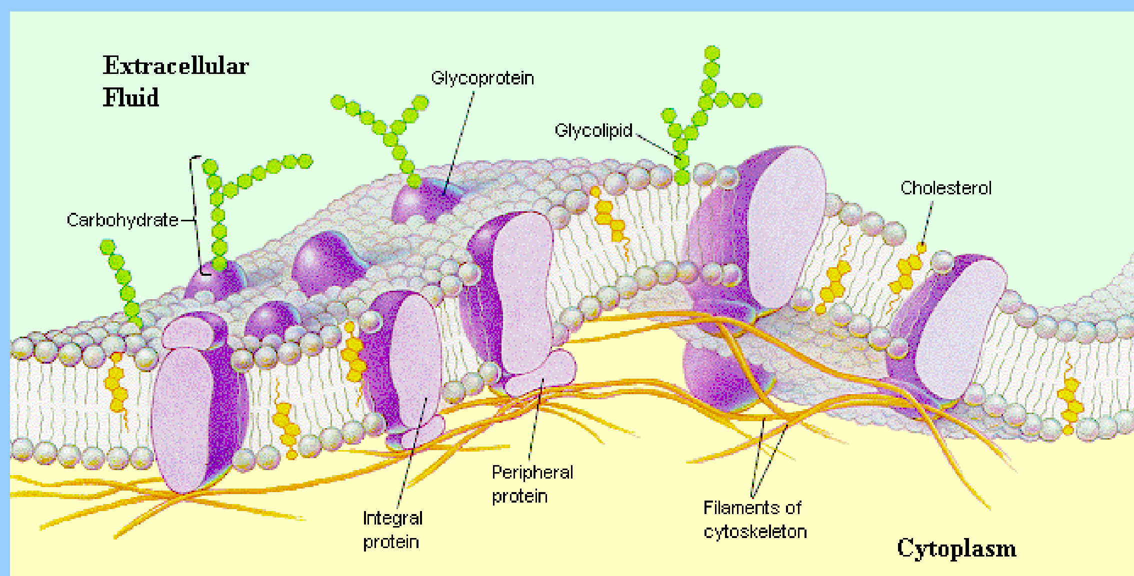


non-polar molecules (2-D squiggles) displace more water molecules dissolved (26 = 13 + 13) than "banded together" (16).

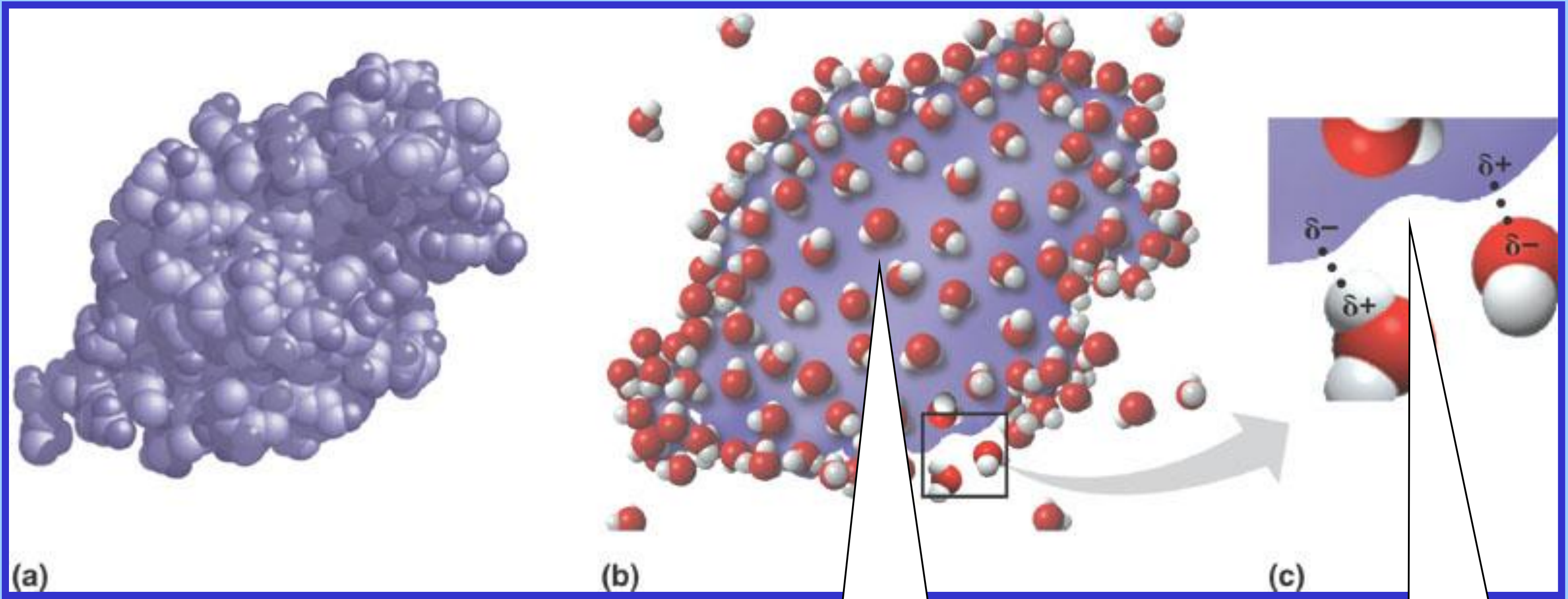
Hydrophobic Exclusion

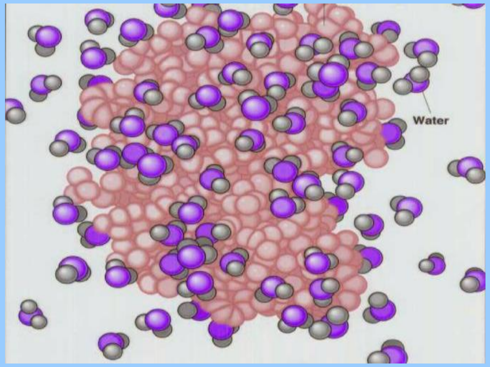






Hydrophobic Excl. of Globular Protein





Hydrophobic Interior Hides from Water

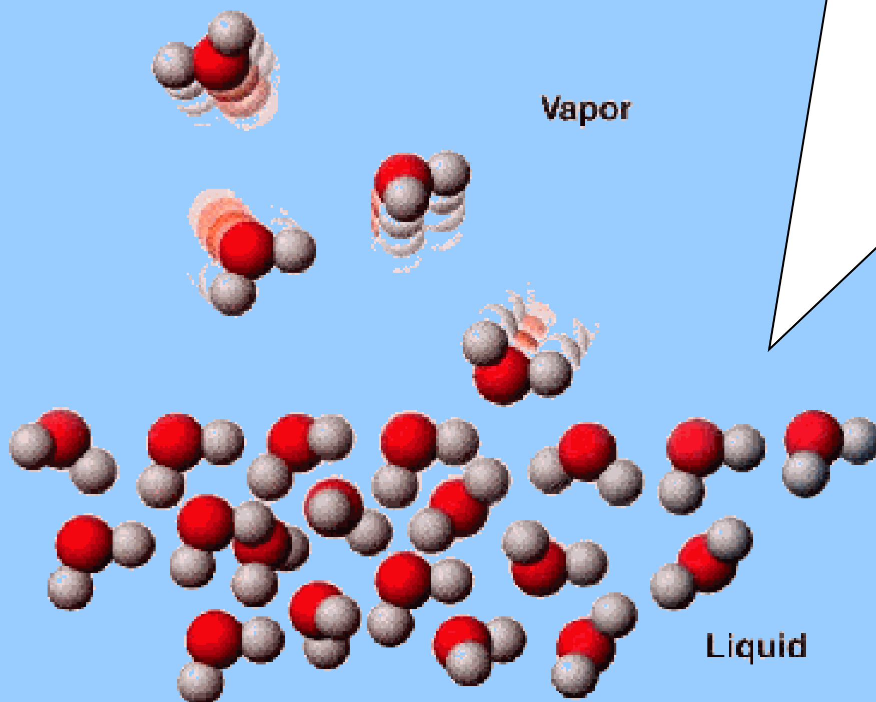
Hydrophilic Exterior “Embraces” Water

H_2O High Specific Heat

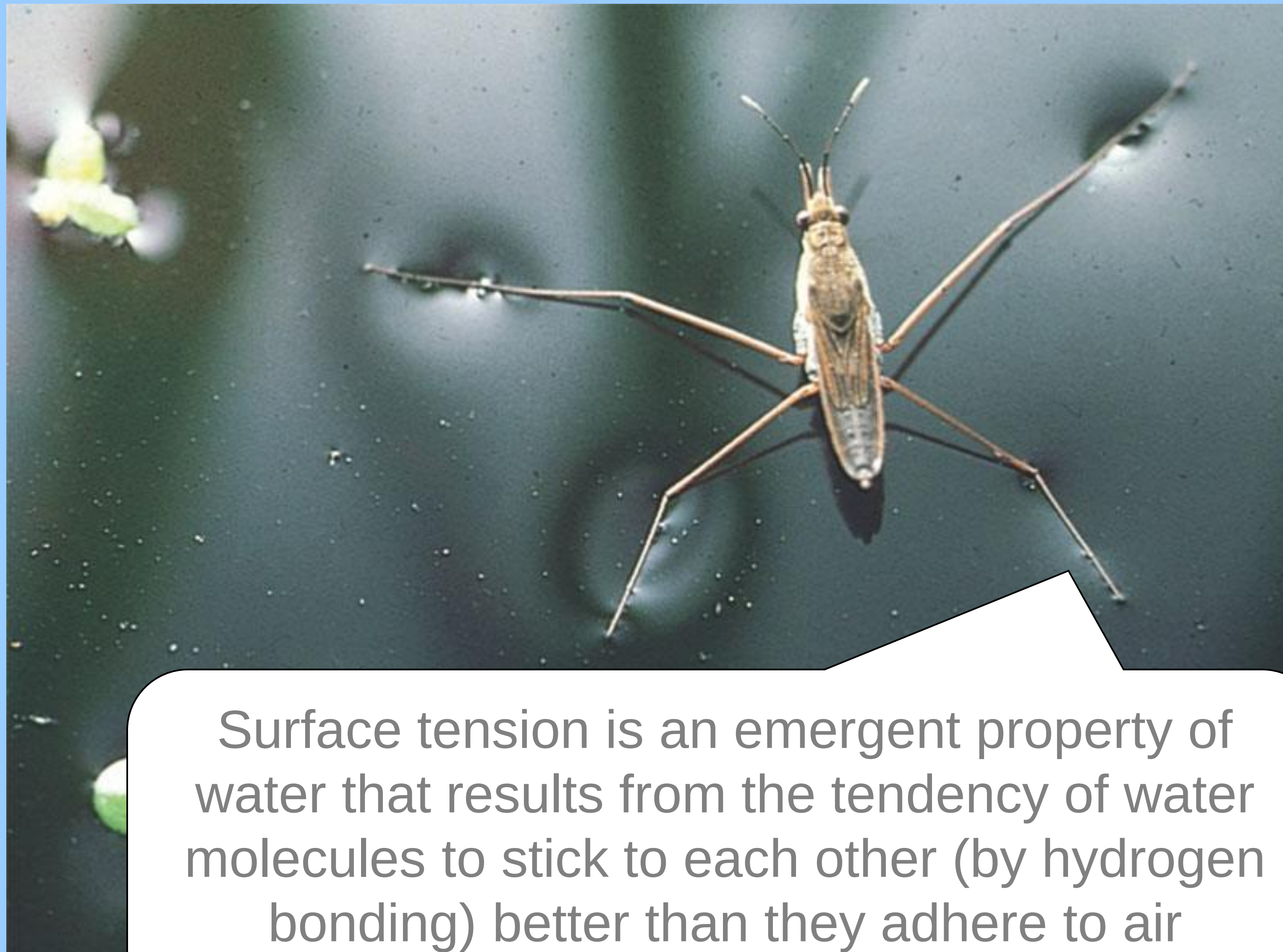
- Temperature is a measure of molecular movement
- To move around more, water molecules must break H bonds
- Breaking H bonds requires energy (water wants to H bond)
- So, much heat that could raise temps instead breaks H bonds
- Now for the less intuitive part…
- If water is to move around, then less then H bonds are formed
- Water wants to form H bonds: bond formation <u>releases</u> energy
- So, as you take heat away from water, water compensates by releasing heat!
- Due to H bonds, water resists heating & cooling—technically, we describe this as water having a high specific heat

High Heat Vaporization

Water resists evaporating (i.e., vaporizing) because hydrogen bonds must be broken in order for water to transition from the liquid to the gas state



Surface Tension



Surface tension is an emergent property of water that results from the tendency of water molecules to stick to each other (by hydrogen bonding) better than they adhere to air molecules

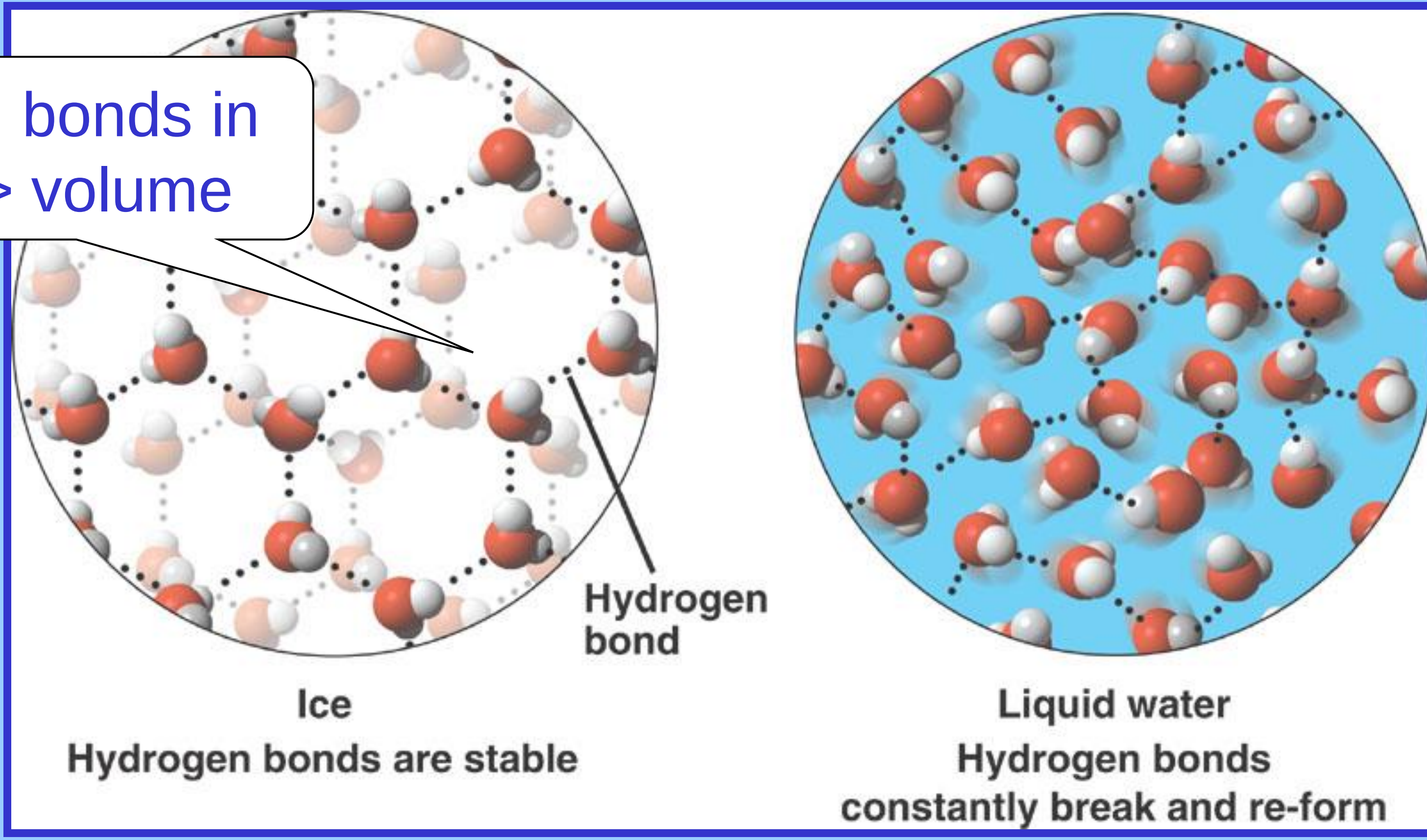
H_2O Liquid at Room Temp

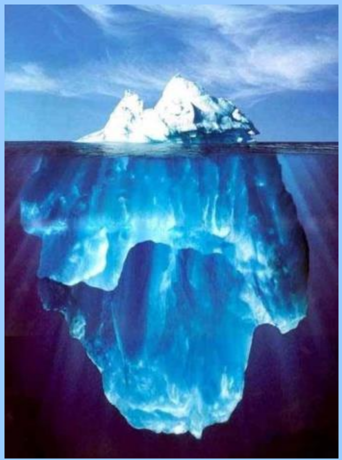
Formula	Mol.Weight	Phys. State
CO_2	44	Gas
O_2	32	Gas
CO	28	Gas
N_2	28	Gas
H_2O	18	Liquid
CH_4	16	Gas
H_2	2	Gas

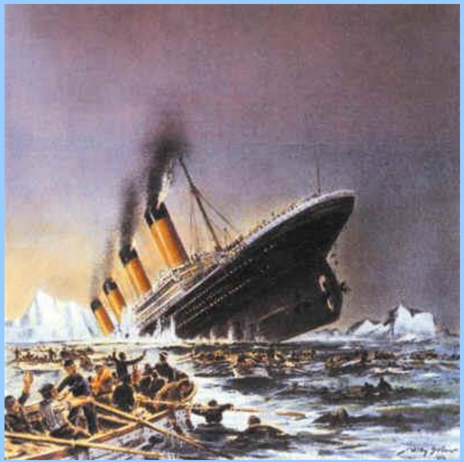
Water is a liquid at room temperature not because of its mass because of hydrogen bonding (cohesion)

Ice Floats

More H bonds in ice = > volume

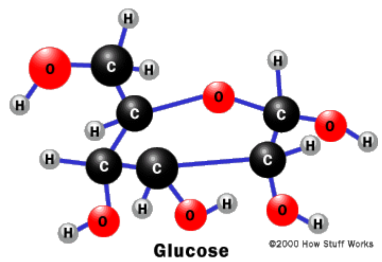


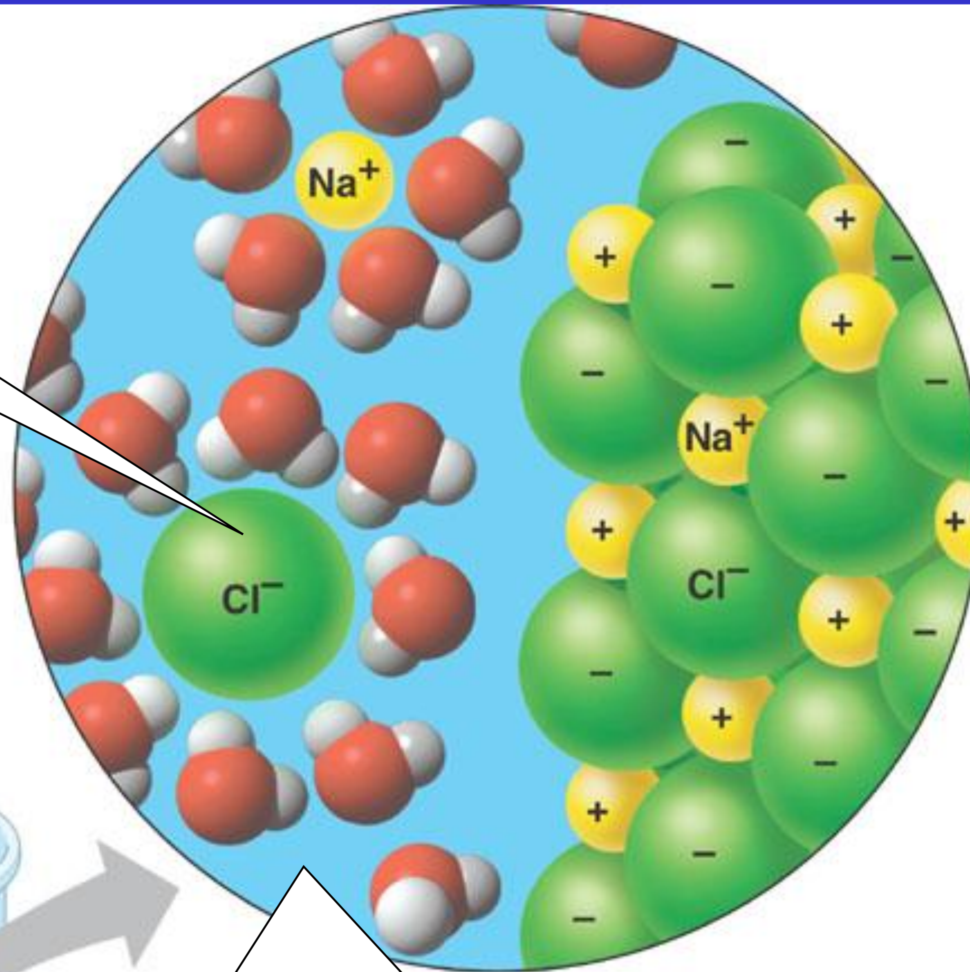


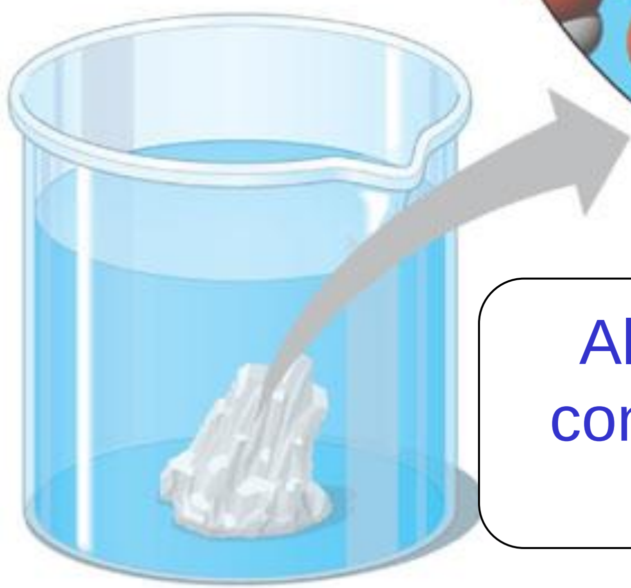


Powerful Polar Solvent

Note hydration shell



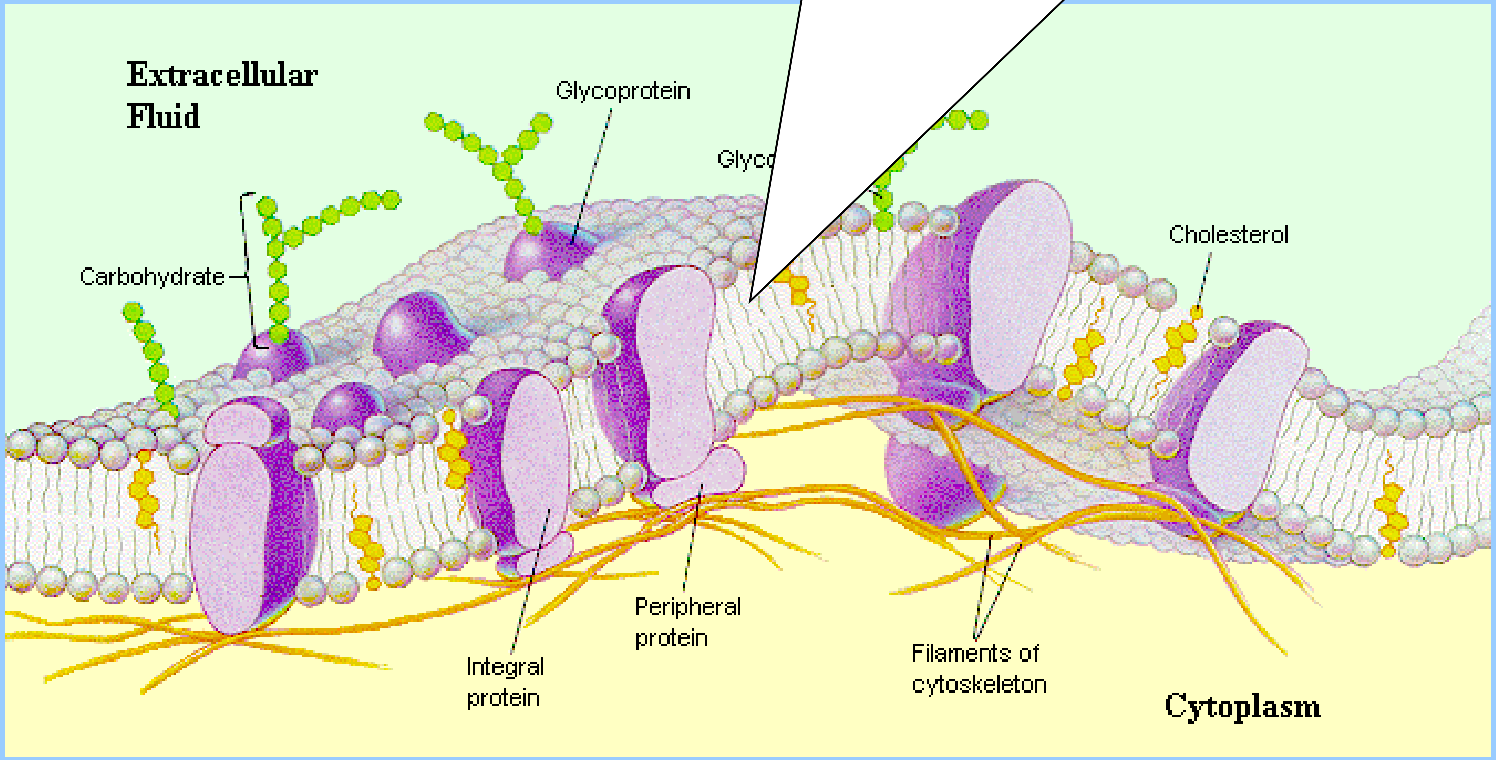




Also Effective with Molecules containing only partial charges, e.g., sugars and alcohols

Crucial to Life

The most important property of water to the existence of life has to do with the ability of water to dissolve some substances and exclude others



Water is considered the "universal solvent"

- Water dissolves substances to which it can readily hydrogen bond (or is otherwise attracted to typically because the substance contains full or partial charges)
- Solute = a substance that dissolves in another substance
- Solvent = the substance the solute dissolves in
- Solution = a solvent in which solutes are dissolved
- Aqueous solution = a solution in which water is the solvent

Molarity and pH

- 342 grams of sucrose = 1 mole of sucrose
- $C_{12}H_{22}O_{11}$ = (12x12) + (22x1) + (11x16)
- A solution of sucrose can be described based on its concentration, i.e., how much sucrose is present in a specific amount of water
- A 1.0 Molar (1M) solution of sucrose is defined as 1.0 mole of sucrose for every 1.0 liter of water

Water as a Solution

- Water dissociates into H^+ and OH^- spontaneously, so all water contains these ions in solution, albeit in very small amounts
- Notation:
  - $[H^+]$ is read "H^+ concentration"
  - $[OH^-]$ is read "OH^- concentration"
- In *any* solution, the **product** of $[H^+]$ and $[OH^-]$ is a constant: $[H^+] \times [OH^-] = 10^{-14}M$
- In a neutral solution, $[H^+] = 10^{-7}M$
- In a neutral solution, $[OH^-] = 10^{-7}M$

A solution in which the $[H^+]$ is **larger** than in a neutral solution is an acidic solution

The range of $[H^+]$ for acids is 10^{-1}M to 10^{-7}M

The pH of acids range from 1 to 7

The pH is found by: pH = (-log $[H^+]$)

An example of an acid is HCl

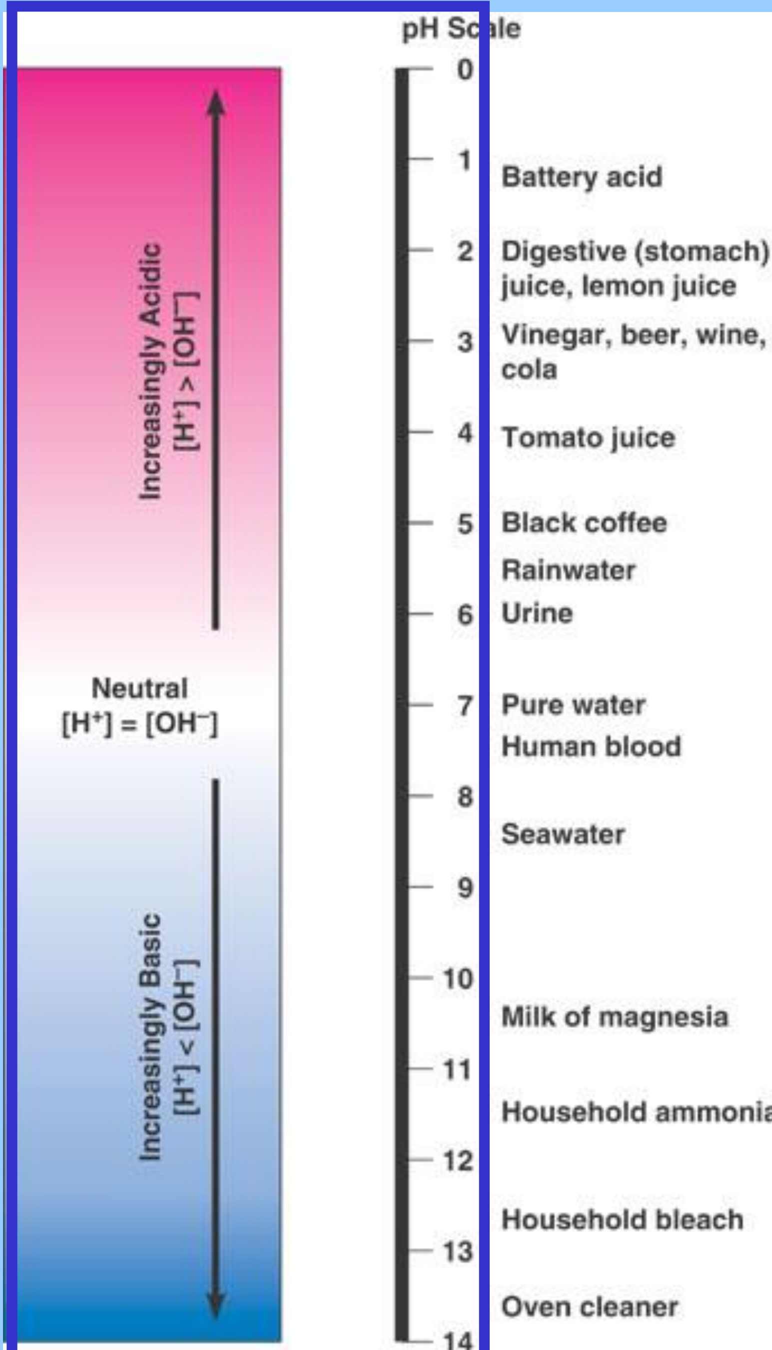
A solution in which the $[H^+]$ is **smaller** than in a neutral solution is a basic solution

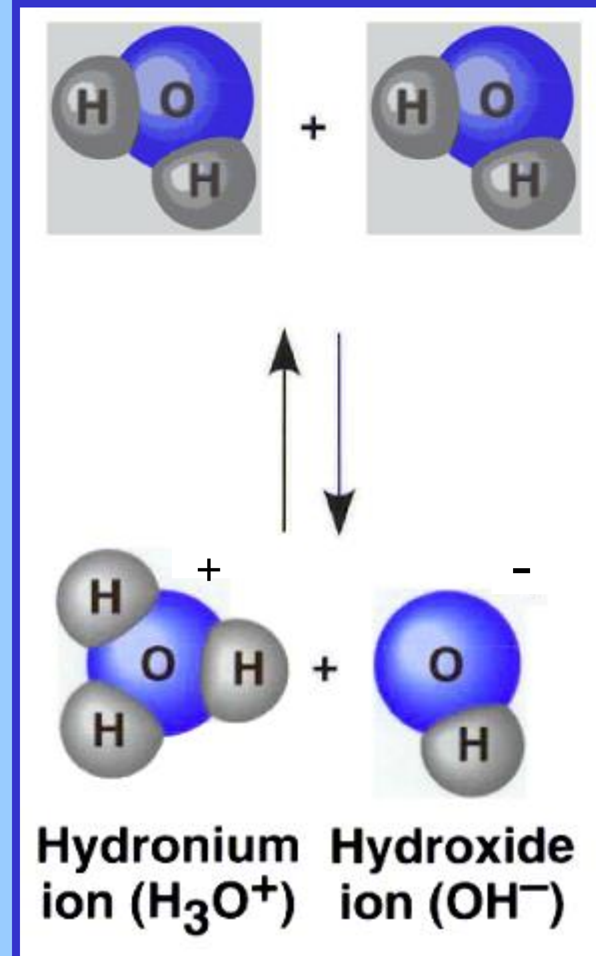
The range of $[H^+]$ for bases is 10^{-7}M to 10^{-14}M

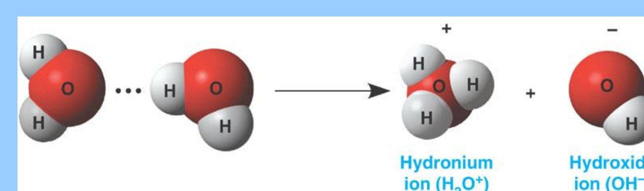
The pH of bases range from 7 to 14

An example of a base is NaOH

pH & Chemical Equilibria





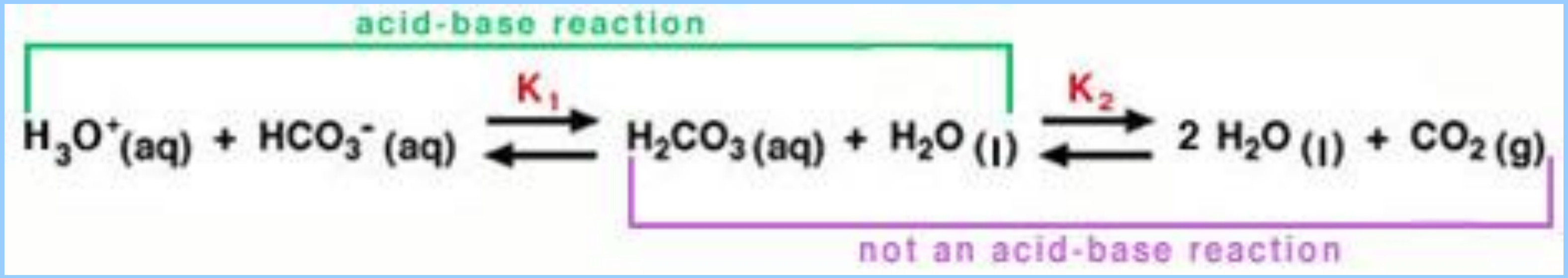


Buffers

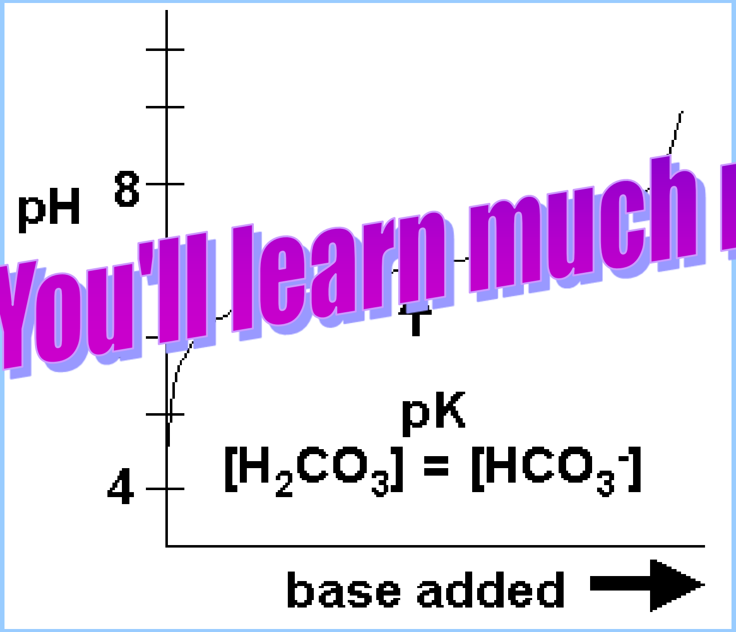
- The pH in living systems is maintained by buffer solutions that can accept or lose H^+ or OH^- without a corresponding change in solution pH
- Blood pH has a value of 7.4
- A change of 0.2 in either direction is serious, and changes to 6.9 or 7.9 are fatal if not corrected immediately
- The blood is buffered by CO_2 and HCO3
- The levels of these molecules is maintained through the action of the lungs and kidneys

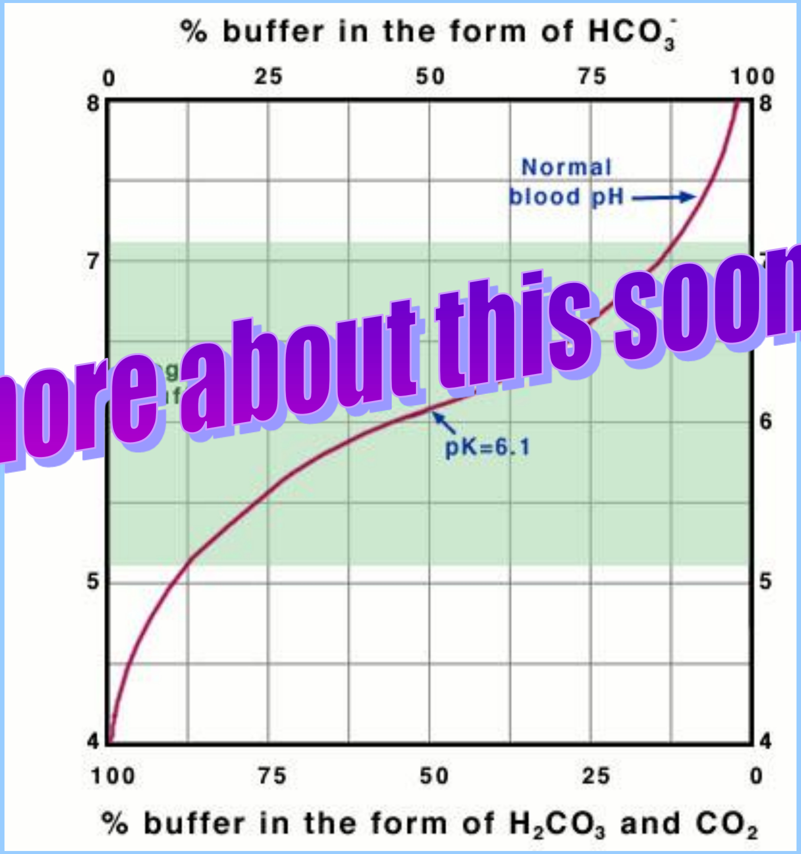
Carbonic-Acid-Bicarbonate Buffering (e.g., of blood)

pH Buffering



>pH = less $H_3O^+ \approx H^+$





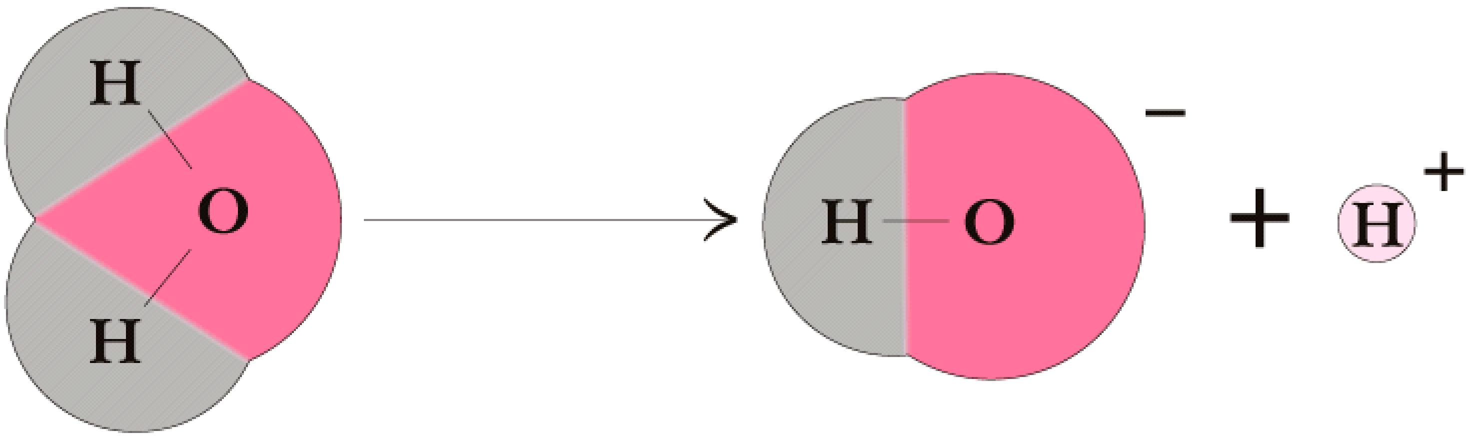
You'll learn much more about this soon

The pH Scale

A convenient means of writing small concentrations:

- $pH = -\log_{10}[H^+]$
- If $[H^+] = 1 \times 10^{-7}\ M$
- Then $pH = 7$

Garrett & Grisham: Biochemistry, 2/e
Figure 2.9



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Dissociation of Weak Electrolytes

Consider a weak acid, HA

- The acid dissociation constant is given by:
- $HA \rightarrow H^+ + A^-$
- $K_a = \dfrac{[\,H^+\,]\,[\,A^-\,]}{[HA]}$

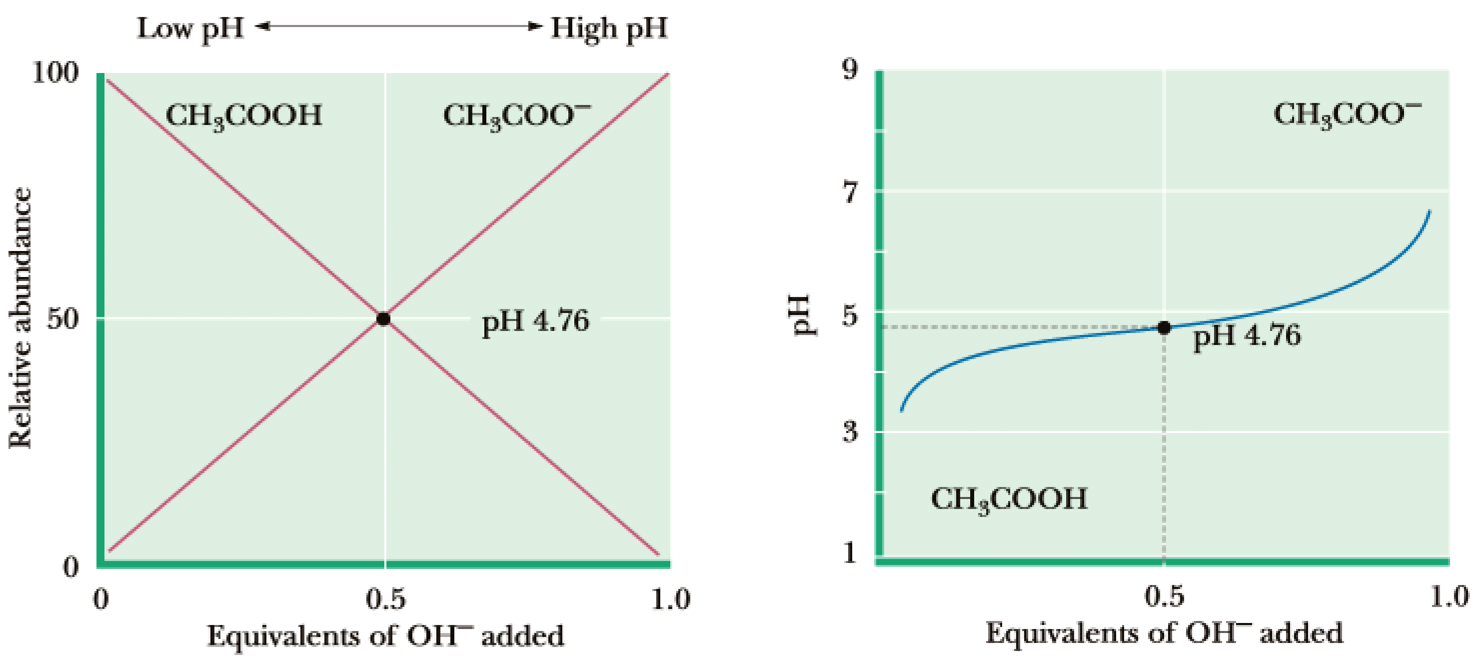
The Henderson-Hasselbalch Equation

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:

- $pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$

Garrett & Grisham: Biochemistry, 2/e
Figure 2.12



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Consider the Dissociation of Acetic Acid

Assume 0.1 eq base has been added to a fully protonated solution of acetic acid

- The Henderson-Hasselbalch equation can be used to calculate the pH of the solution:

With 0.1 eq OH^- added:

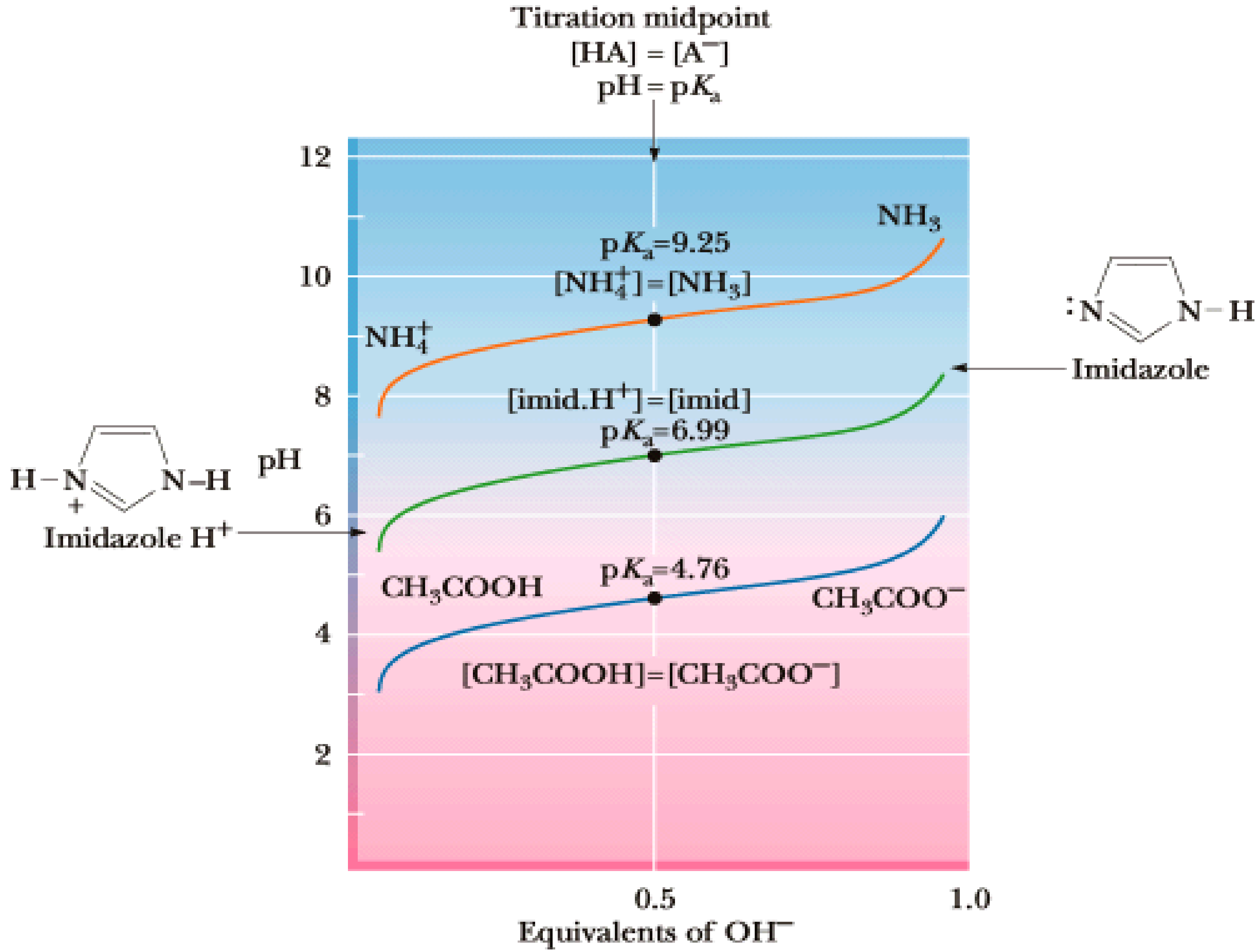
- $pH = pK_a + \log_{10} \frac{[0.1]}{[0.9]}$
- $pH = 4.76 + (-0.95)$
- $pH = 3.81$

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:
  - $pH = pK_a + \log_{10} \frac{[0.5]}{[0.5]}$
  - $pH = 4.76 + 0$
  - $pH = 4.76 = pK_a$

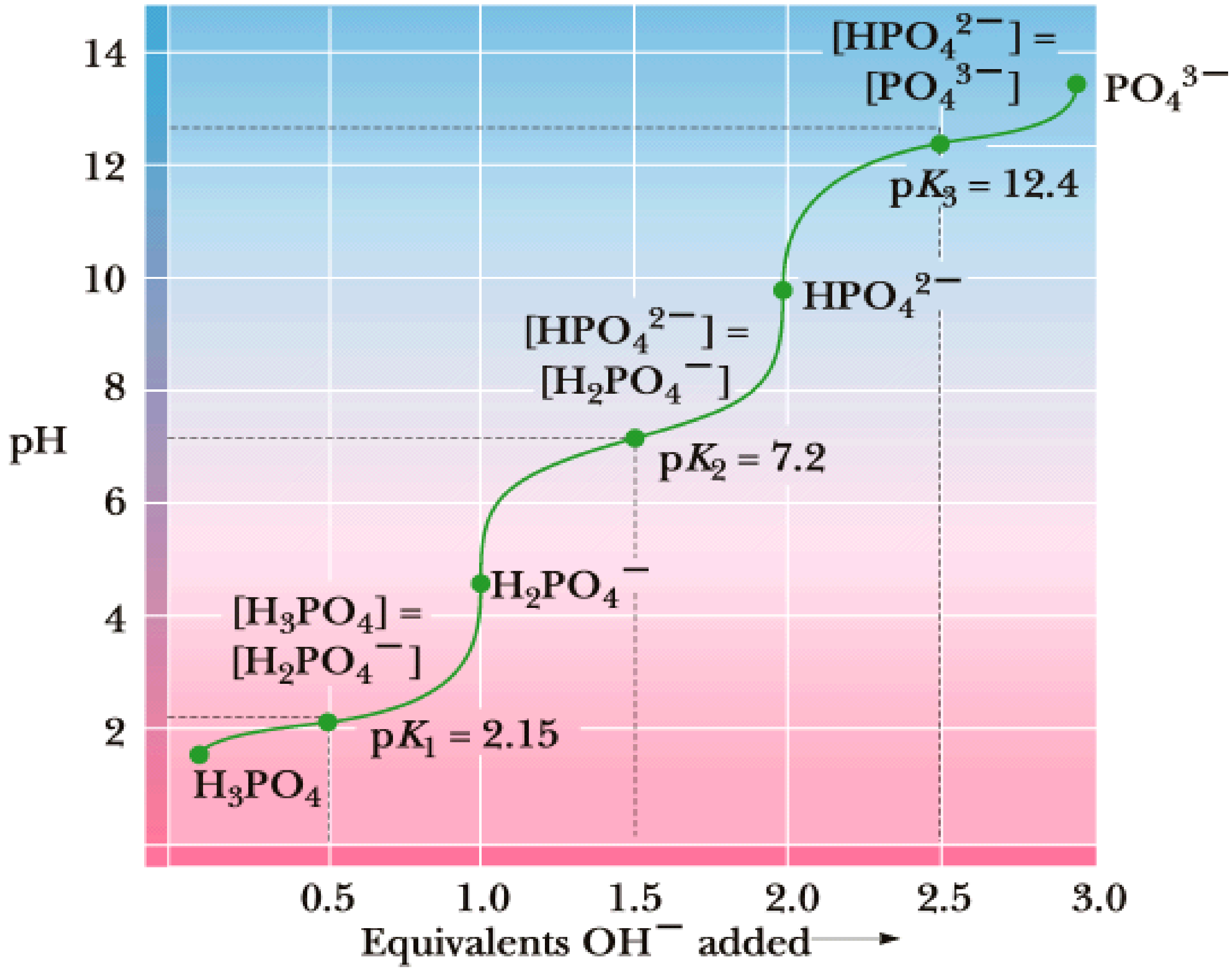
A final case to consider....

- What is the pH if 0.9 eq of base is added to a solution of the fully protonated acid?
- With 0.9 eq OH^{-} added:
  - $pH = pK_a + \log_{10} \frac{[0.9]}{[0.1]}$
  - pH = 4.76 + 0.95
  - pH = 5.71



Titration midpoint
[HA] = [A⁻]
pH = pKa
12
10
8
6
4
2
pH
0.5
1.0
Equivalents of OH⁻
NH3
pKa=9.25
[NH4+]=[NH3]
NH4+
Imidazole
[imid.H+]=[imid]
pKa=6.99
Imidazole H+
CH3COOH
pKa=4.76
CH3COO⁻
[CH3COOH]=[CH3COO⁻]

Garrett & Grisham: Biochemistry, 2/e
Figure 2.14



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Buffers

- 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 in Figure 2.15 how the 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

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Figure 2.15

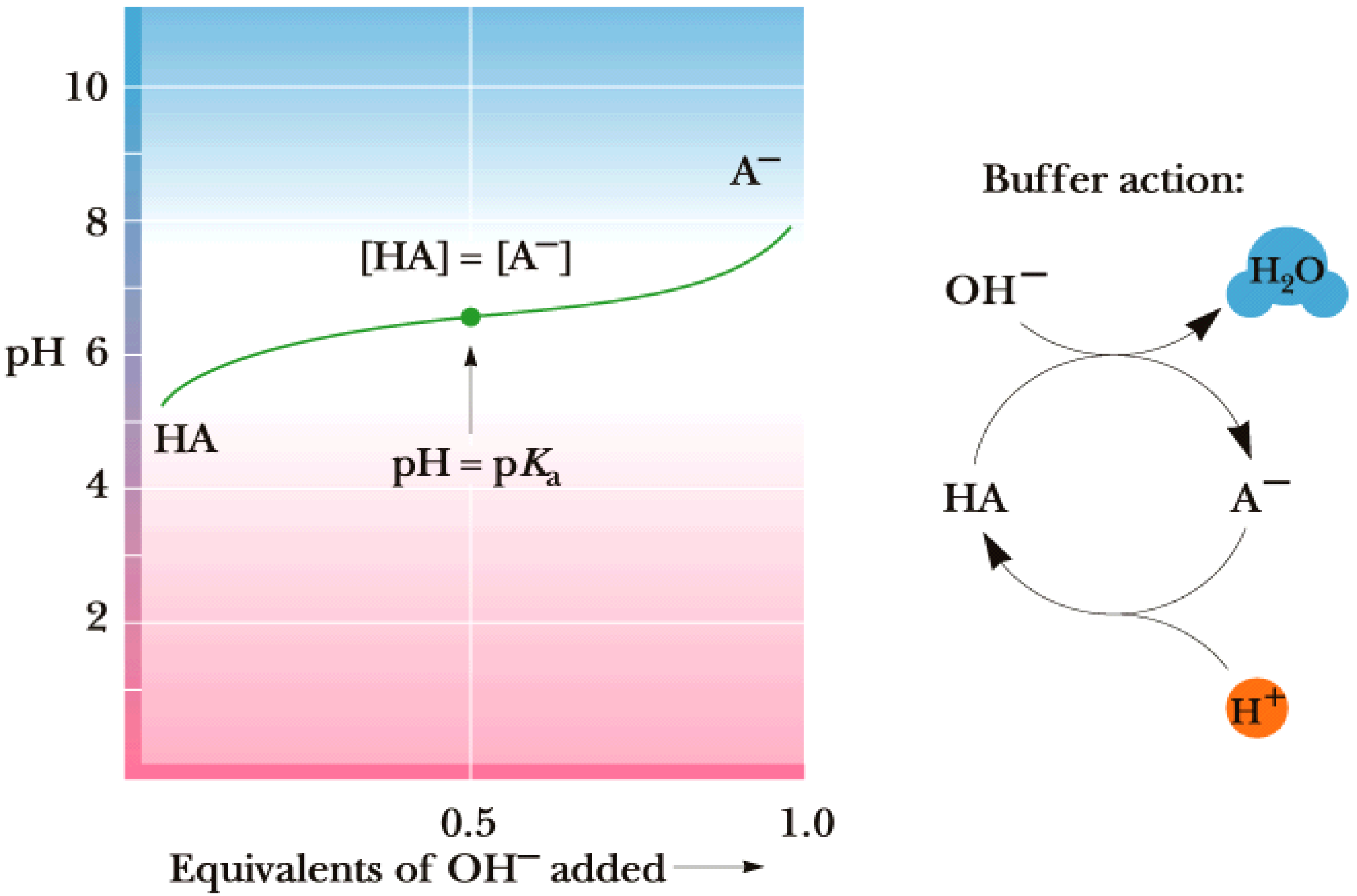

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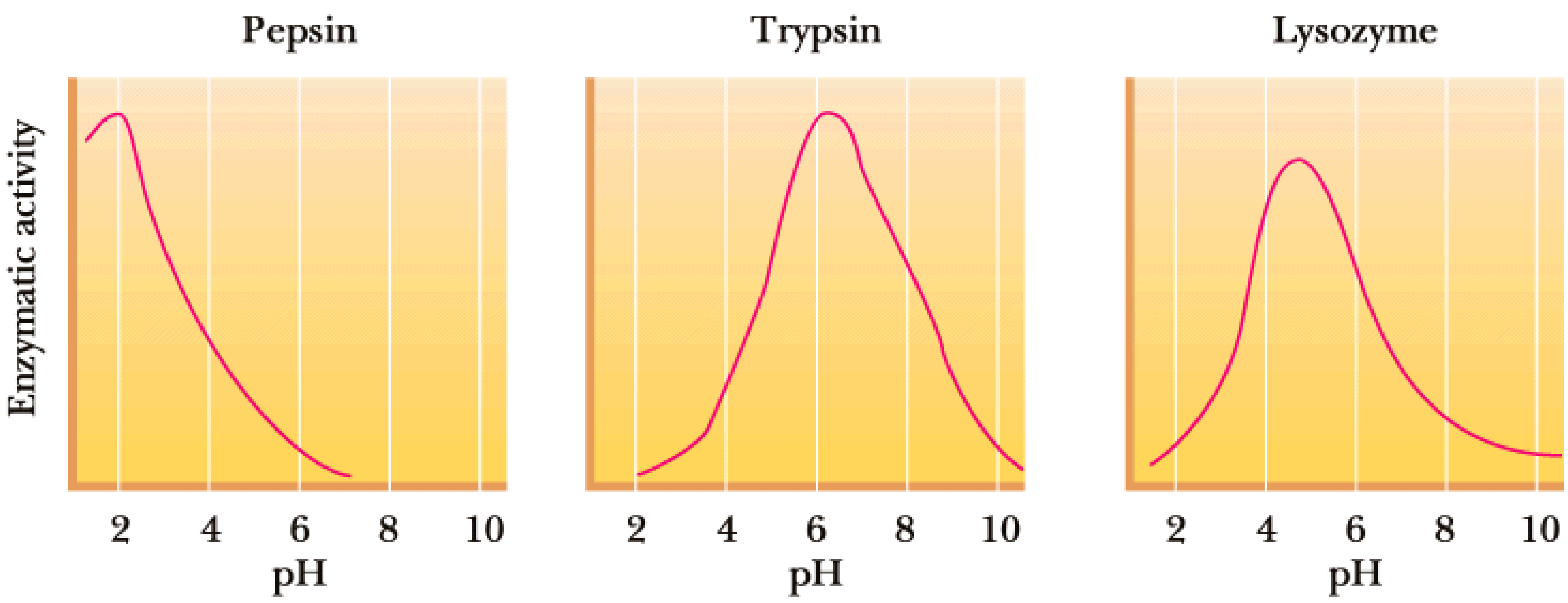
Figure 12.16



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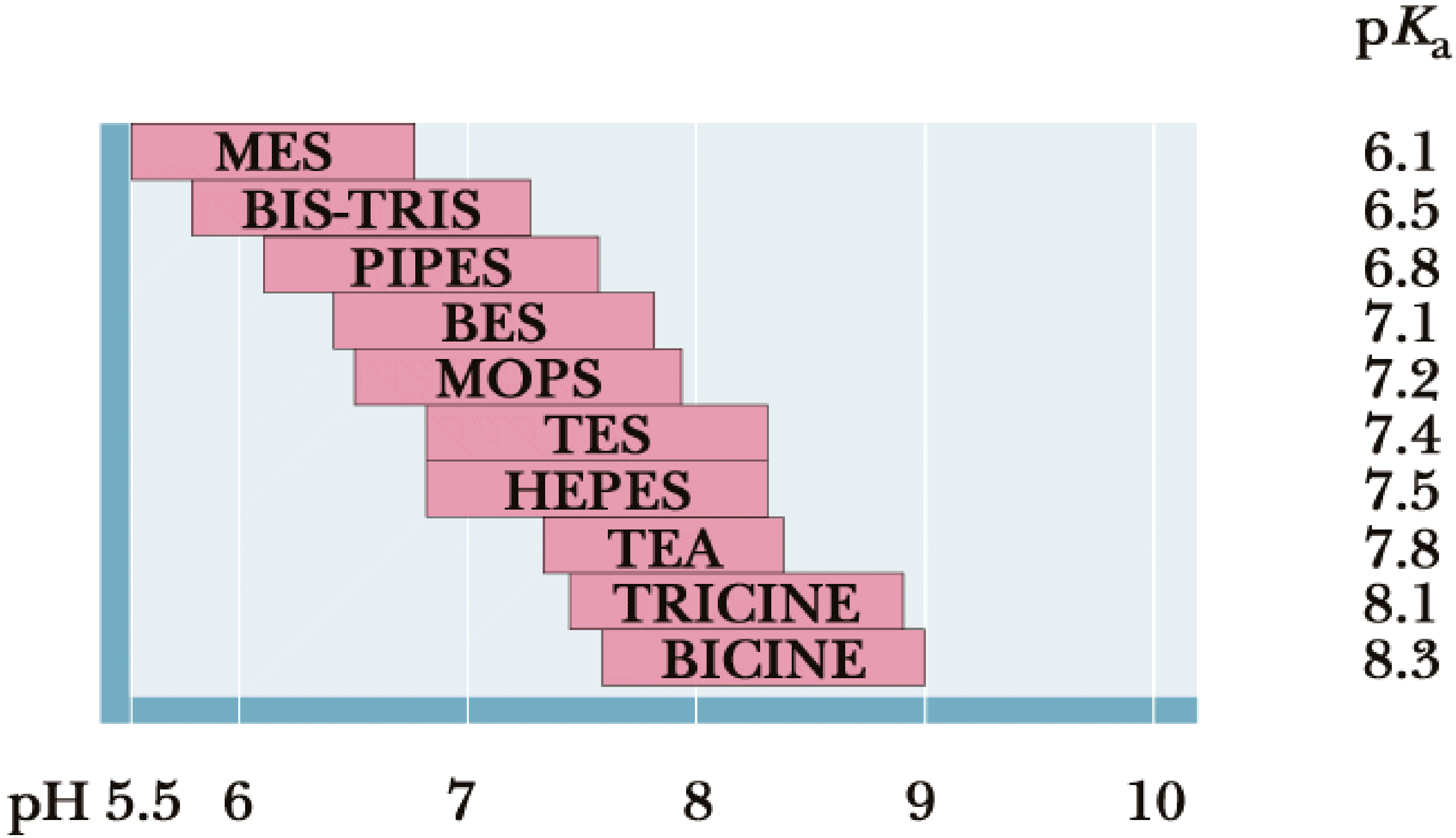

Useful pH range of selected biological buffers (25°C, 0.1 M)

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The End