Chapter 3

Water: The Matrix of Life

Overview

- Water, water everywhere,; not a drop to drink
  - Only 3% of world's water is fresh
- How has this happened
  - Consumption resulting from how environment inhabited
  - Deforestation disrupts water cycle
    - Plants transpire fresh water, fresh water evaporates from soil
    - Deforestation removes plants therefore erodes soil
- Earth's water supply is why we exist
  - Life arose from *primordial pudding*
  - First bio-molecules formed, combined into macromolecules

- **Water's** – matrix of life; major role as solvent
  - Chemical stability & polarity
    - Key to solvent properties
  - Role as a biochemical reactant
    - Hydrolysis, dehydration,
  - Hydration – structured water
    - Stabilization & function of macromolecules

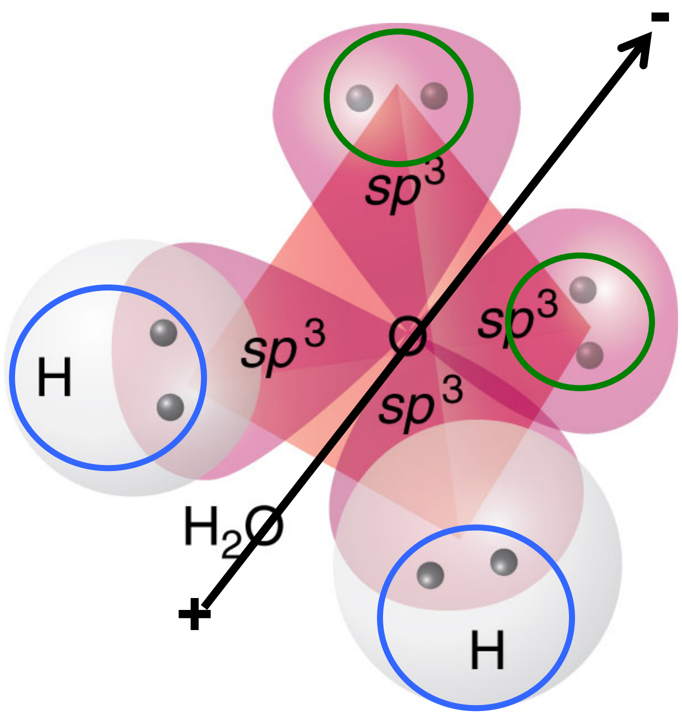


Figure 3.2 Tetrahedral Structure of Water

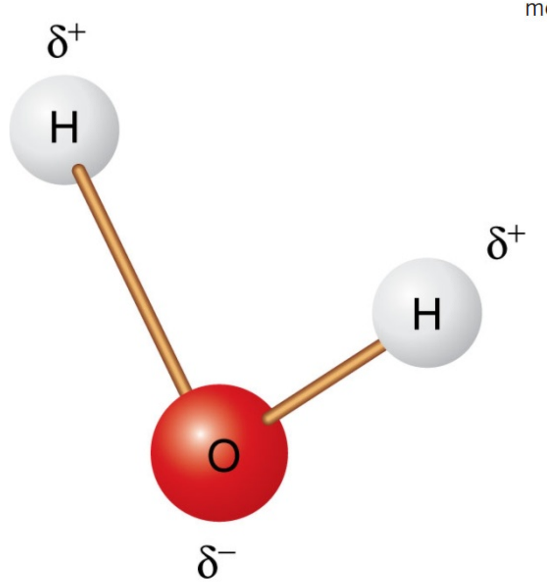
- Composition: 2H, 1O
- Tetrahedral geometry: sp^3 hybridization
- Oxygen is more electronegative than hydrogen
- Polar bonds; dipoles & hydrogen bonds

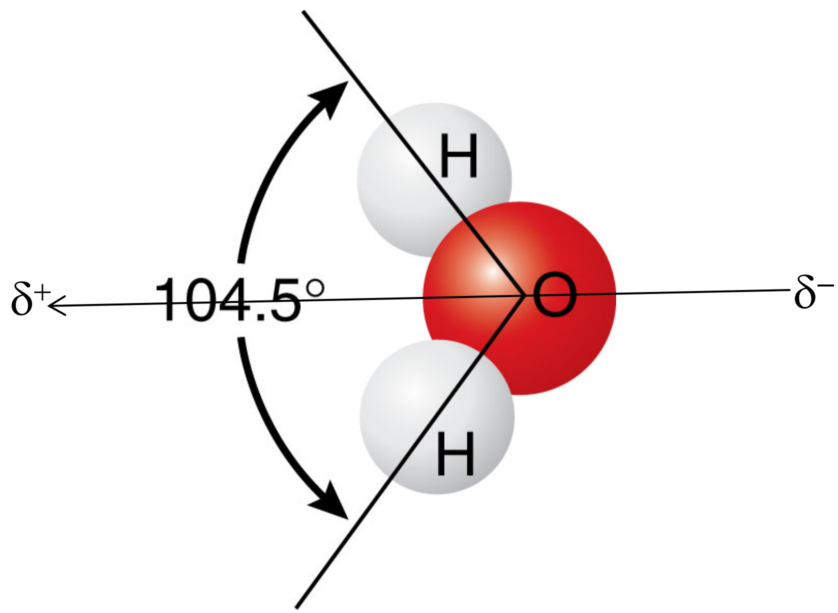
Electronegativity – measure of force of an atom's attraction for electrons is shares

Electronegativities of Selected Elements

Element	Electronegativity*
Oxygen	3.5
Nitrogen	3.0
Sulfur	2.6
Carbon	2.5
Phosphorus	2.2
Hydrogen	2.1

* Electronegativity values are relative, and are chosen to be positive numbers ranging from less than 1 for some metals to 4 for fluorine.





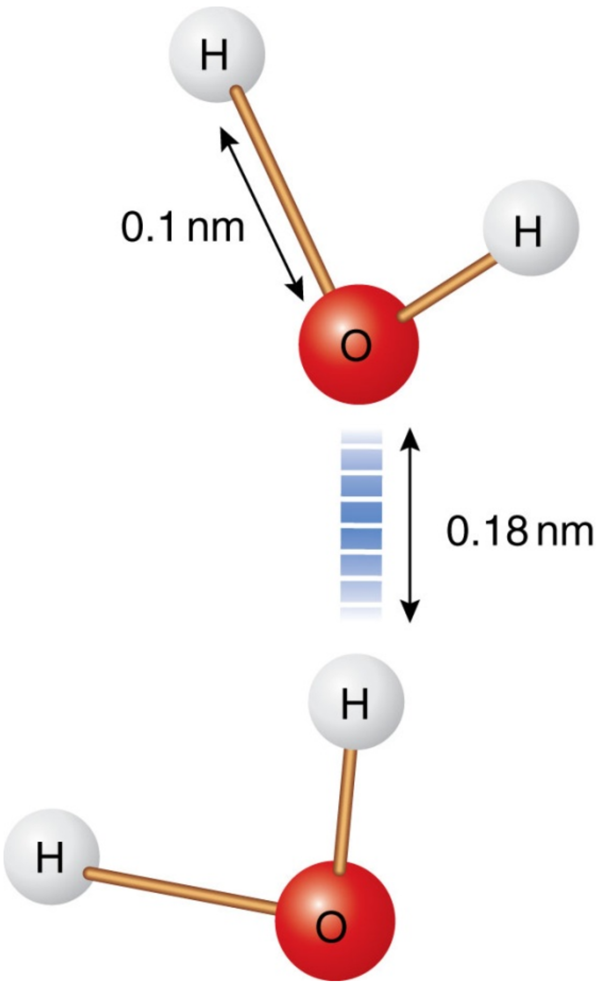
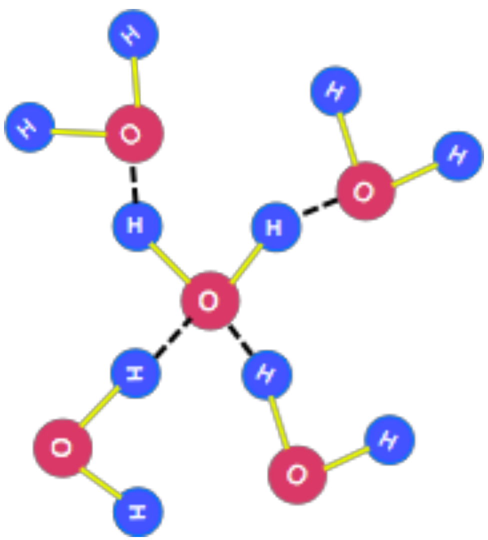


Figure 3.6 Hydrogen Bond

- **Hydrogen bond:** relatively strong electrostatic bond between electron-deficient H of one water and unshared electrons of O on another
  - Can occur with oxygen, nitrogen, and fluorine
  - Water can form 4 hydrogen bonds



Section 3.2: Noncovalent Bonding

TABLE 3.1 Bond Strengths of Bonds Typically Found in Living Organisms*

Bond Type	Bond Strength kcal/mol	Bond Strength kJ/mol*
Covalent	>50	>210
Noncovalent		
Ionic interactions†	1–20	4–80
Van der Waals forces	<1–2.7	<4–11.3
Mixed: hydrogen bonds	3–7	12–29

* The actual strength varies considerably with the identity of the interacting species.

† 1 cal = 4.184 J.

- Noncovalent interactions are electrostatic
  - Weak individually, play vital role in biomolecules (cumulative effects)
- Three most important noncolvalent bonds:
  - Ionic interactions
  - Van der Waals forces
  - Hydrogen bonds

- **Ionic Interactions** – “Like dissolves like”
  - Oppositely charged ions attract one another
    - Ionic compounds – NaCl
    - Ion-dipole interaction – KCl dissolved in H_2O
    - Dipole-dipole interactions - Low-molecular weight polar covalent compounds – C_2H_5OH (ethanol) & CH_3COCH_3 (acetone)
  - Ionized amino acid side chains
    - Glutamic acid $–CH_2CH_2COO^-$
    - Lysine - $-CH_2CH_2CH_2CH_2NH_3^+$
    - Salt bridges: $-COO^-$ $^+H_2N-$
  - Repulsive forces important in biological processes
    - Protein folding, enzyme catalysis, molecular recognition

Section 3.2: Noncovalent Bonding

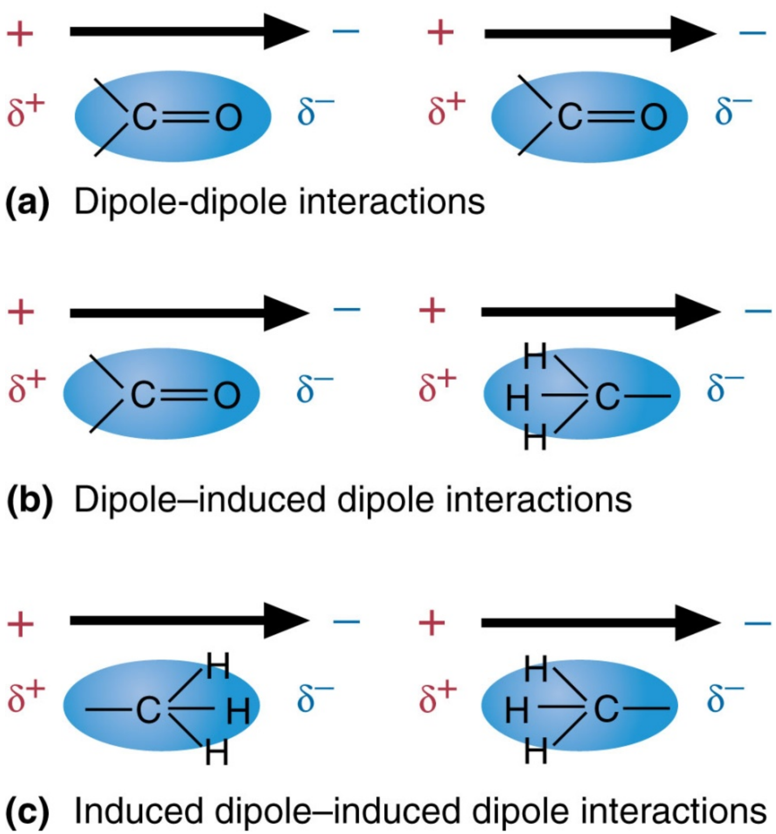


Figure 3.8 Dipolar Interactions

- **Van der Waals Forces**
  - Occur between neutral, permanent, and/or induced dipoles

Three types:

- Dipole-dipole interactions
  - Between 2 permanent dipoles
- Dipole-induced dipole interactions
  - Between permanent dipole/transient dipole
- Induced dipole-induced dipole interactions
  - Between transient dipoles from electron cloud overlap

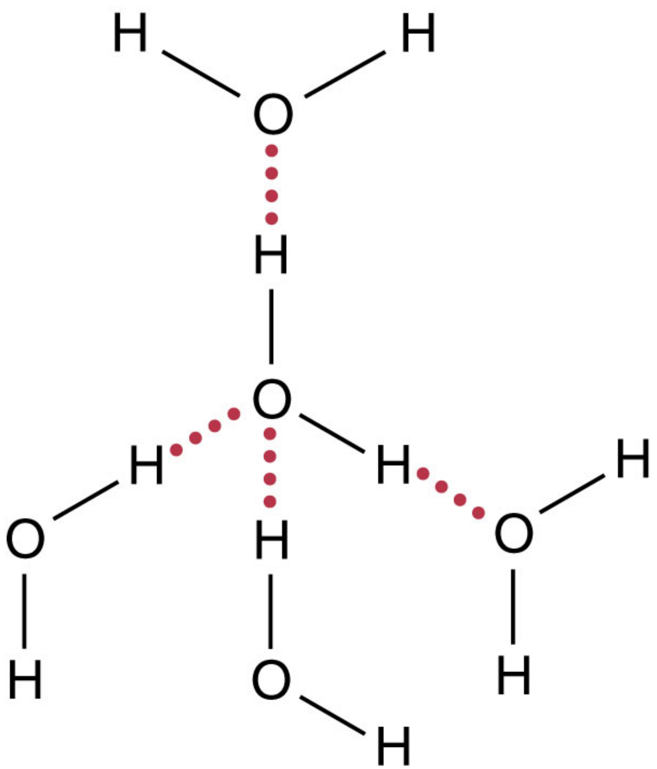


Figure 3.7 Tetrahedral Aggregate of Water Molecules

- **Hydrogen Bonds**
  - Electron-deficient hydrogen is weakly attracted to unshared electrons of another oxygen or nitrogen
  - Large numbers of hydrogen bonds lead to extended network

TABLE 3.2 Melting and Boiling Points of Water and Three Other Group VI Hydrogen-Containing Compounds

Name	Formula	Molecular Weight (D)*	Melting Point (°C)	Boiling Point (°C)
Water	H_2O	18	0	100
Hydrogen sulfide	H_2S	34	–85.5	–60.7
Hydrogen selenide	H_2Se	81	–50.4	–41.5
Hydrogen telluride	H_2Te	129.6	–49	–2

* I dalton (D) = 1 atomic mass unit (amu).

- Melting and boiling points are exceptionally high due to **hydrogen bonding**
  - Each water molecule can form four hydrogen bonds with other water molecules
  - Extended network of hydrogen bonds requires more energy to change state

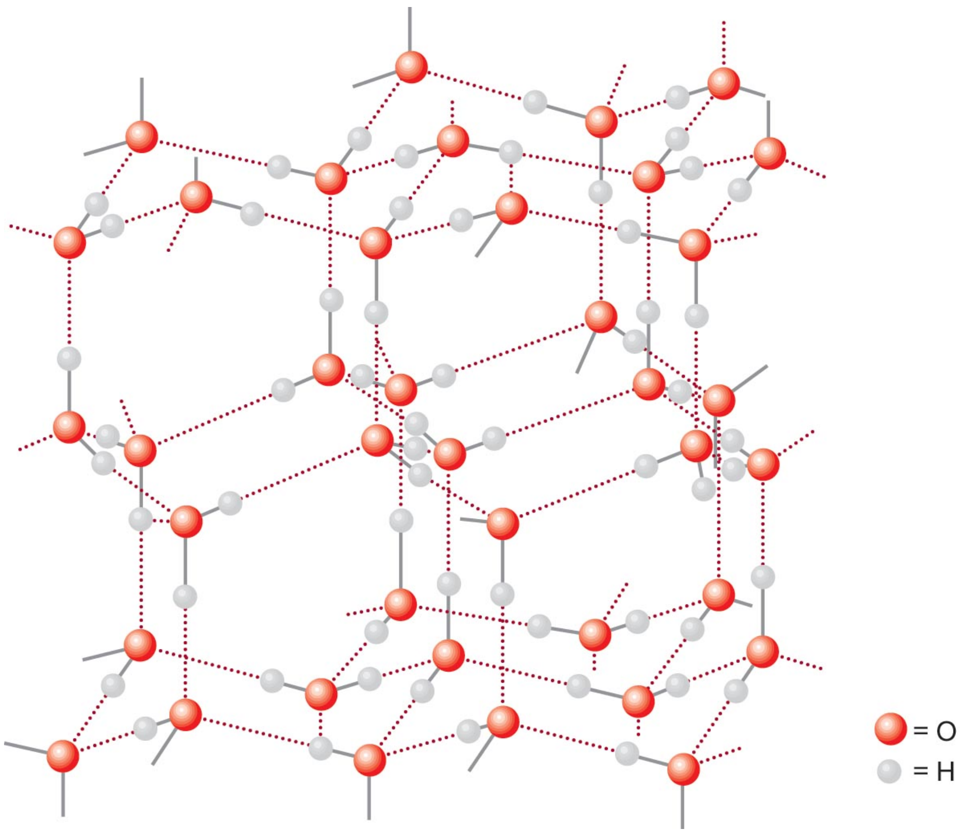


Figure 3.9 Hydrogen Bonding Between Water Molecules in Ice

- Maximum number of hydrogen bonds form is frozen into ice
  - Open, less-dense structure

Section 3.3: Thermal Properties of Water

TABLE 3.3 Heat of Fusion of Water and Two Other Group VI Hydrogen-Containing Compounds

Name	Formula	Molecular Weight (D)	Heat of Fusion* cal/g	J/g
Water	H_2O	18	80	335
Hydrogen sulfide	H_2S	34	16.7	69.9
Hydrogen selenide	H_2Se	81	7.4	31

* The heat of fusion is the amount of heat required to change 1 g of a solid into a liquid at its melting point; 1 cal = 4.184 J.

- Exceptionally **high heat of fusion (melt)** and **heat of vaporization (vaporize)**
- **High heat capacity** – energy added or removed to change temperature by 1C^o
  - Helps to maintain an organism's internal temperature

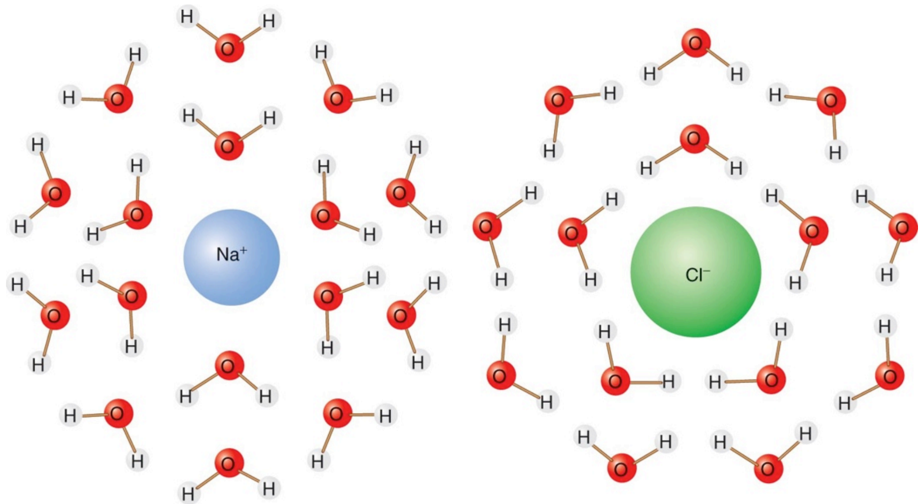


Figure 3.10 Solvation Spheres

Ideal biological solvent

- Hydrophilic Molecules – water loving
- Hydropholic molecules – water fearing
  - **Solvation spheres** - dissolve ionic and polar substances
    - Shells of water molecules form around ions
    - Substance positive – sphere large, $Na^+ > Cl^-$
    - Ion diameter – smaller diameter larger hydration sphere

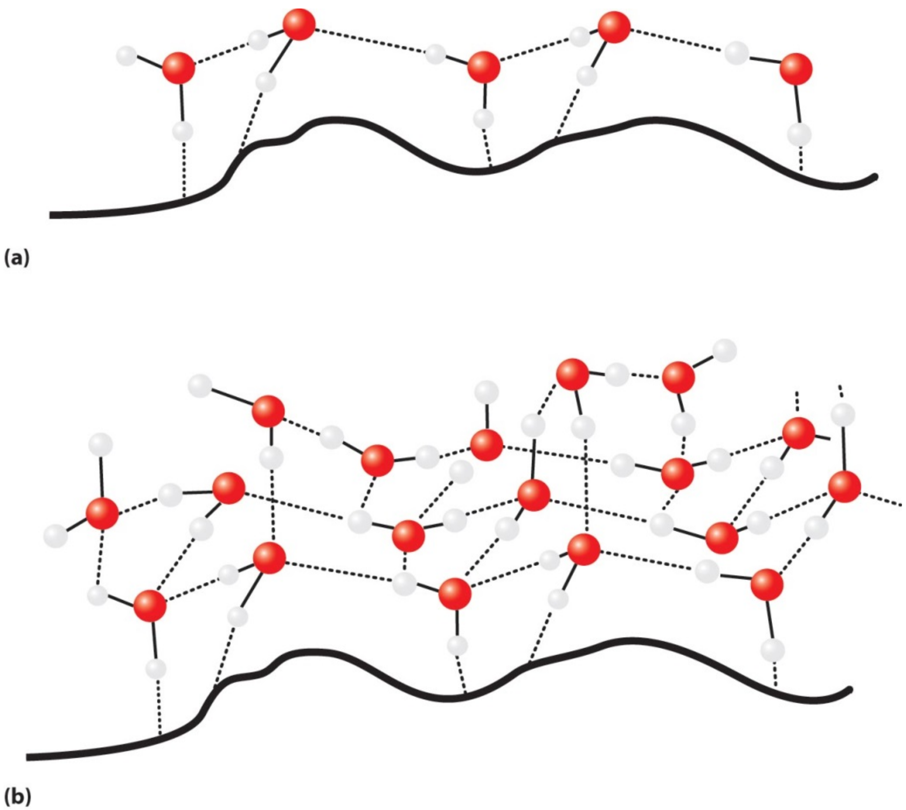


Figure 3.11 Diagrammatic View of Structured Water

- **Structured Water**
  - Rarely free flowing
  - Associated with macromolecules and other cellular components
  - Forms complex three-dimensional bridges between cellular components

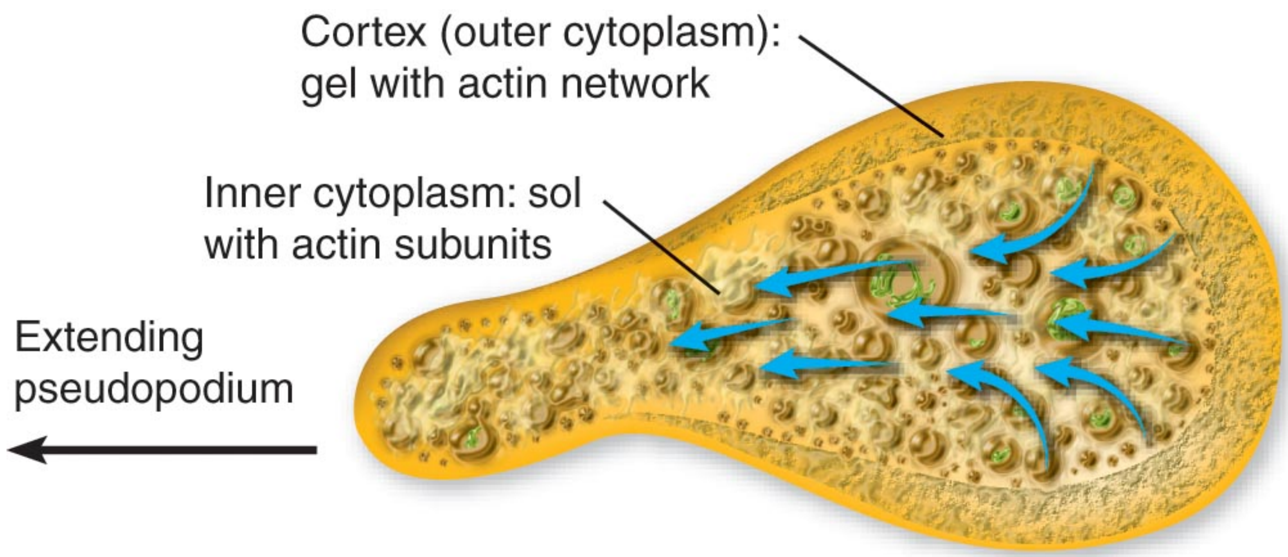


Figure 3.12 Amoeboid Motion

- **Sol-Gel Transitions**
  - Cytoplasm has properties of a gel (colloidal mixture)
  - Transition from gel to sol important in cell movement
    - Amoeboid motion provides an example of regulated, cellular, sol-gel transitions

Section 3.4: Solvent Properties of Water

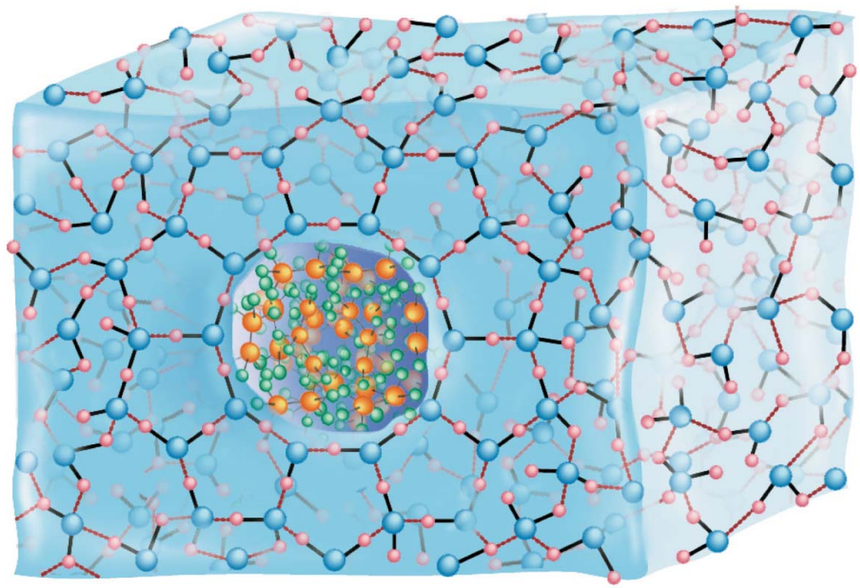


Figure 3.13 The Hydrophobic Effect

- **Hydrophobic Effect**
  - Hydrophobic molecules– coalesce into droplets
  - Stabilized by van der Waals interactions
    - Generation of stable lipid membranes
    - Contributes to fidelity of protein folding

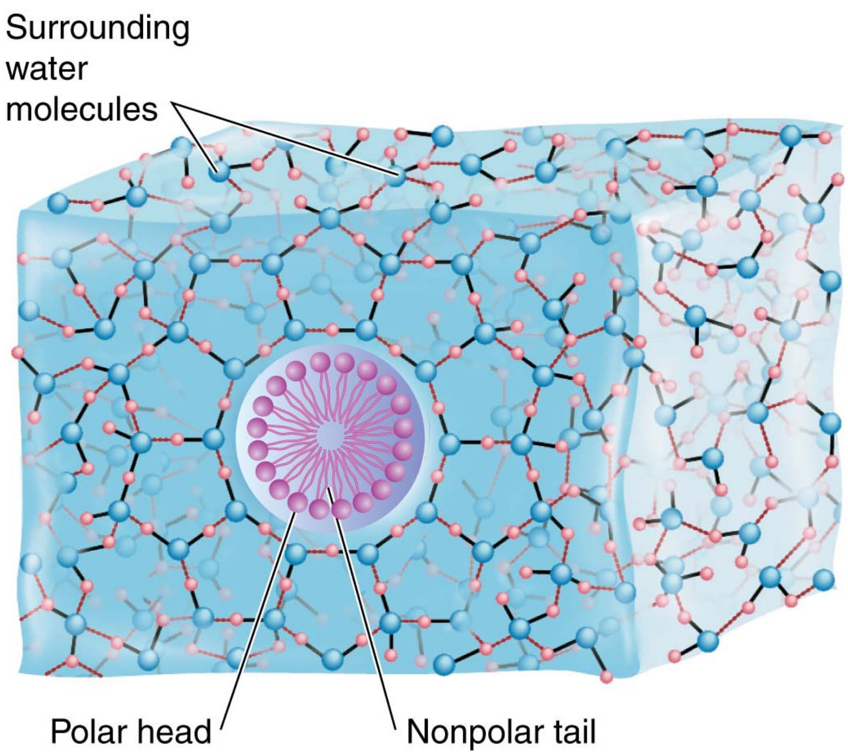


Figure 3.14 Formation of Micelles

- **Amphipathic Molecules**
  - Both hydrophobic & hydrophilic
  - Form **micelles** when mixed with water
  - Important feature for formation of cellular membranes

Section 3.4: Solvent Properties of Water

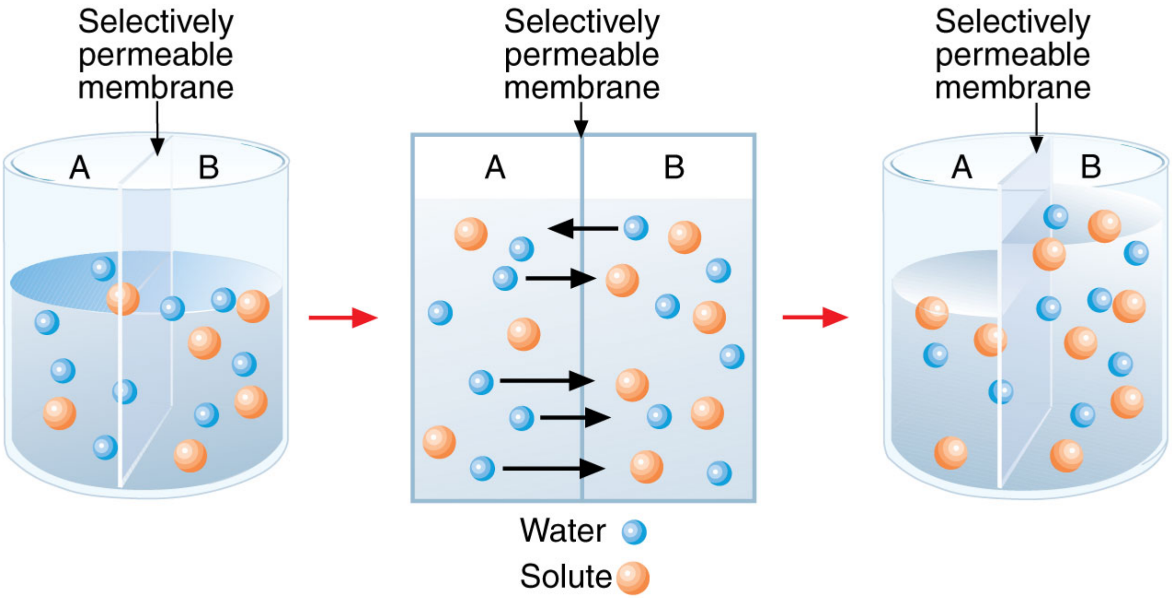
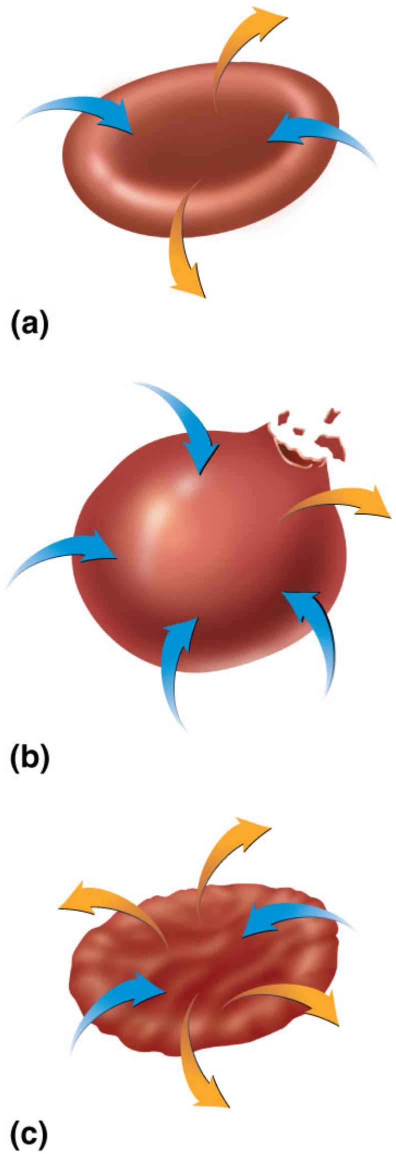


Figure 3.15 Osmotic Pressure

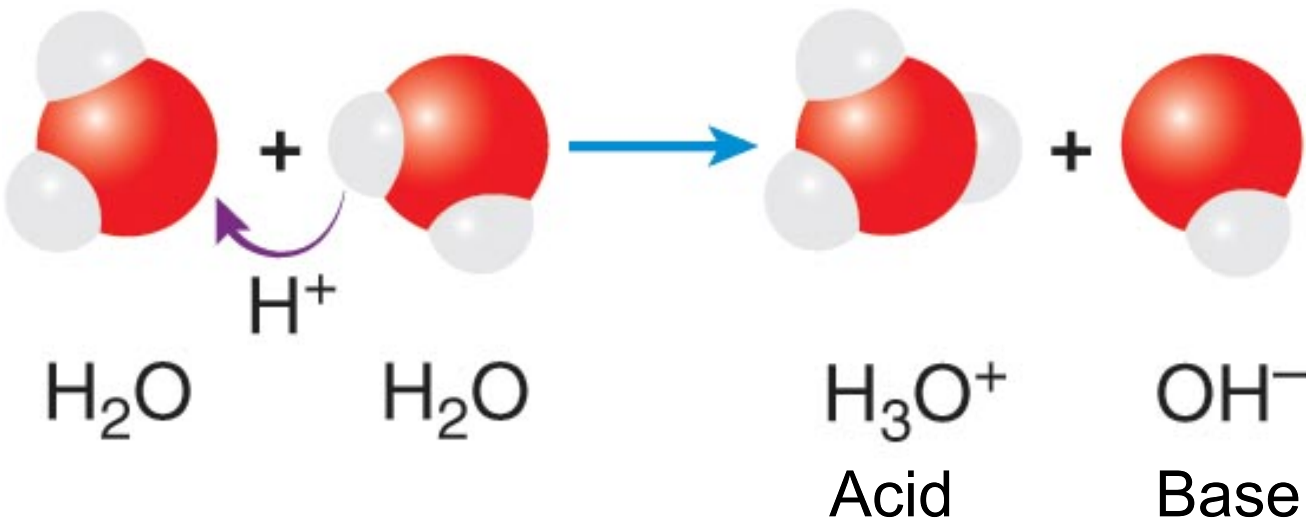
- **Osmotic Pressure**
  - Osmosis - spontaneous passage of solvent molecules through a semipermeable membrane
    - Moves down concentration gradient – hi to low
  - Osmotic pressure - pressure required to stop the net flow across the membrane
    - Equilibrium – no net flow from side to side
    - Osmotic pressure depends on solute concentration



- Cells may gain or lose water because of the environmental solute concentration
- Consequences of solute concentration differences between the cell and the environment
  - **Isotonic solution** – solute concentration equal
  - **Hypotonic solution –** solute concentration lower outside; water in; lysis
  - **Hypertonic solution** – solute concentration higher outside; water out; crenation

Figure 3.17 Effect of Solute Concentration on Animal Cells

- **Amphoteric** – acts as acid and base
  - **Acid** – proton donor; **Base** – proton acceptor
  - $H_2O \Leftrightarrow H^+ + OH^-$ (reversible)



Equilibrium constant, K_{eq} = [products] / [reactants]

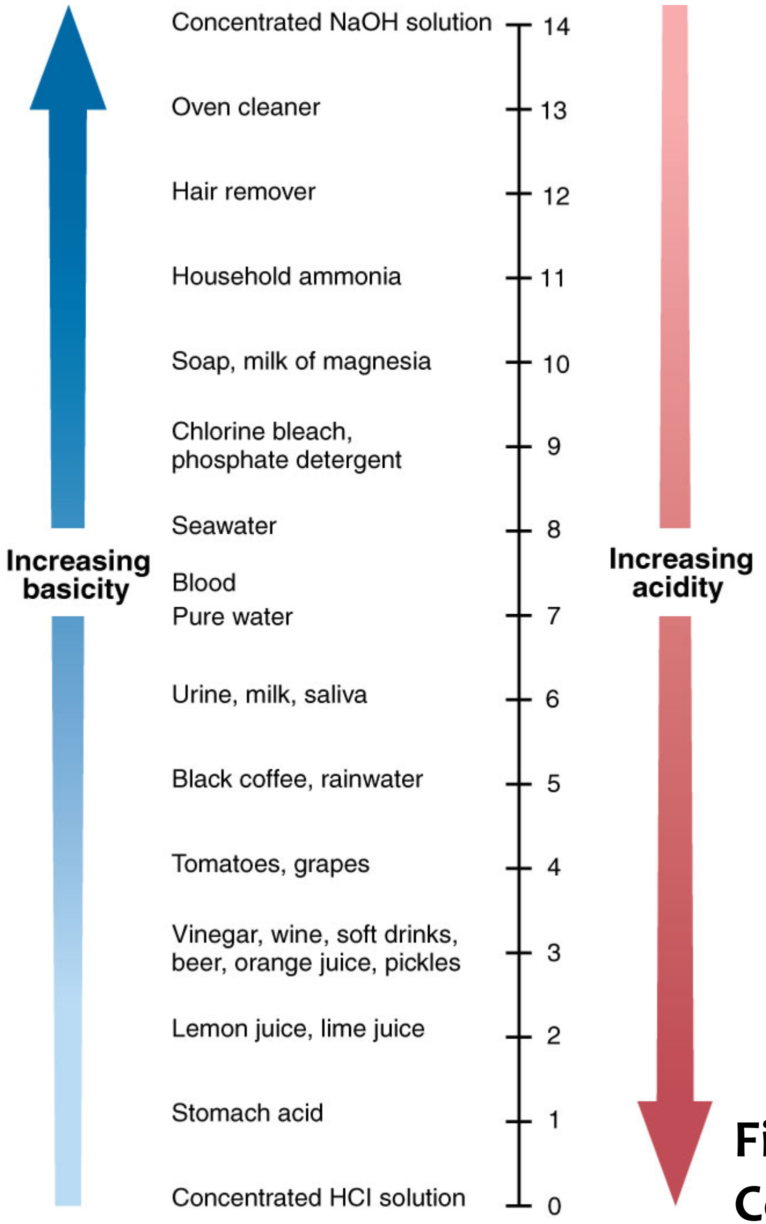
- $H_2O \Leftrightarrow H^+ + OH^-$
  - $K_{eq} = [H^+][OH^-] / [H_2O]$
  - $K_{eq}[H_2O] = [H^+][OH^-]$
- Ion product of water is $K_{eq}[H_2O]$ or K_w
  - $K_w = [H^+][OH^-]$
  - K_w at 25°C and 1 atm pressure = 1.0×10^{-14}
  - K_w is temperature-dependent; therefore, pH is temperature-dependent as well

- **Acids, Bases, and pH**
  - Most organic molecules are **weak acids** or **weak bases**
    - Reaction of weak acid in water

      $HA(aq) + H_2O(l) \leftarrow \rightarrow H_3O^+(aq) + A^-(aq)$

      w.a. c.b.
    - Measure of weak acid strength - K_a

      $K_a = [H_3O^+][A^-] /HA]$
    - $pK_a = -logK_a$ Lower pK_a stronger acid



- **pH scale** reflects hydrogen ion concentration
  - $pH=-\log[H^+]$

Figure 3.19 The pH Scale and the pH Values of Common Fluids

TABLE 3.4 Dissociation Constants and pK_a Values for Common Weak Acids*

Acid	HA	A^-	K_a	pK_a
Acetic acid	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.76
Carbonic acid	H_2CO_3	HCO_3^-	4.5×10^{-7}	6.35
Bicarbonate	HCO_3^-	CO_3^{2-}	5.61×10^{-11}	10.33
Lactic acid	$CH_3CH(OH)COOH$	$CH_3CH(OH)COO^-$	1.38×10^{-4}	3.86
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	7.25×10^{-3}	2.14
Dihydrogen phosphate	$H_2PO_4^-$	HPO_4^{2-}	6.31×10^{-8}	7.20

* Equilibrium constants should be expressed in terms of activities rather than concentrations (activity is the effective concentration of a substance in a solution). However, in dilute solutions, concentrations may be substituted for activities with reasonable accuracy.

- **Buffers** – resist changes in pH
  - Regulation of pH is universal and essential for all living things, normal blood pH 7.4
  - Certain diseases can cause changes in pH that can be disastrous
    - **Acidosis** – pH <7.35
    - **Alkalosis** – pH >7.45
  - Composed of a weak acid and its conjugate base

$$CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$$

weak acid conjugate base

✓ Added base reacts with weak acid; added acid reacts with conjugate base

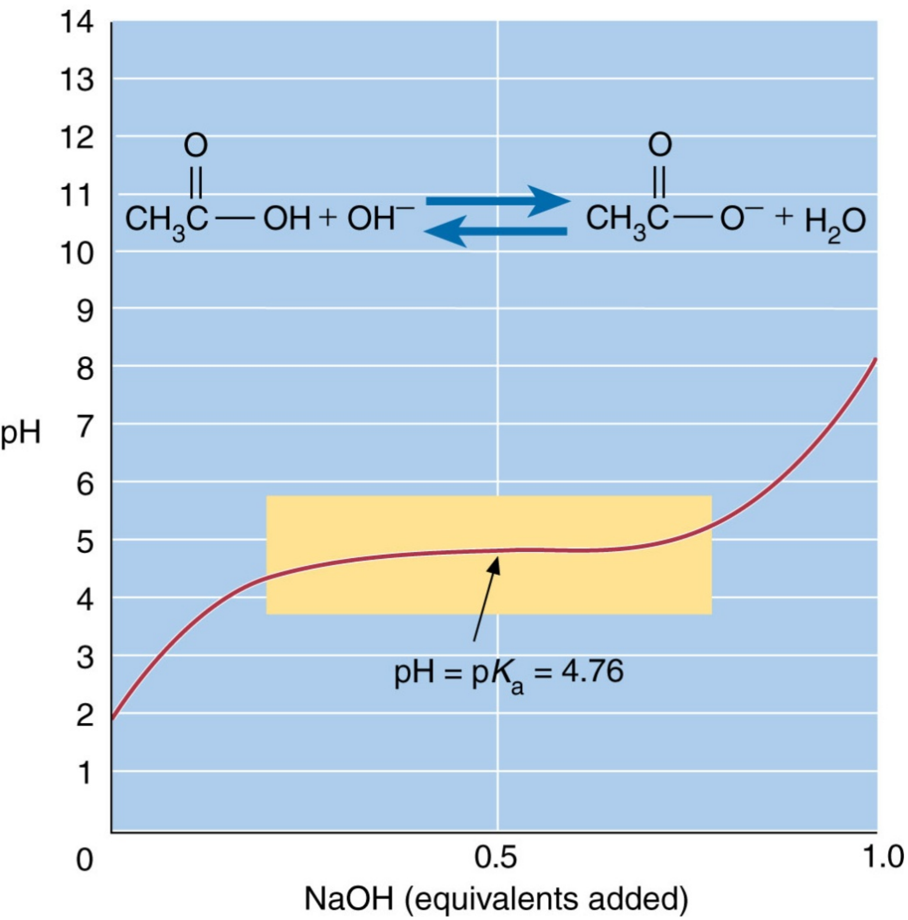


Figure 3.20 Titration of Acetic Acid with NaOH

- **Buffers Capacity**
  - Molar concentration of weak acid-conjugate base pair
  - Most effective - equal parts weak acid and conjugate base
  - Best buffering occurs 1 pH unit above and below the pK_a

Henderson-Hasselbalch Equation

- Establishes the relationship between pH and pK_a for selecting a buffer

Henderson-Hasselbalch Equation

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

- Optimum buffer should have pK_a equal to pH being maintained
- Best buffering occurs 1 pH unit above and below the pK_a

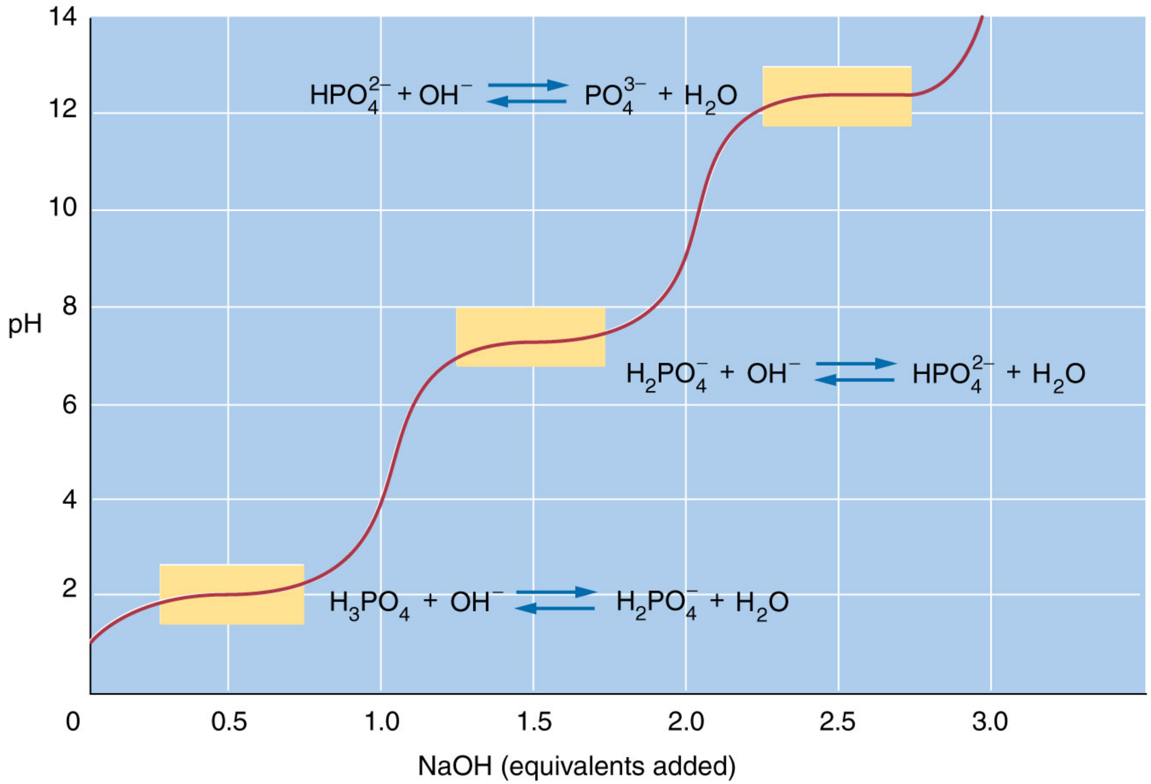


Figure 3.21 Titration of Phosphoric Acid with NaOH

- **Weak Acids with Multiple Ionizable Groups**
  - Each has its own pK_a
  - Protons are released in a stepwise fashion

- **Physiological Buffers**
  - Buffers adapted to solve specific physiological problems within the body
  - **Bicarbonate Buffer**
    - One of the most important buffers in the blood

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-\ \text{(bicarbonate)}$$

    - Carbonic anhydrase is the enzyme responsible

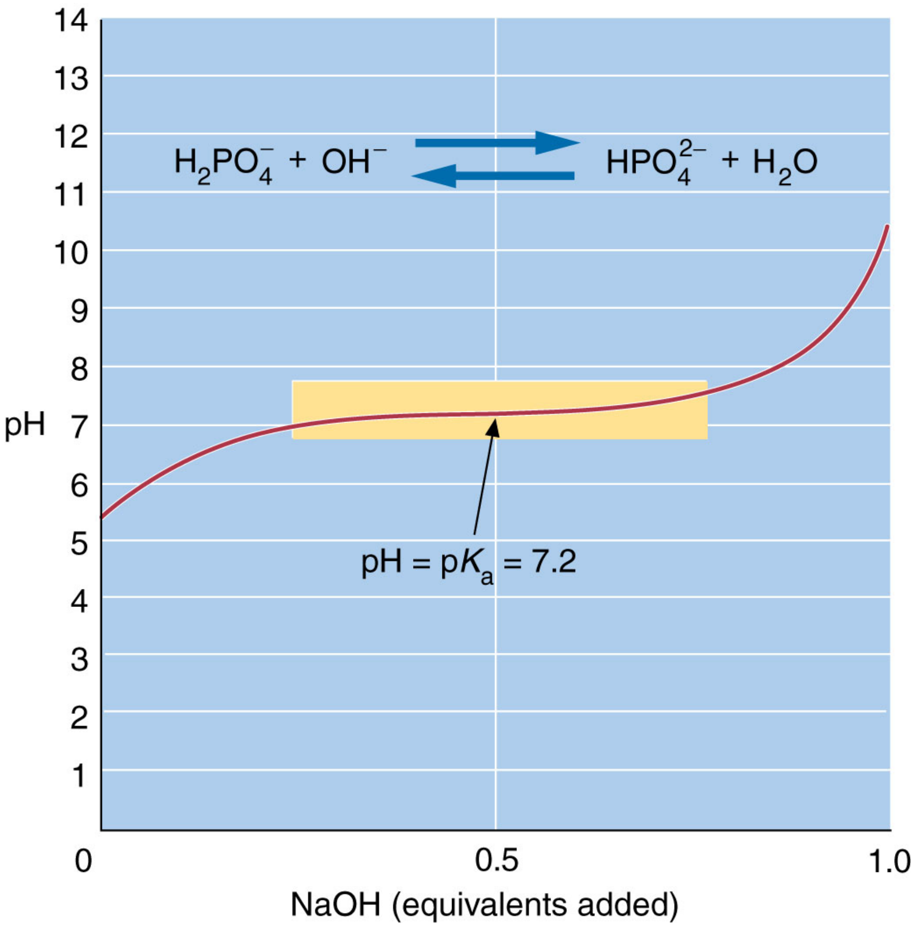


Figure 3.22 Titration of $H_2PO_4^-$ by Strong Base

- **Phosphate Buffer**
  - Important buffer for intracellular fluids
  - Consists of $H_2PO_4^-/HPO_4^{2-}$ (weak acid/conjugate base)
  - $H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$
- **Protein Buffer**
  - Proteins are a significant source of buffering capacity (e.g., hemoglobin)