

Review of Biochemistry



[illegible]

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

+ Actinide
Series

Legend - click to find out more...

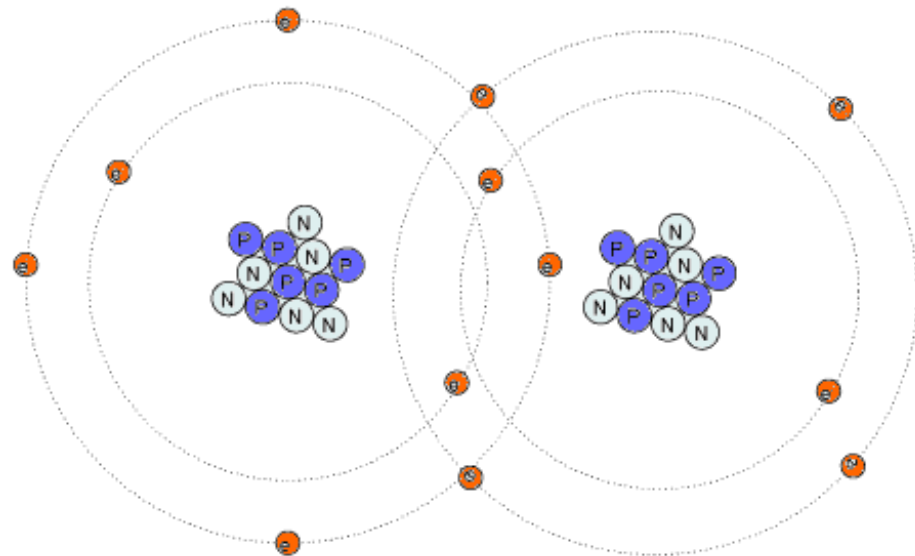
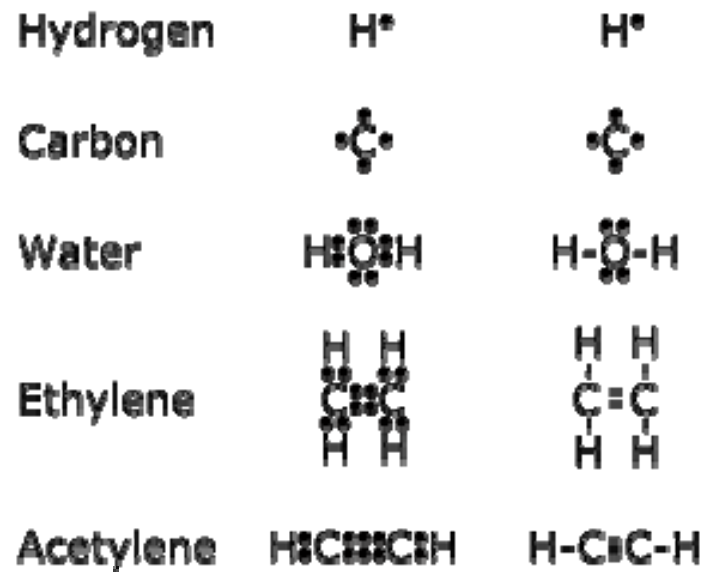
Tc - synthetic

Halogens

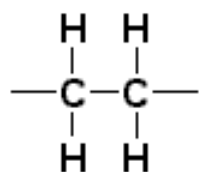
Inert Elements



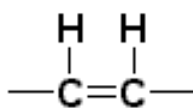
Chemical bond



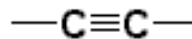
Functional Groups



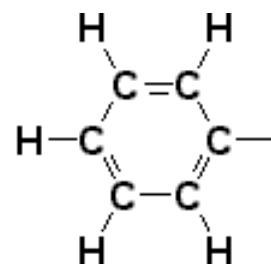
alkane



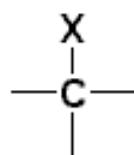
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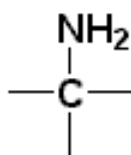
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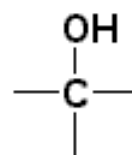
phenyl



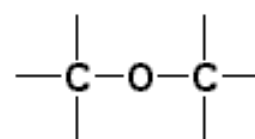
alkyl halide
(X = F, Cl, Br, I)



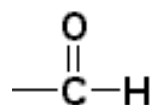
amine



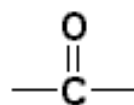
alcohol



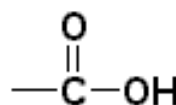
ether



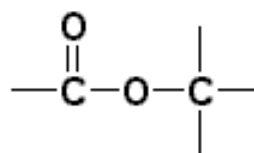
aldehyde



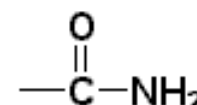
ketone



carboxylic
acid



ester



amide

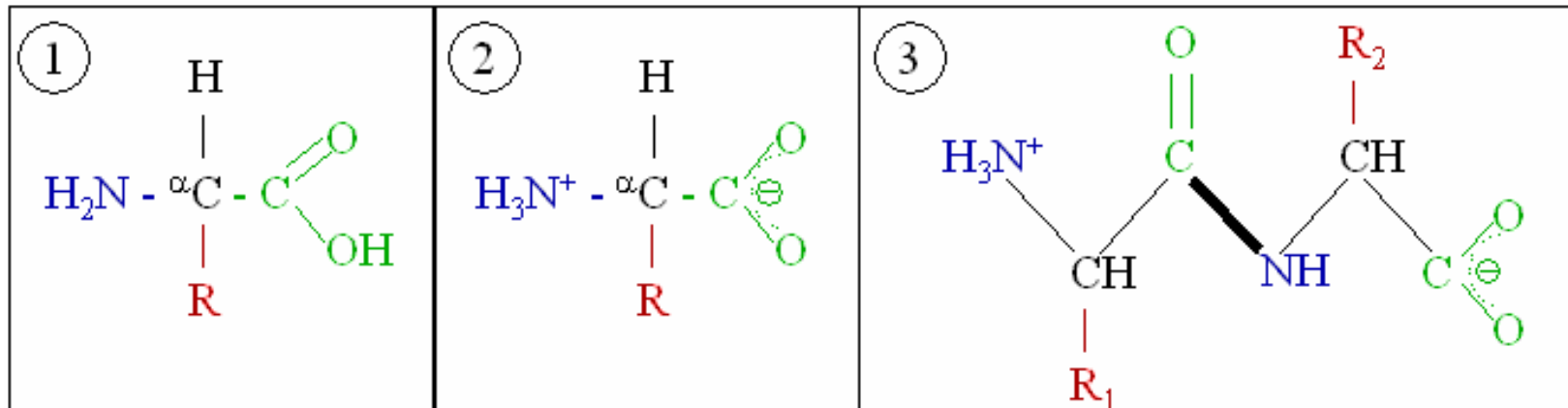
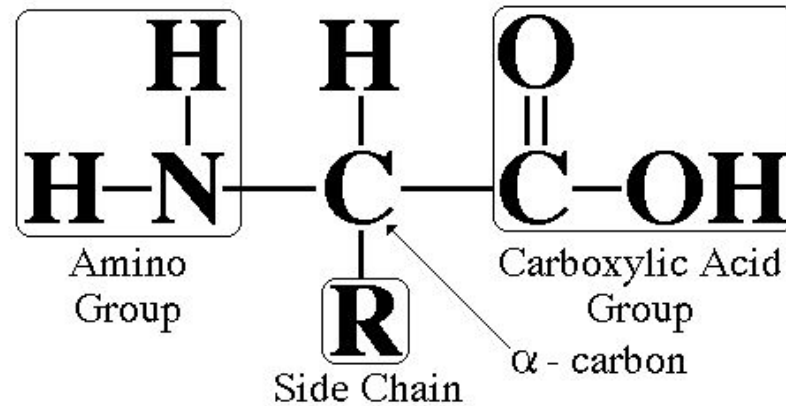


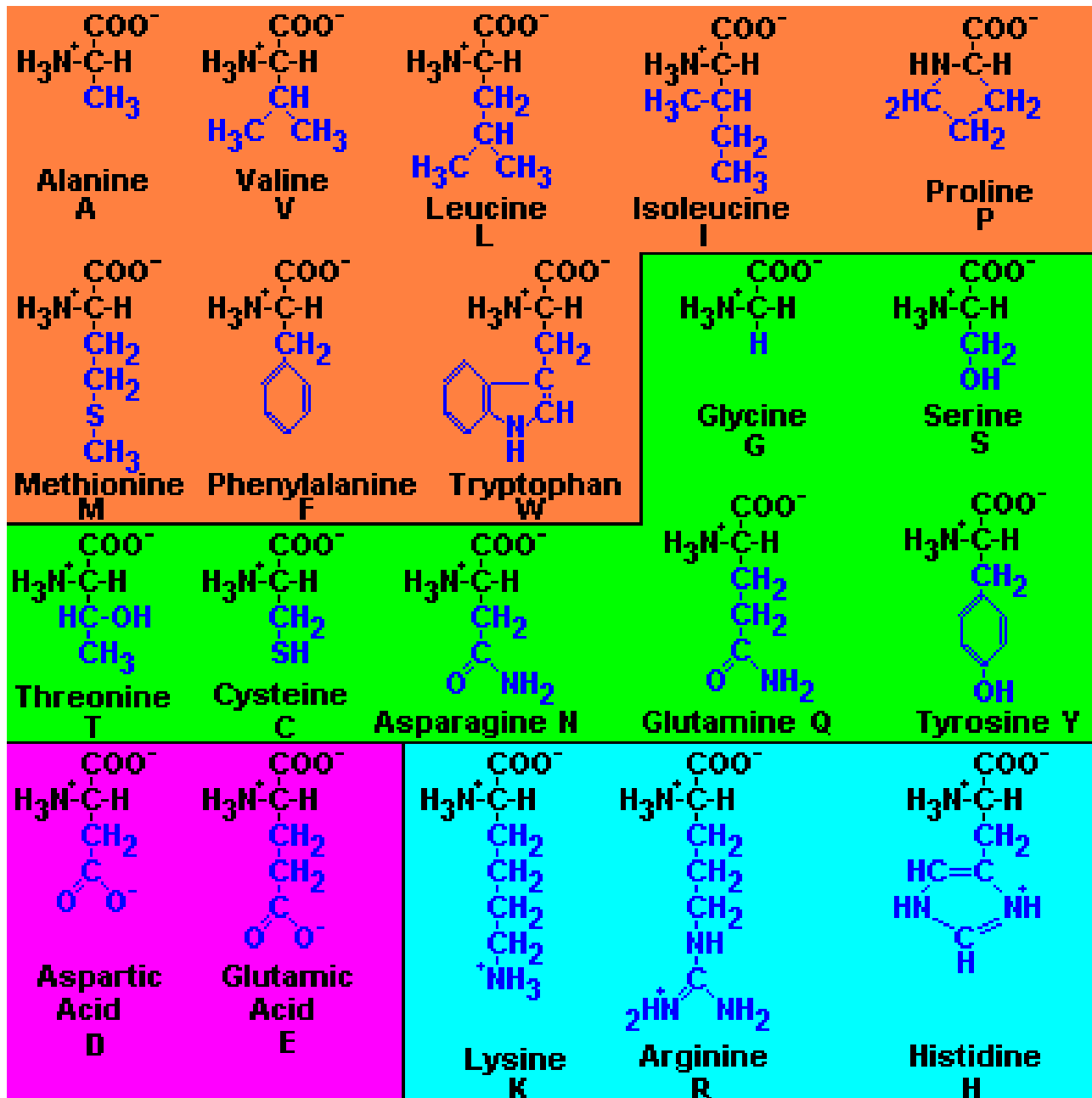
TABLE 18.1 Functional Groups of Importance in Biochemical Molecules

Functional Group	Structure	Type of Biomolecule
Amino group	$-\text{NH}_3^+, -\text{NH}_2$	Amino acids and proteins (Sections 18.3, 18.7)
Hydroxyl group	$-\text{OH}$	Monosaccharides (carbohydrates) and glycerol: a component of triacylglycerols (lipids) (Sections 22.4, 24.2)
Carbonyl group	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	Monosaccharides (carbohydrates); in acetyl group (CH_3CO) used to transfer carbon atoms during catabolism (Sections 22.4, 21.4, 21.8)
Carboxyl group	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH}, \end{array} \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}^- \end{array}$	Amino acids, proteins, and fatty acids (lipids) (Sections 18.3, 18.7, 24.2)
Amide group	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}- \\ \end{array}$	Links amino acids in proteins; formed by reaction of amino group and carboxyl group (Section 18.7)
Carboxylic acid ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R} \end{array}$	Triacylglycerols (and other lipids); formed by reaction of carboxyl group and hydroxyl group (Section 24.2)
Phosphates, mono-, di-, tri-	$\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}^- \\ \end{array}$ $\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}^- \\ \quad \end{array}$ $\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}^- \\ \quad \quad \end{array}$	ATP and many metabolism intermediates (Sections 17.8, 21.5, and throughout metabolism sections)
Hemiacetal group	$\begin{array}{c} \\ -\text{C}-\text{OH} \\ \\ \text{OR} \end{array}$	Cyclic forms of monosaccharides; formed by a reaction of carbonyl group with hydroxyl group (Sections 16.7, 22.4)
Acetal group	$\begin{array}{c} \\ -\text{C}-\text{OR} \\ \\ \text{OR} \end{array}$	Connects monosaccharides in disaccharides and larger carbohydrates; formed by reaction of carbonyl group with hydroxyl group (Sections 16.7, 22.7, 22.9)

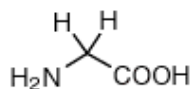
Amino Acid

Amino Acid Structure

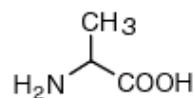




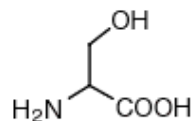
Small



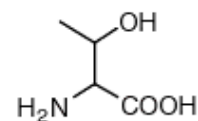
Glycine (Gly, G)
MW: 57.05



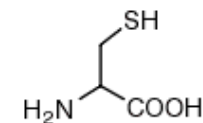
Alanine (Ala, A)
MW: 71.09



Serine (Ser, S)
MW: 87.08, $pK_a \sim 16$

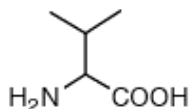


Threonine (Thr, T)
MW: 101.11, $pK_a \sim 16$

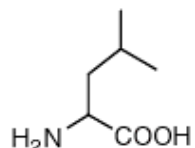


Cysteine (Cys, C)
MW: 103.15, $pK_a = 8.35$

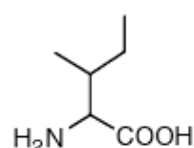
Hydrophobic



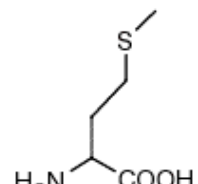
Valine (Val, V)
MW: 99.14



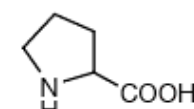
Leucine (Leu, L)
MW: 113.16



Isoleucine (Ile, I)
MW: 113.16

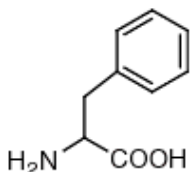


Methionine (Met, M)
MW: 131.19

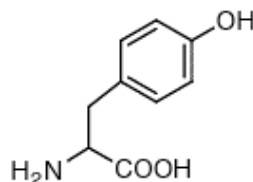


Proline (Pro, P)
MW: 97.12

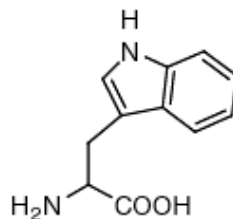
Aromatic



Phenylalanine (Phe, F)
MW: 147.18

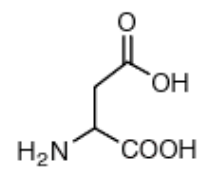


Tyrosine (Tyr, Y)
MW: 163.18

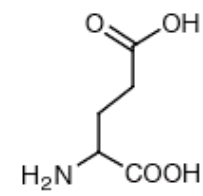


Tryptophan (Trp, W)
MW: 186.21

Acidic

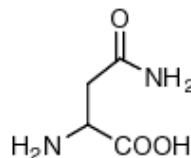


Aspartic Acid (Asp, D)
MW: 115.09, $pK_a = 3.9$

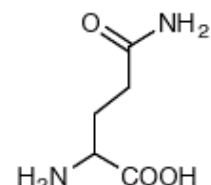


Glutamic Acid (Glu, E)
MW: 129.12, $pK_a = 4.07$

Amide

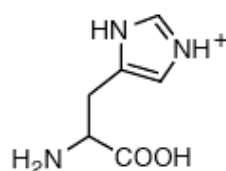


Asparagine (Asn, N)
MW: 114.11

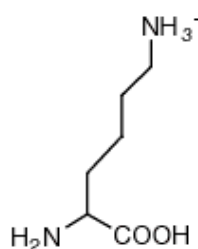


Glutamine (Gln, Q)
MW: 128.14

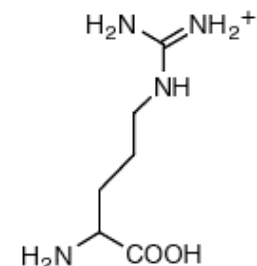
Basic



Histidine (His, H)
MW: 137.14, $pK_a = 6.04$



Lysine (Lys, K)
MW: 128.17, $pK_a = 10.79$



Arginine (Arg, R)
MW: 156.19, $pK_a = 12.48$

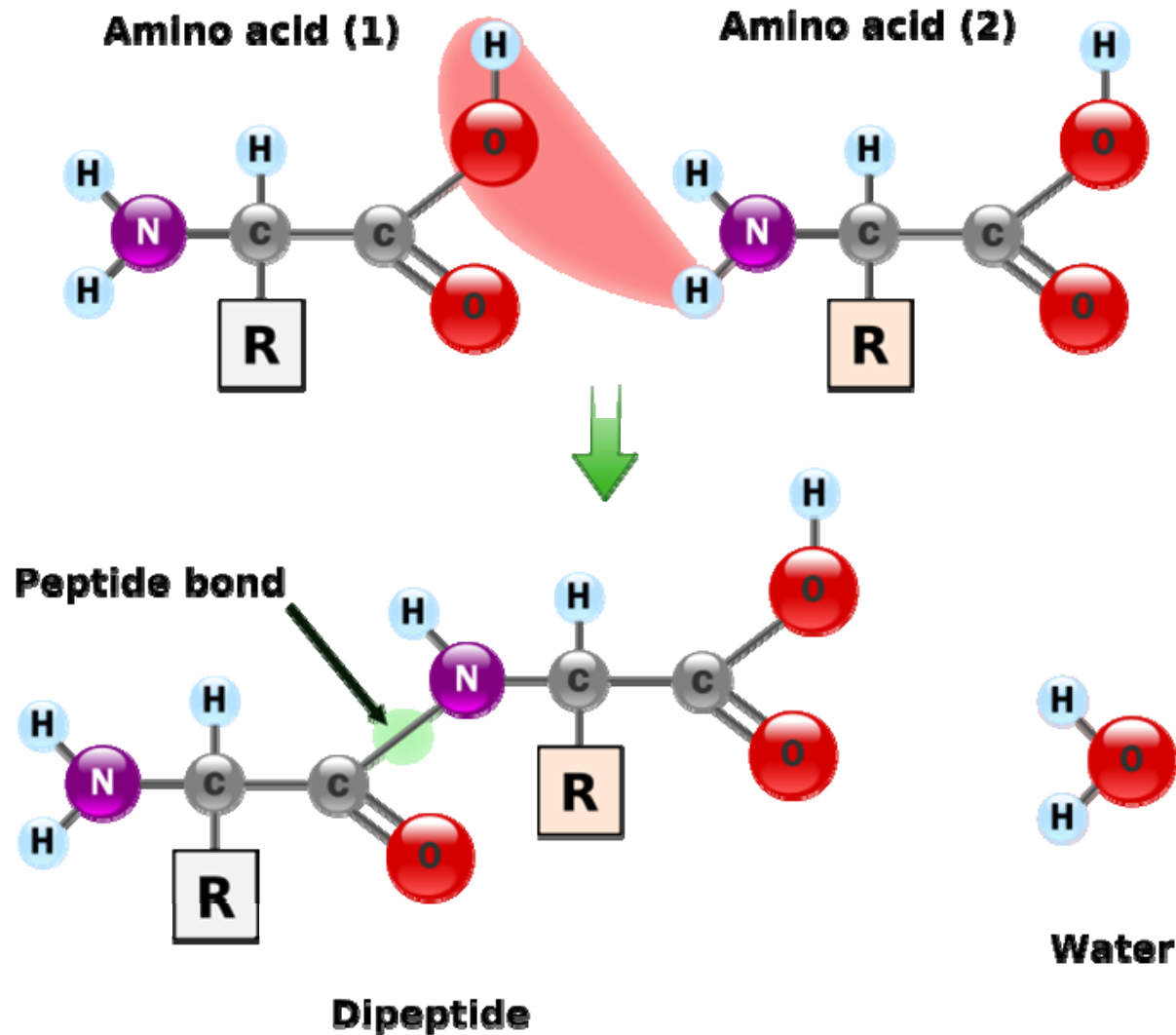


Protein Structure and Function

- Proteins are **polymers** of amino acids.
- Each amino acids in a protein contains a amino group, -NH₂, a carboxyl group, -COOH, and an R group, all bonded to the central carbon atom. The R group may be a hydrocarbon or they may contain functional group.
- All amino acids present in a proteins are ***α-amino acids*** in which the amino group is bonded to the carbon next to the carboxyl group.
- Two or more amino acids can join together by forming amide bond, which is known as a ***peptide bond*** when they occur in proteins.

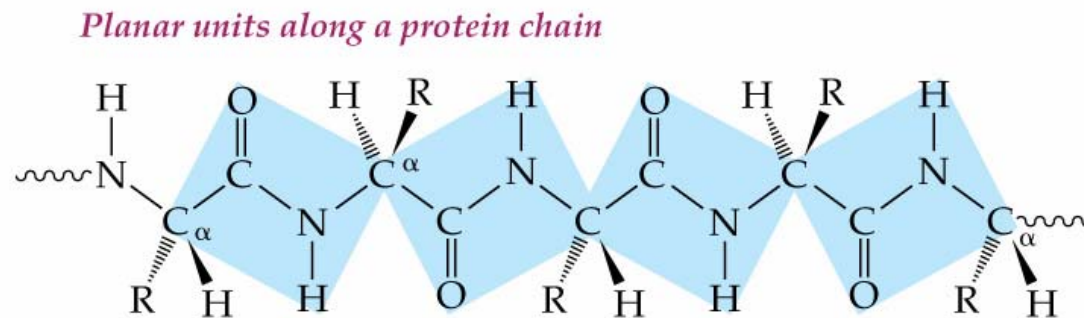


Peptide bond

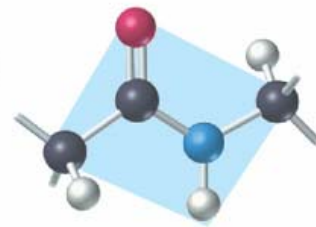


Primary Protein Structure

- Primary structure of a proteins is the sequence of amino acids connected by **peptide bonds**. Along the backbone of the proteins is a chain of alternating peptide bonds and α -carbons and the amino acid side chains are connected to these



One planar unit



- By convention, peptides and proteins are always written with the amino terminal amino acid (N-terminal) on the left and carboxyl-terminal amino acid (C-terminal) on the right.

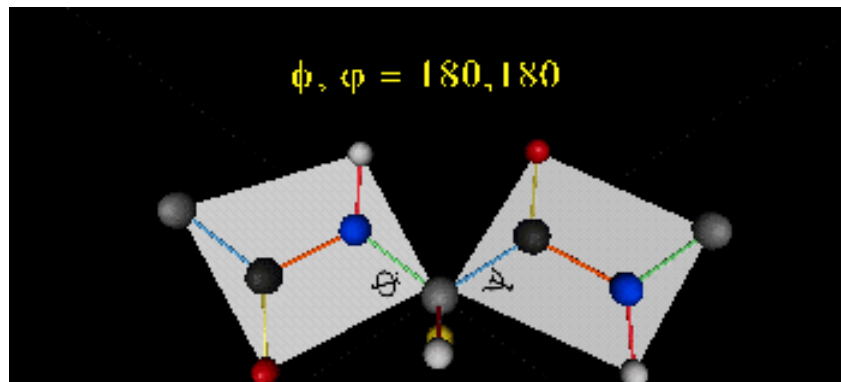
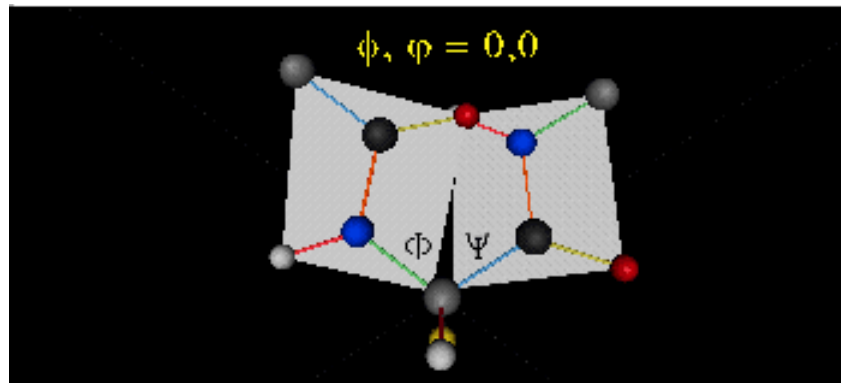
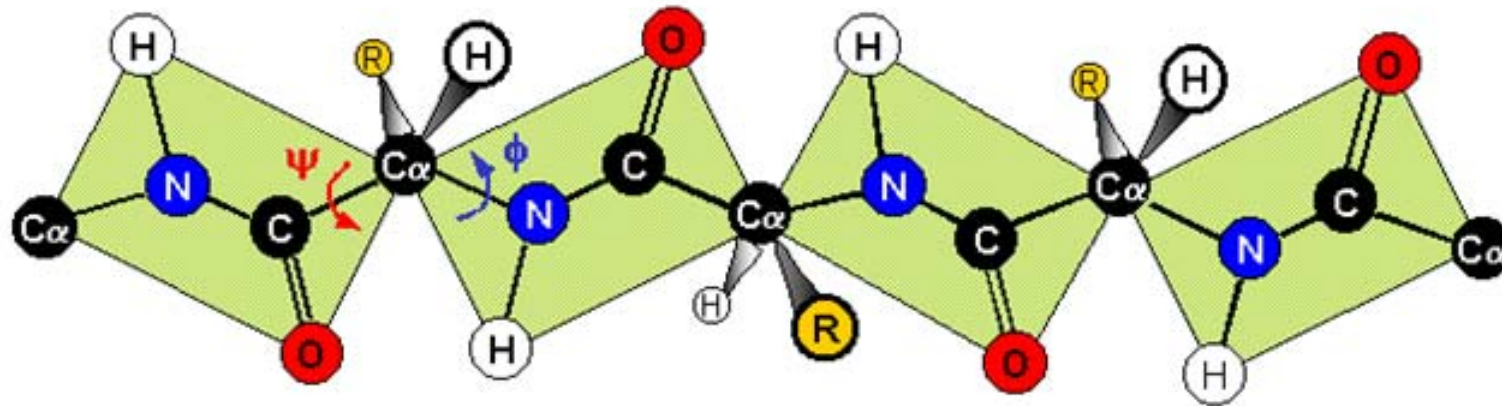


Secondary Protein Structure

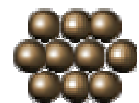
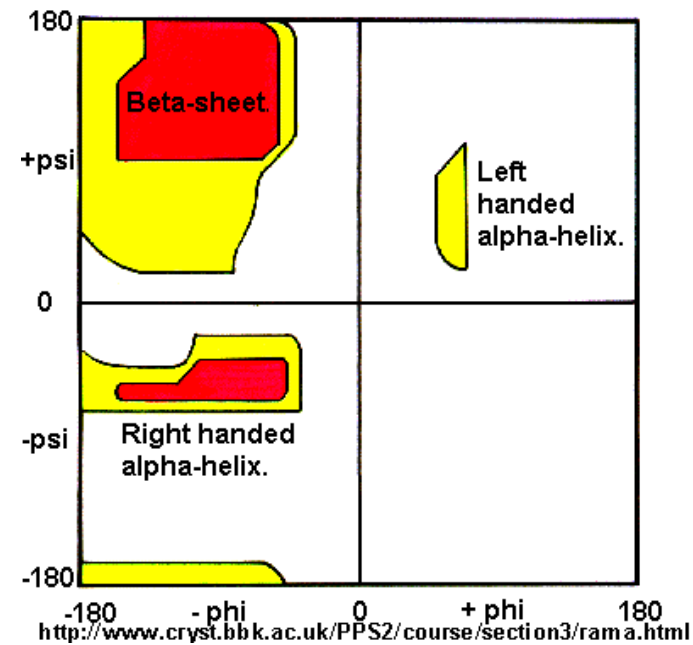
- Secondary structure of a protein is the arrangement of polypeptide backbone of the protein in space. The secondary structure includes two kinds of repeating pattern known as the *α -helix and β -sheet*.
- Hydrogen bonding between backbone atoms are responsible for both of these secondary structures.



FULLY EXTENDED POLYPEPTIDE CHAIN

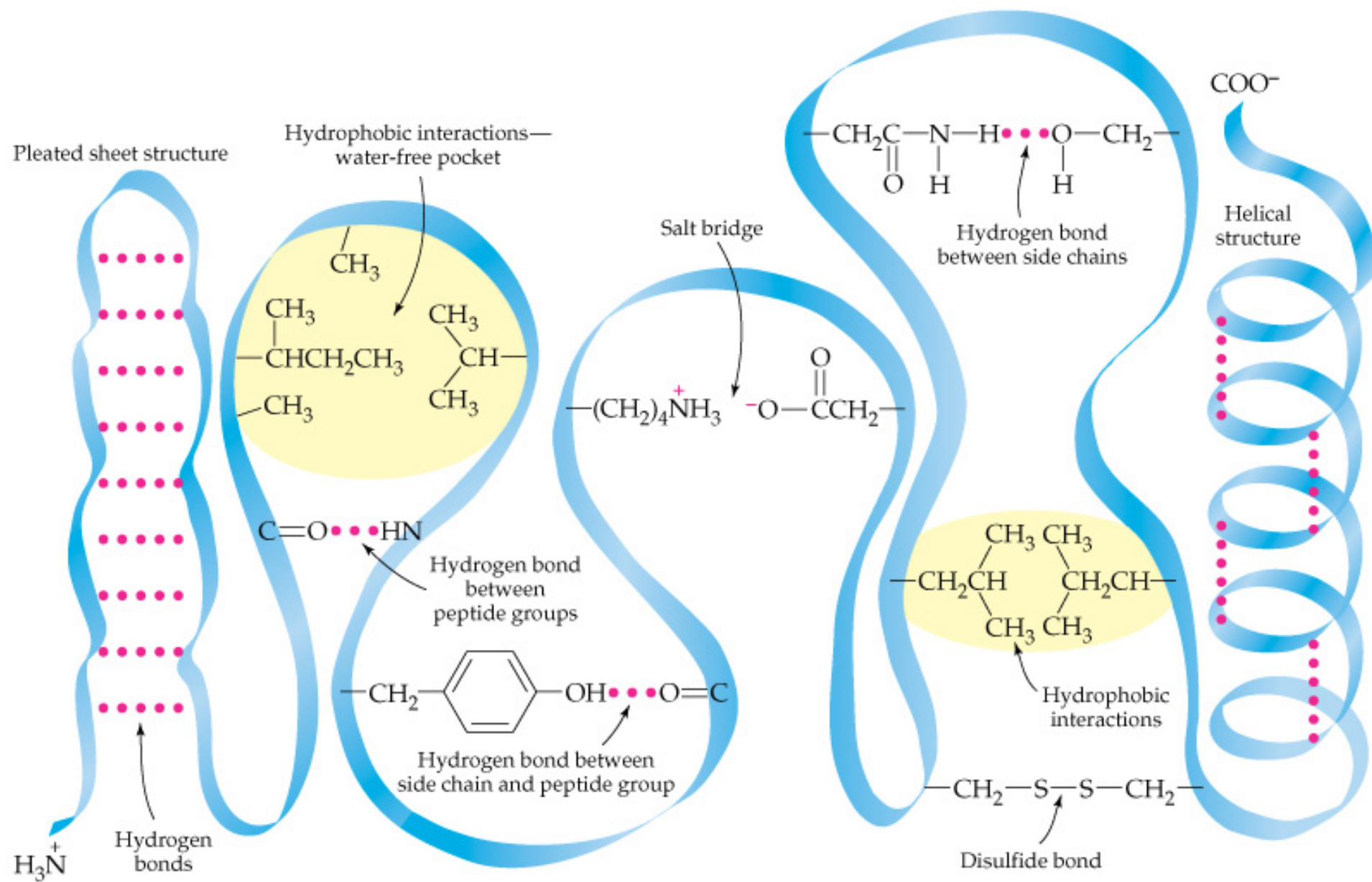


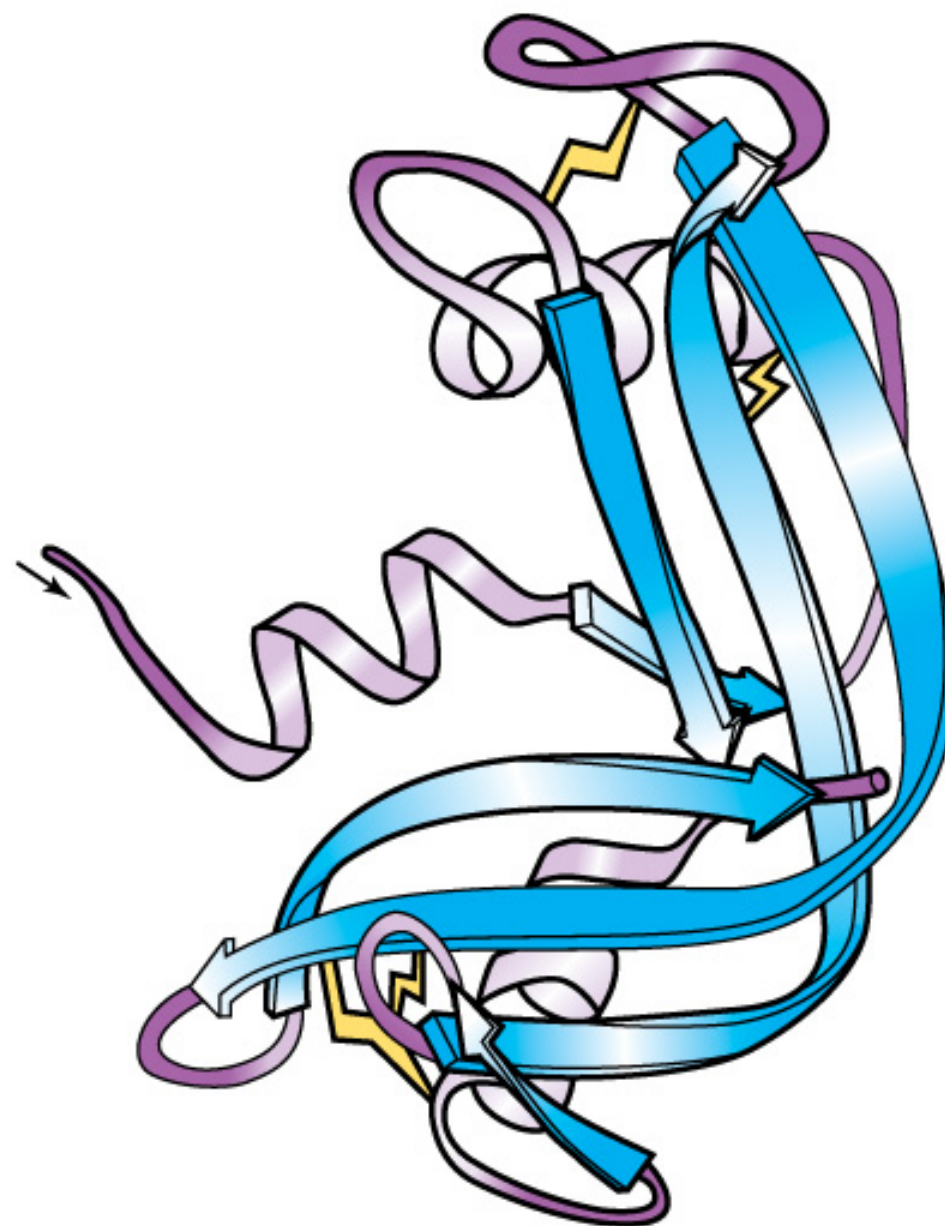
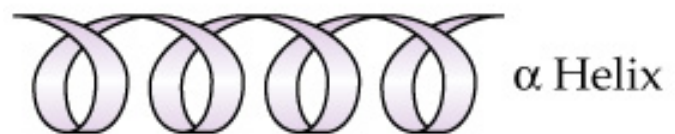
The Ramachandran Plot.



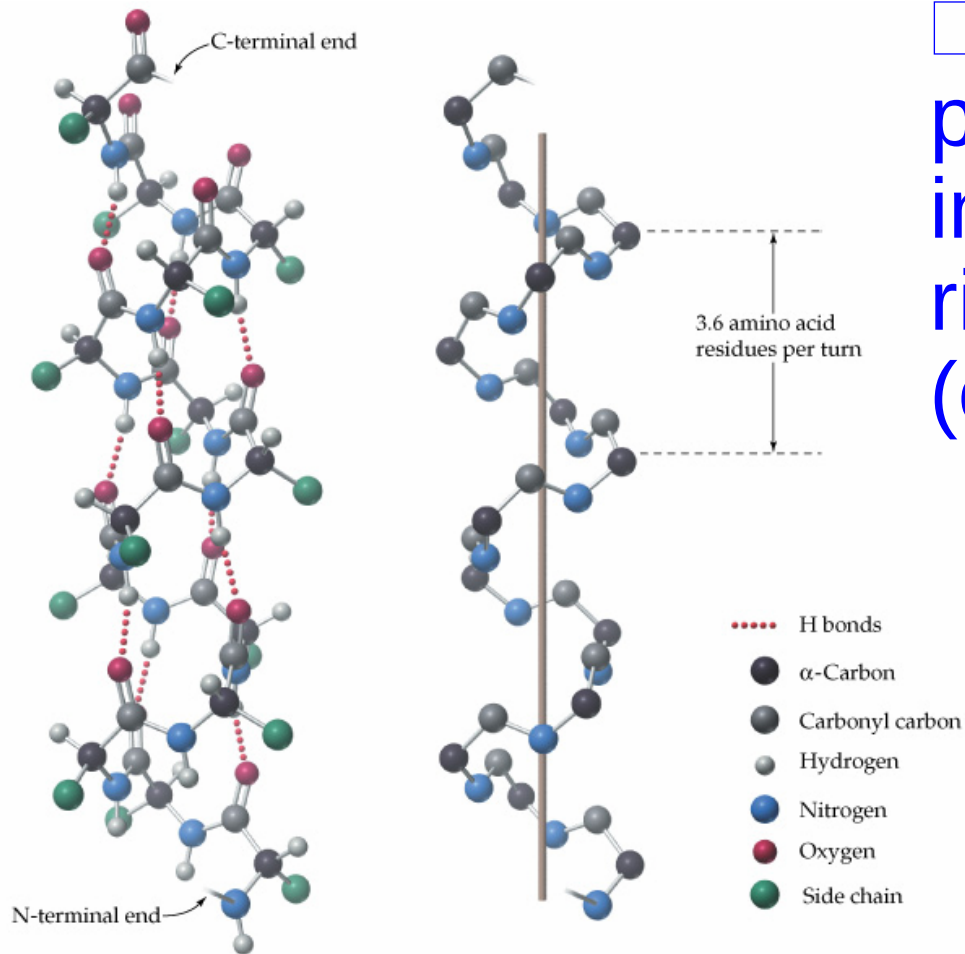
- Protein shape determining interactions are summarized below:
- **Hydrogen bond** between neighboring backbone segments.
- Hydrogen bonds of side chains with each other or with backbone atoms.
- **Ionic attractions** between side chain groups or salt bridge.
- **Hydrophobic** interactions between side chain groups.
- Covalent **sulfur-sulfur** bonds.



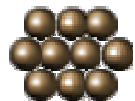




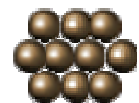
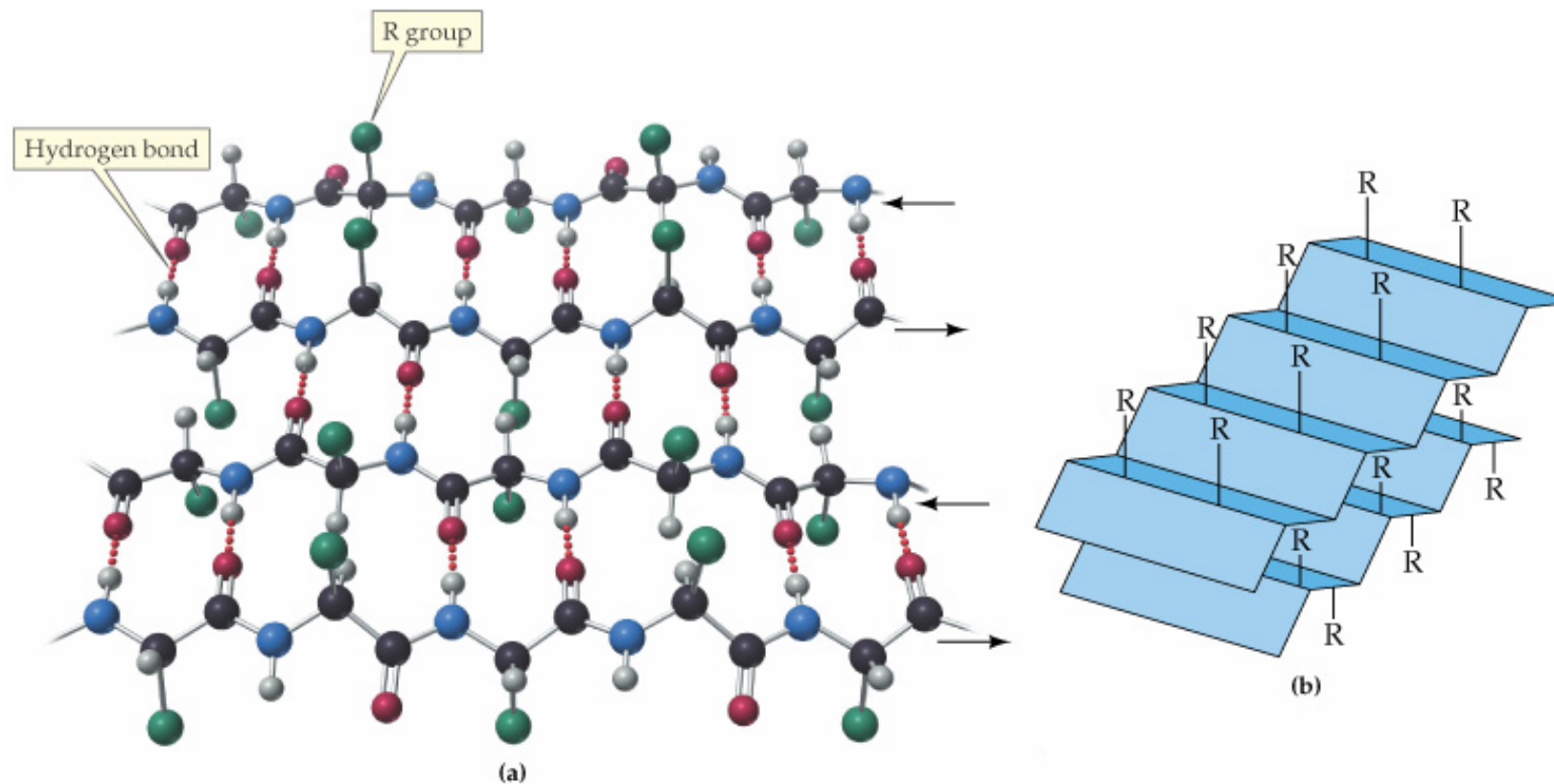
Ribonuclease



□ **α -Helix:** A single protein chain coiled in a spiral with a right-handed (clockwise) twist.

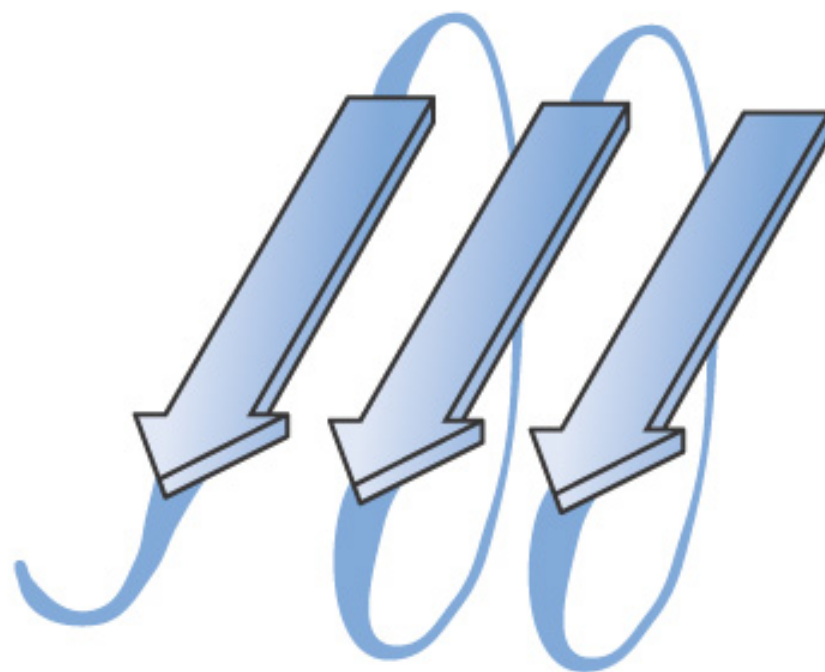


□ **β -Sheet:** The polypeptide chain is held in place by hydrogen bonds between pairs of peptide units along neighboring backbone segments.





α helix



β sheet

Shape-Determining Interactions in Proteins

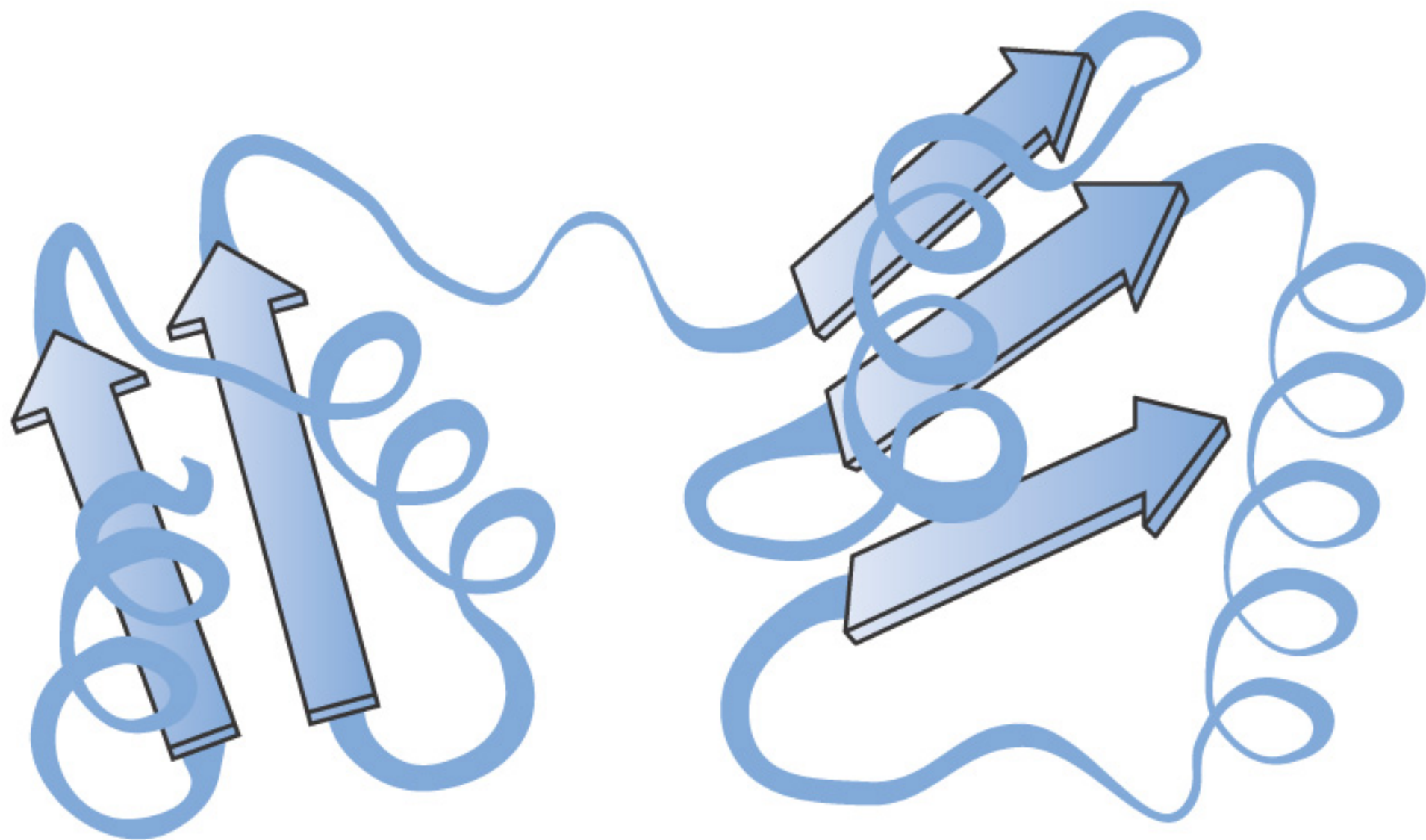
- The essential structure-function relationship for each protein depends on the polypeptide chain being held in its necessary shape by the interactions of atoms in the side chains.

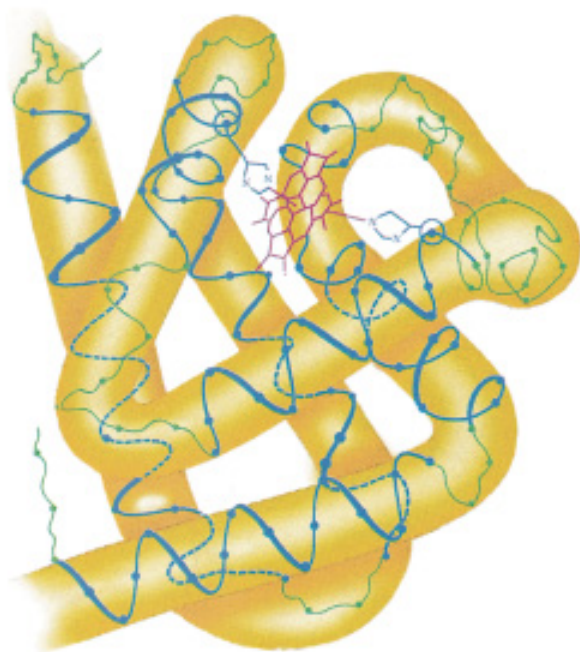


Tertiary Protein Structure

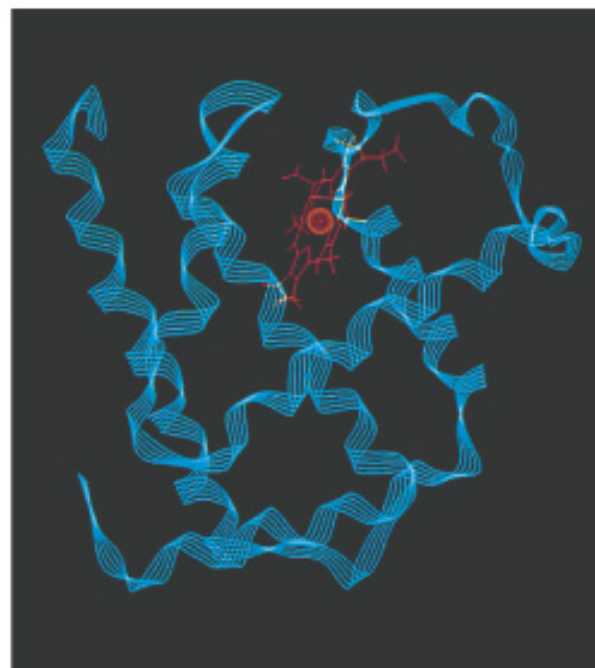
- ***Tertiary Structure of a proteins*** The overall three dimensional shape that results from the folding of a protein chain. Tertiary structure depends mainly on attractions of amino acid side chains that are far apart along the same backbone. Non-covalent interactions and disulfide covalent bonds govern tertiary structure.
- A protein with the shape in which it exist naturally in living organisms is known as a *native protein*.



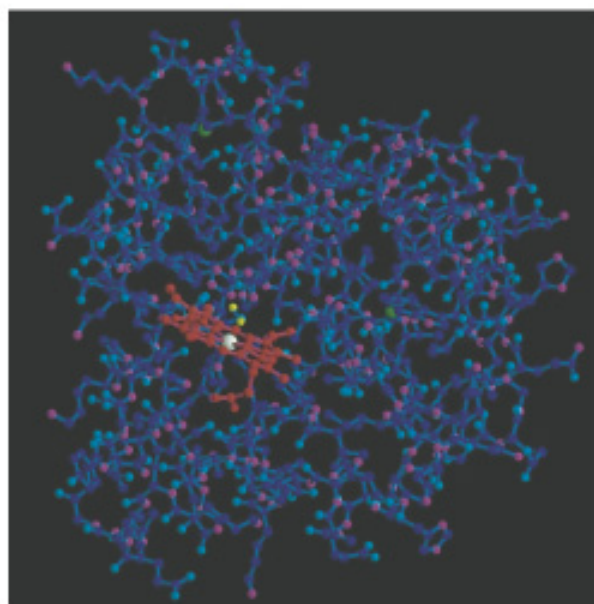




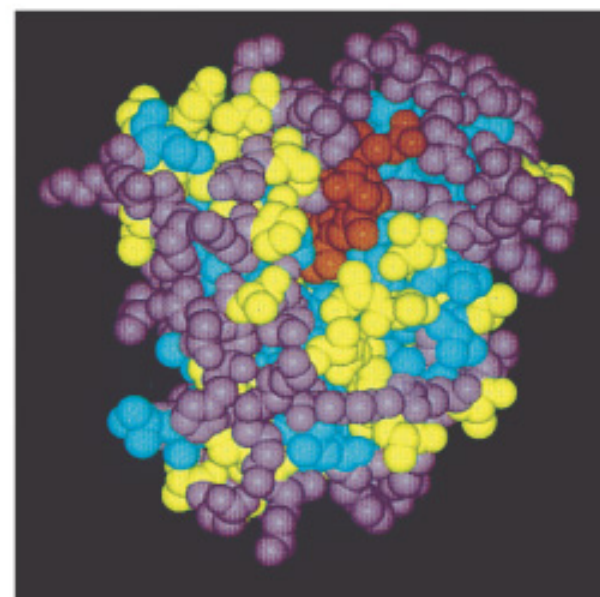
(a)



(b)



(c)

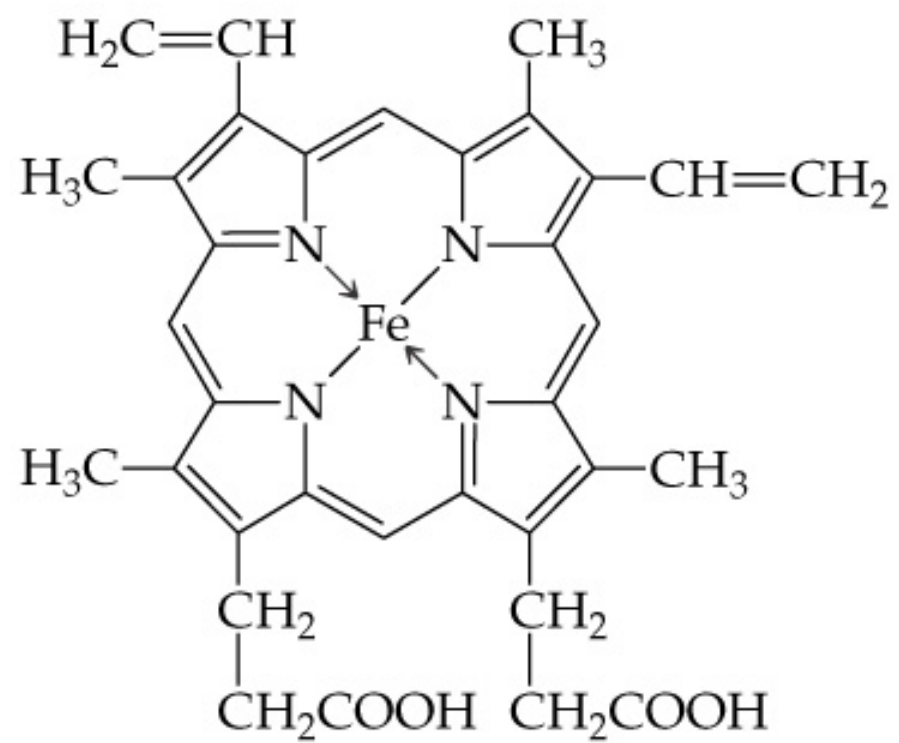


(d)

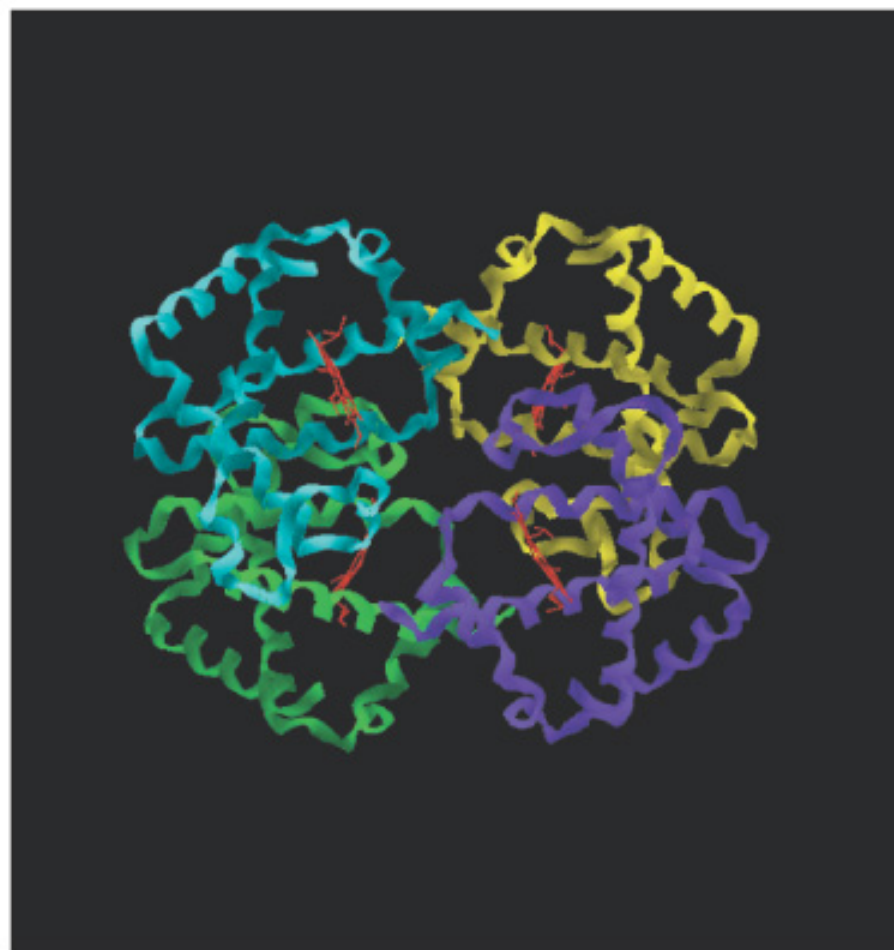
Quaternary Protein Structure

• ***Quaternary protein structure***: The way in which two or more polypeptide sub-units associate to form a single three-dimensional protein unit. Non-covalent forces are responsible for quaternary structure essential to the function of proteins.

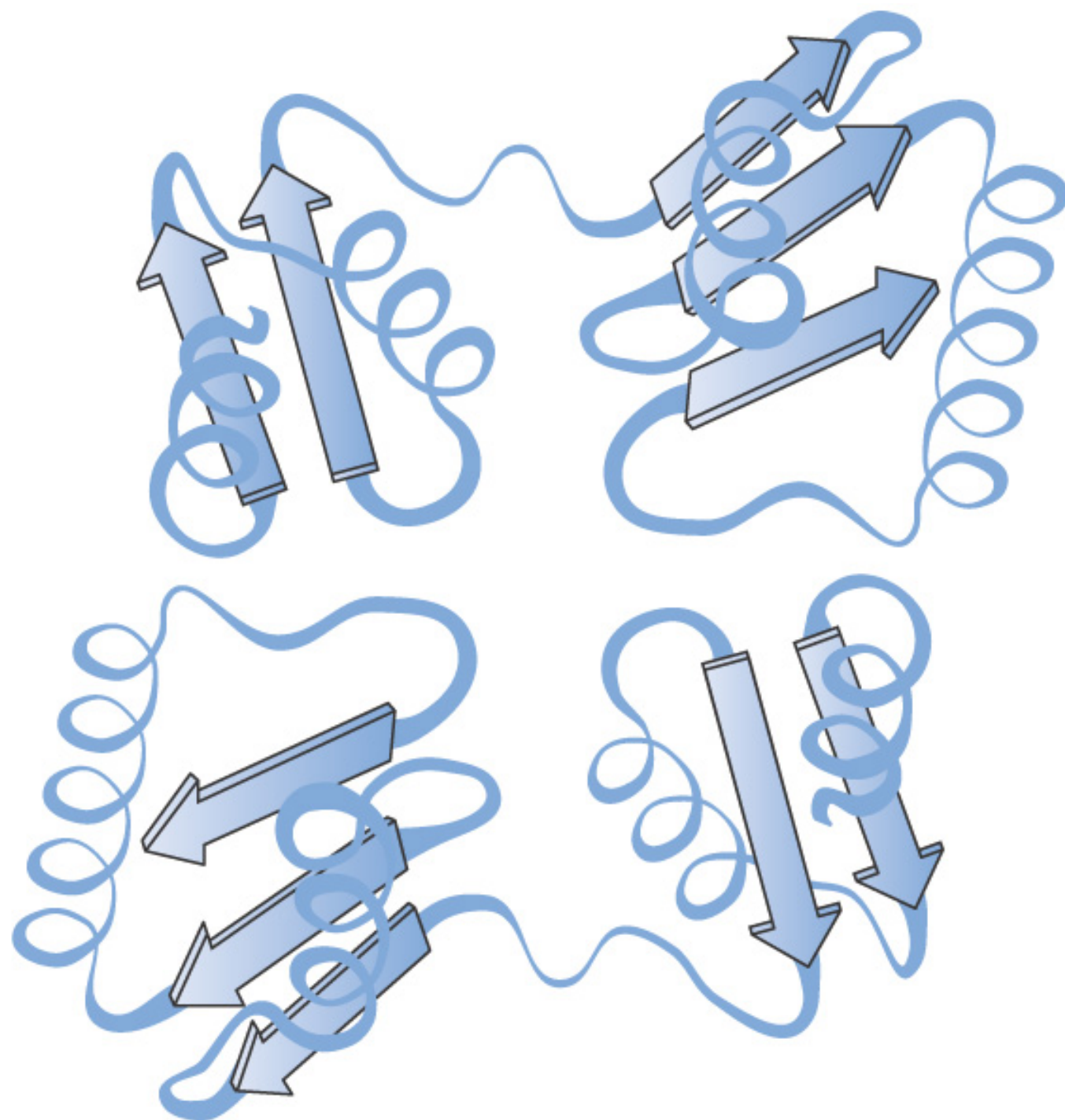


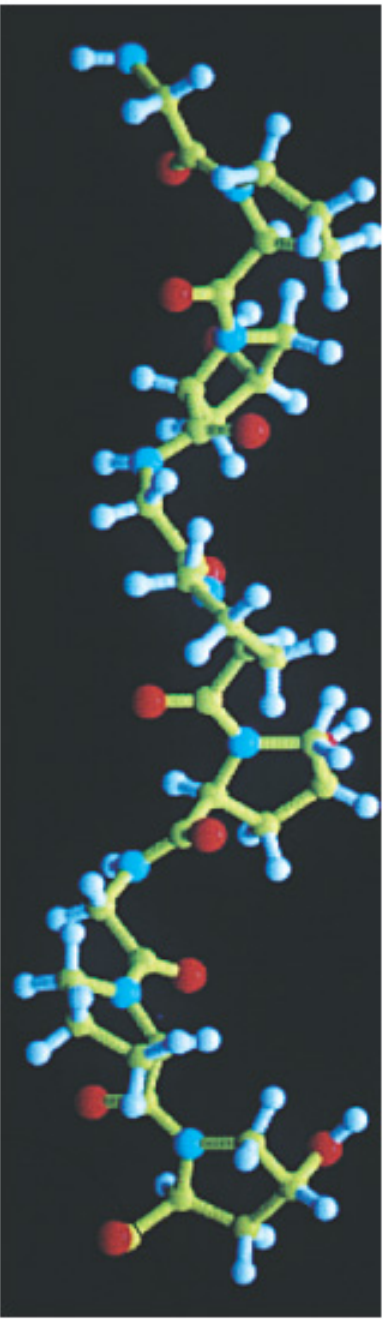


(a)

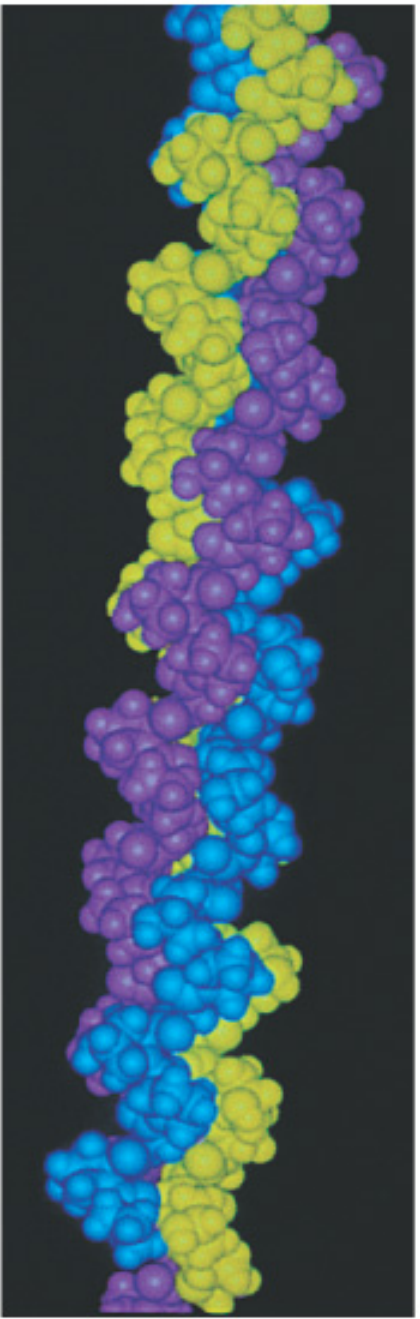


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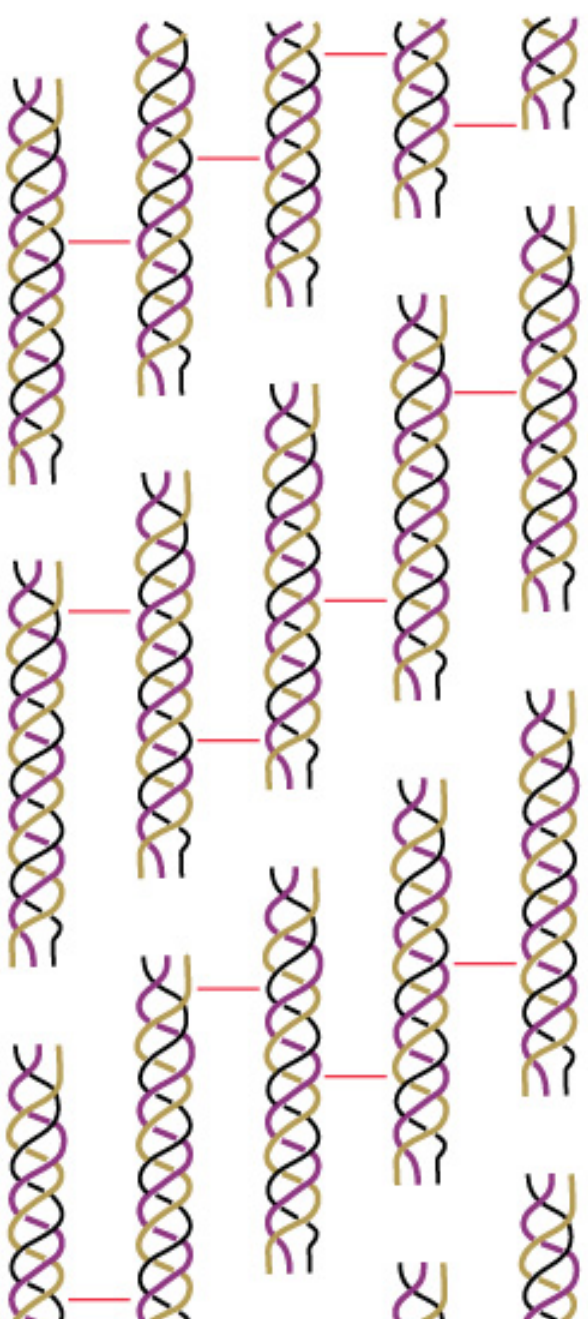




(a)



(b)



(c)

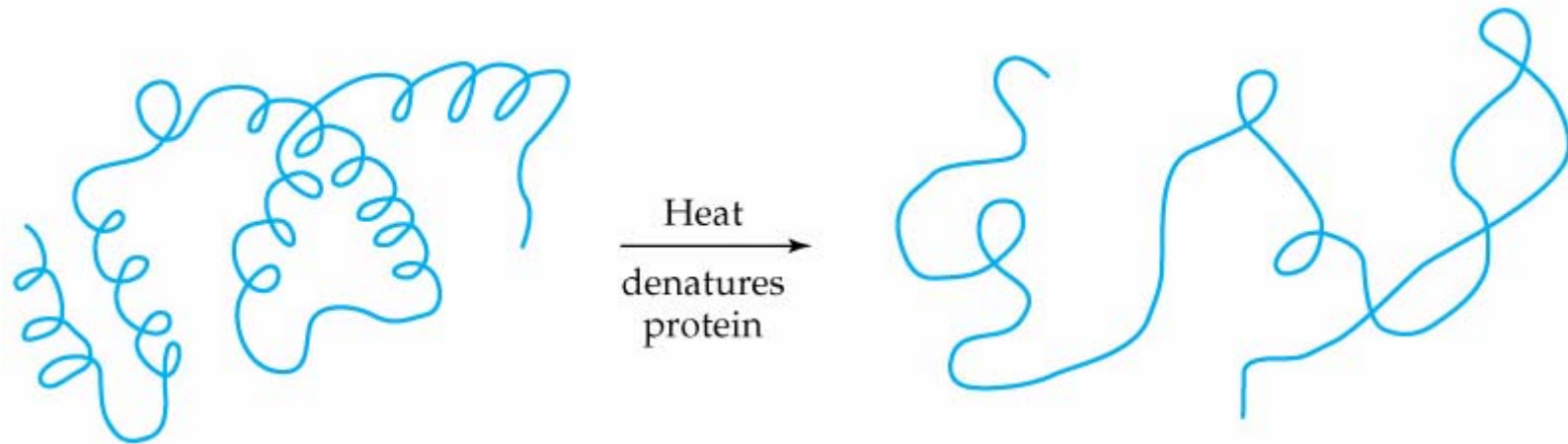
Chemical Properties of Proteins

- *Protein hydrolysis:* In protein hydrolysis, peptide bonds are hydrolyzed to yield amino acids. This is reverse of protein formation.





- *Protein denaturation*: The loss of secondary, tertiary, or quaternary protein structure due to disruption of non-covalent interactions and or disulfide bonds that leaves peptide bonds and primary

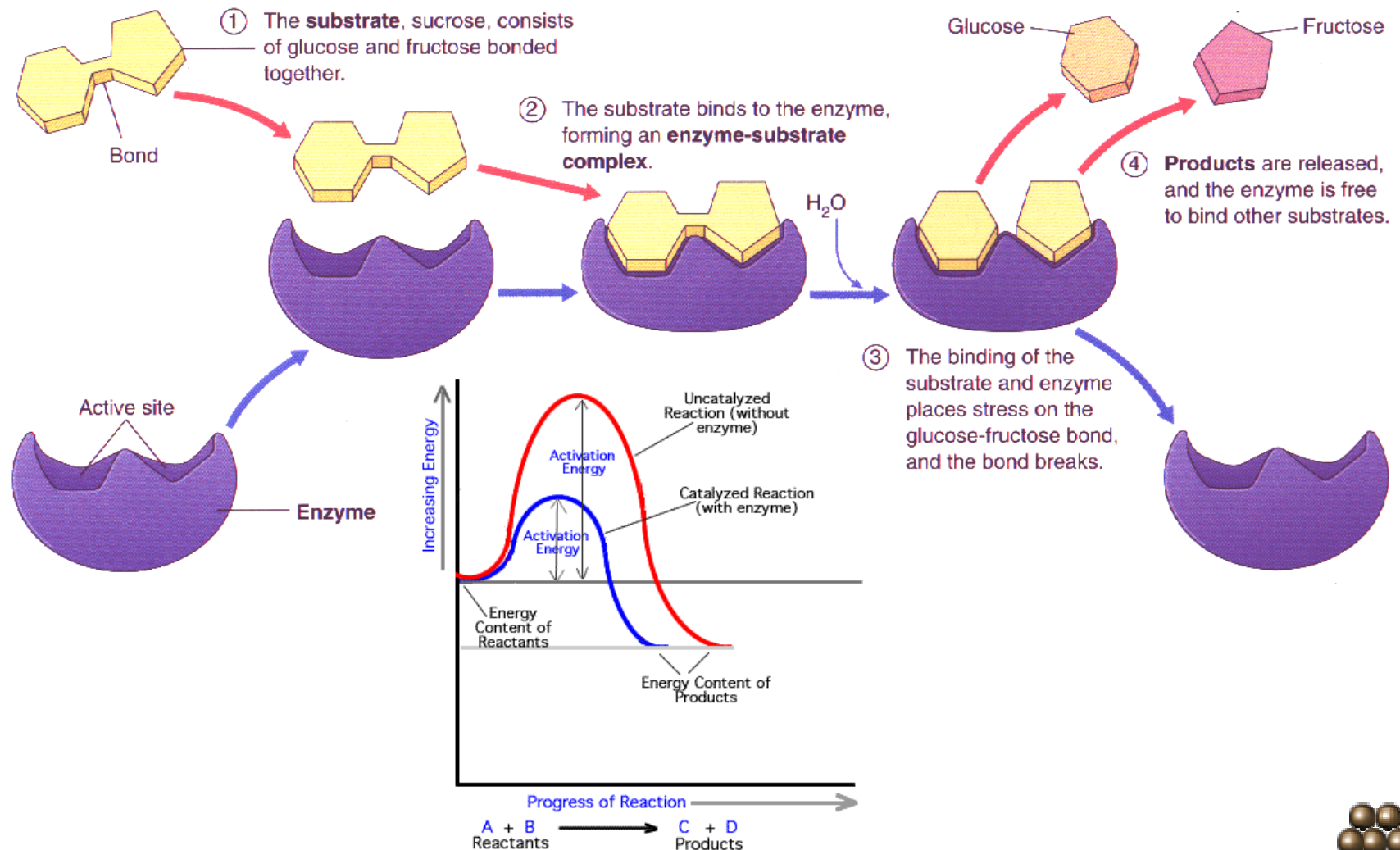


Catalysis by Enzymes

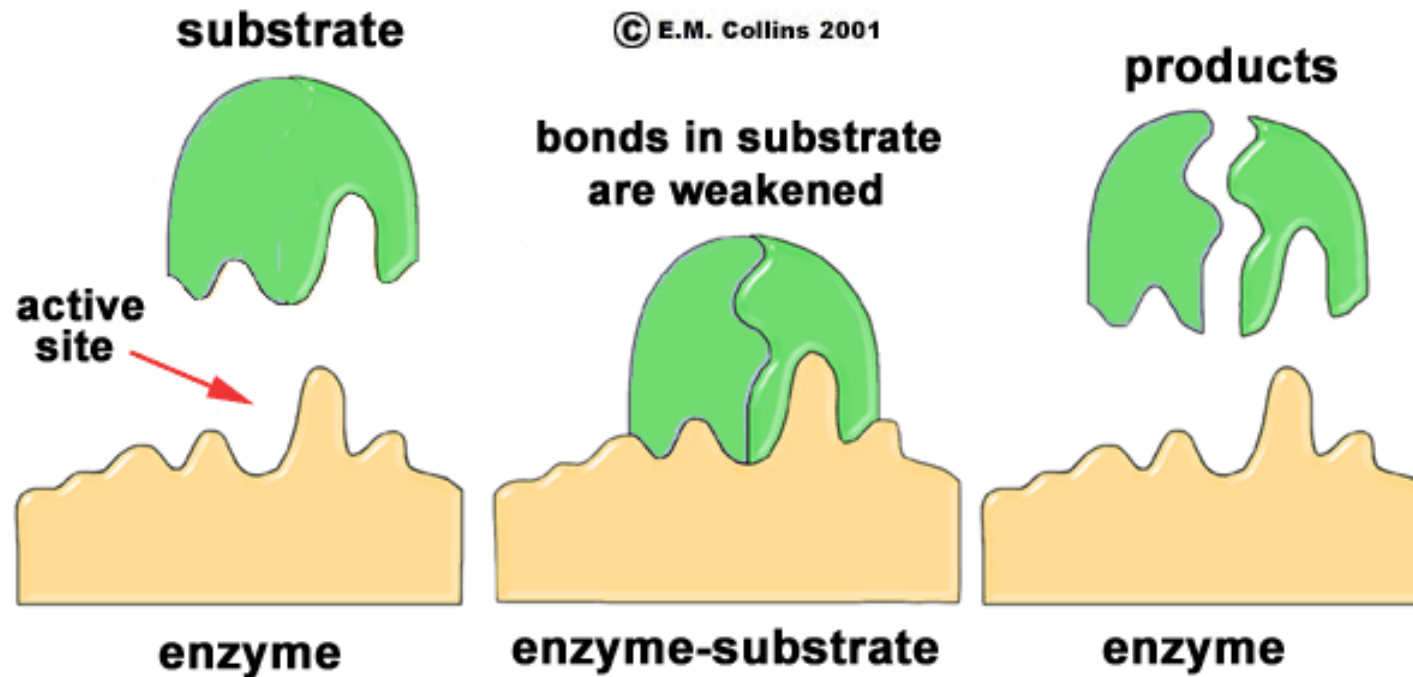
- ***Enzyme*** A protein that acts as a catalyst for a biochemical reaction.



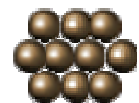
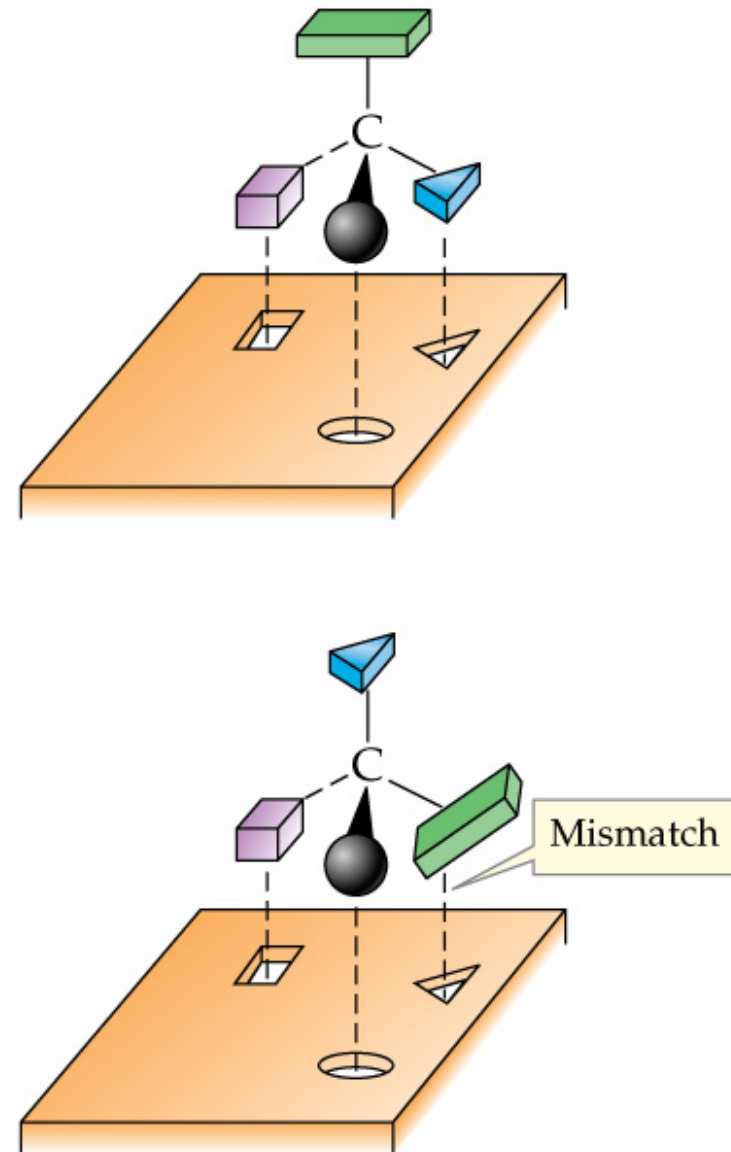
Enzymatic Reaction



Specificity



The specificity of an enzyme for one of two enantiomers is a matter of fit. One enantiomer fits better into the active site of the enzyme than the other enantiomer. Enzyme catalyzes reaction of the enantiomer that fits better into the active site of the enzyme.

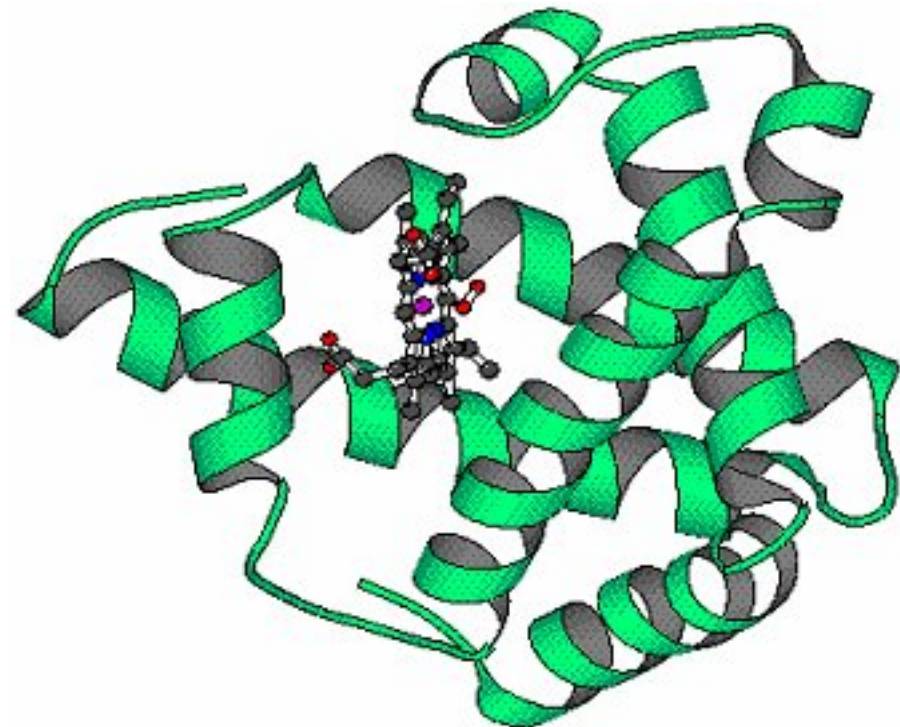
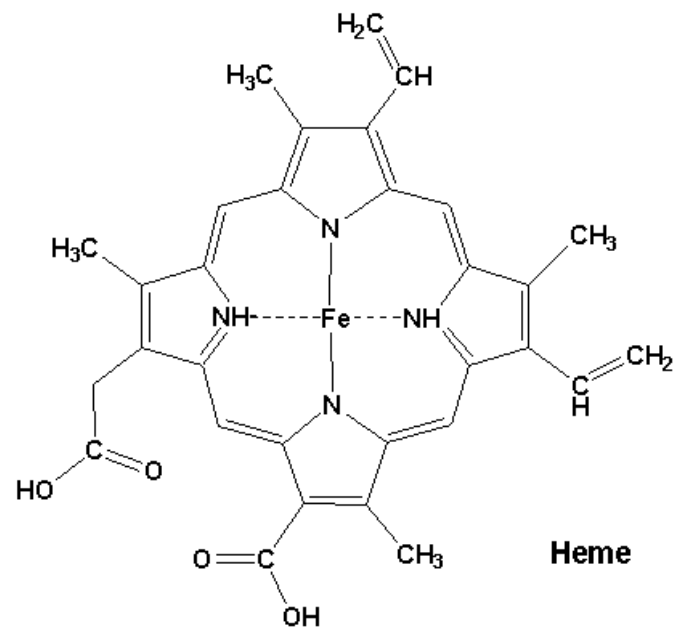
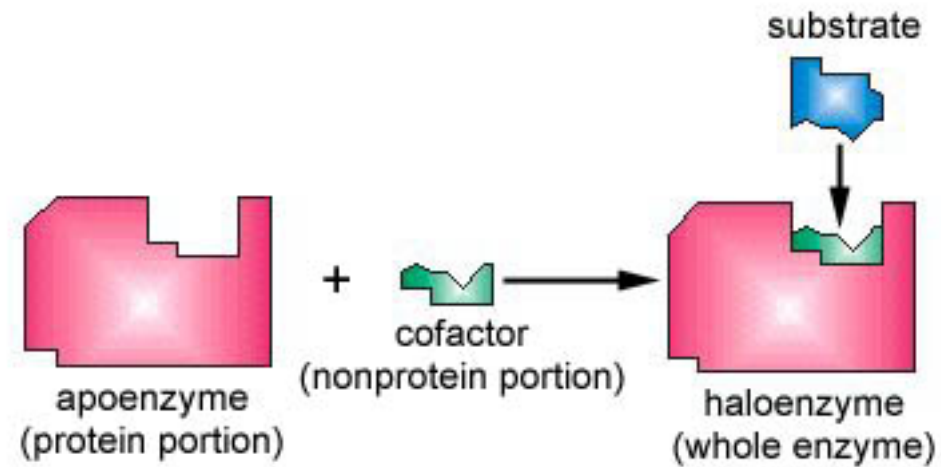


Enzyme Cofactors

- Many enzymes are conjugated proteins that require **nonprotein** portions known as ***cofactors***.
- Some cofactors are metal ions, others are nonprotein **organic molecules** called ***coenzymes***.
- An enzyme may require a metal-ion, a coenzyme, or both to function.



Cofactor



- Cofactors provide additional chemically active functional groups which are not present in the side chains of amino acids that made up the enzyme.
- Metal ions may anchor a substrate in the active site or may participate in the catalyzed reaction.



How Enzyme Work

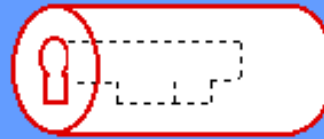
- Two modes are invoked to represent the interaction between substrate and enzymes. These are:
- ***Lock-and-key model***: The substrate is described as fitting into the active site as a key fit into a lock.
- ***Induced-fit-model***: The enzyme has a flexible active site that changes shape to accommodate the substrate and facilitate the reaction.



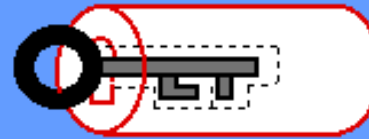
Lock and Key Analogy



key = substrate



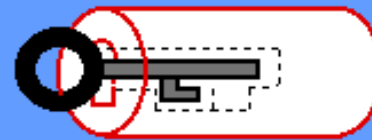
lock = enzyme



correct fit,
will react

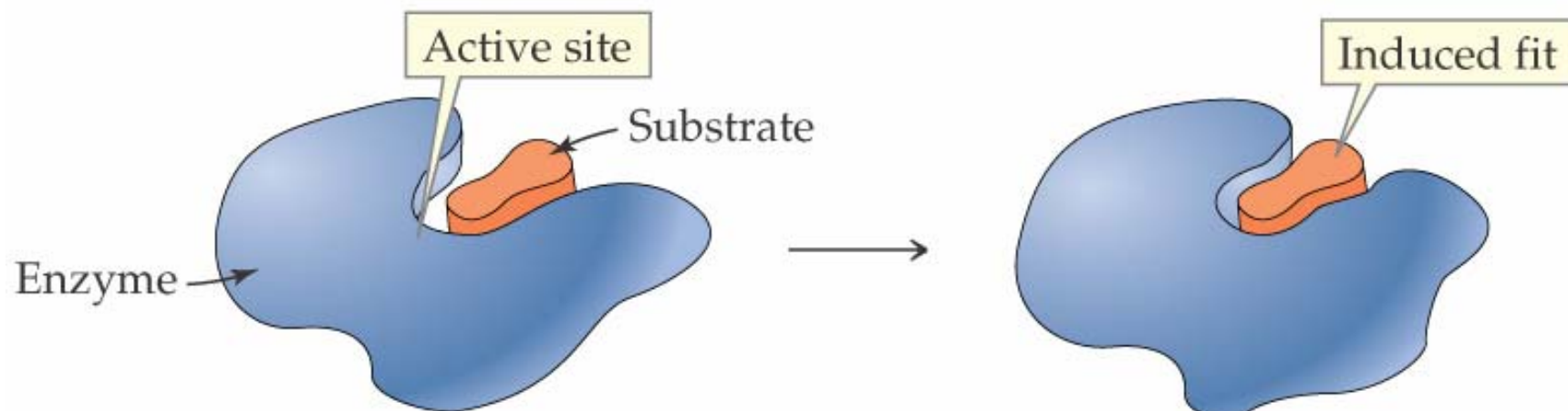


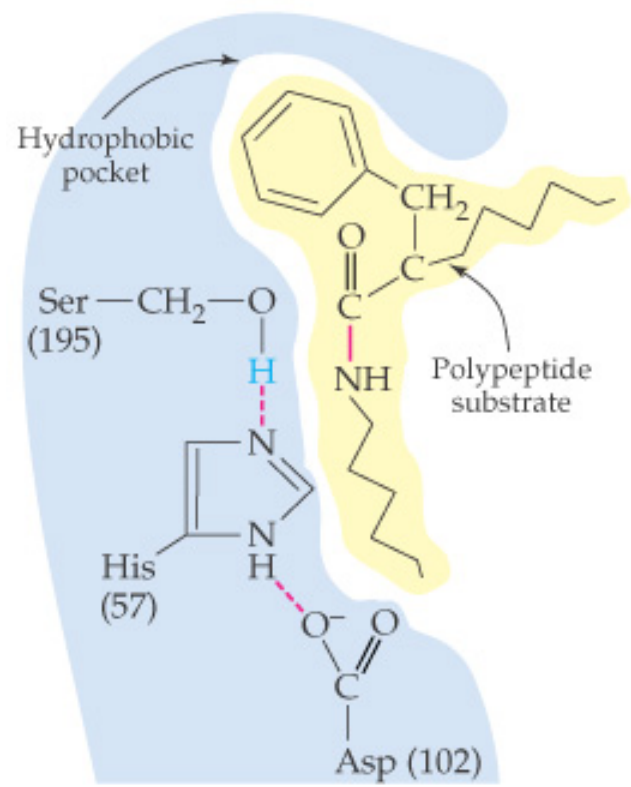
incorrect substrate



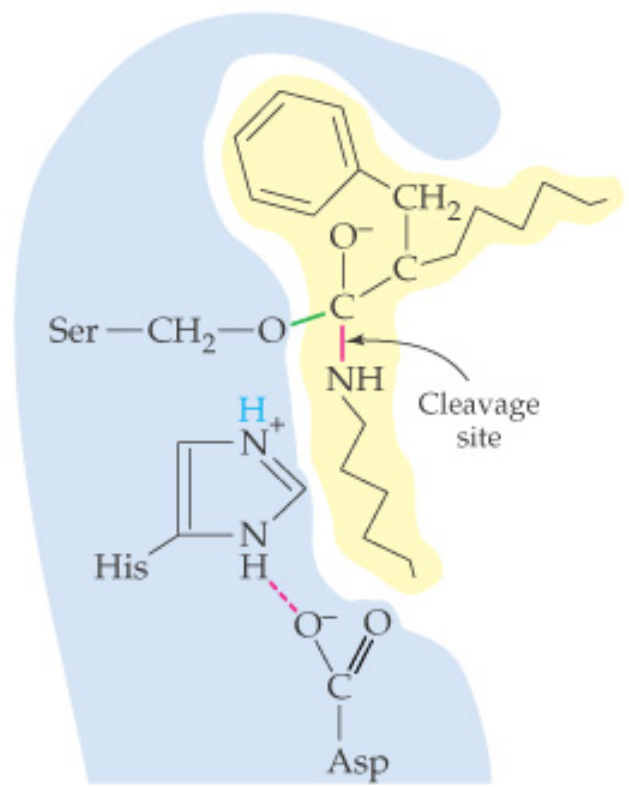
no reaction

C. Ophardt, c. 2003

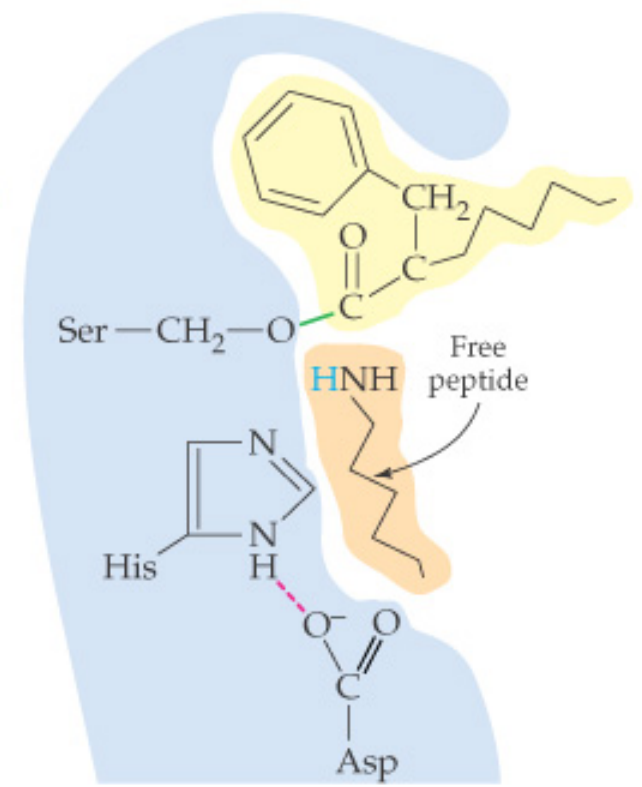




(a)



(b)



(c)

19.5 Effect of Concentration on Enzyme Activity

- Variation in concentration of enzyme or substrate alters the rate of enzyme catalyzed reactions.
- *Substrate concentration:* At low substrate concentration, the reaction rate is directly proportional to the substrate concentration. With increasing substrate concentration, the rate drops off as more of the active sites are occupied.



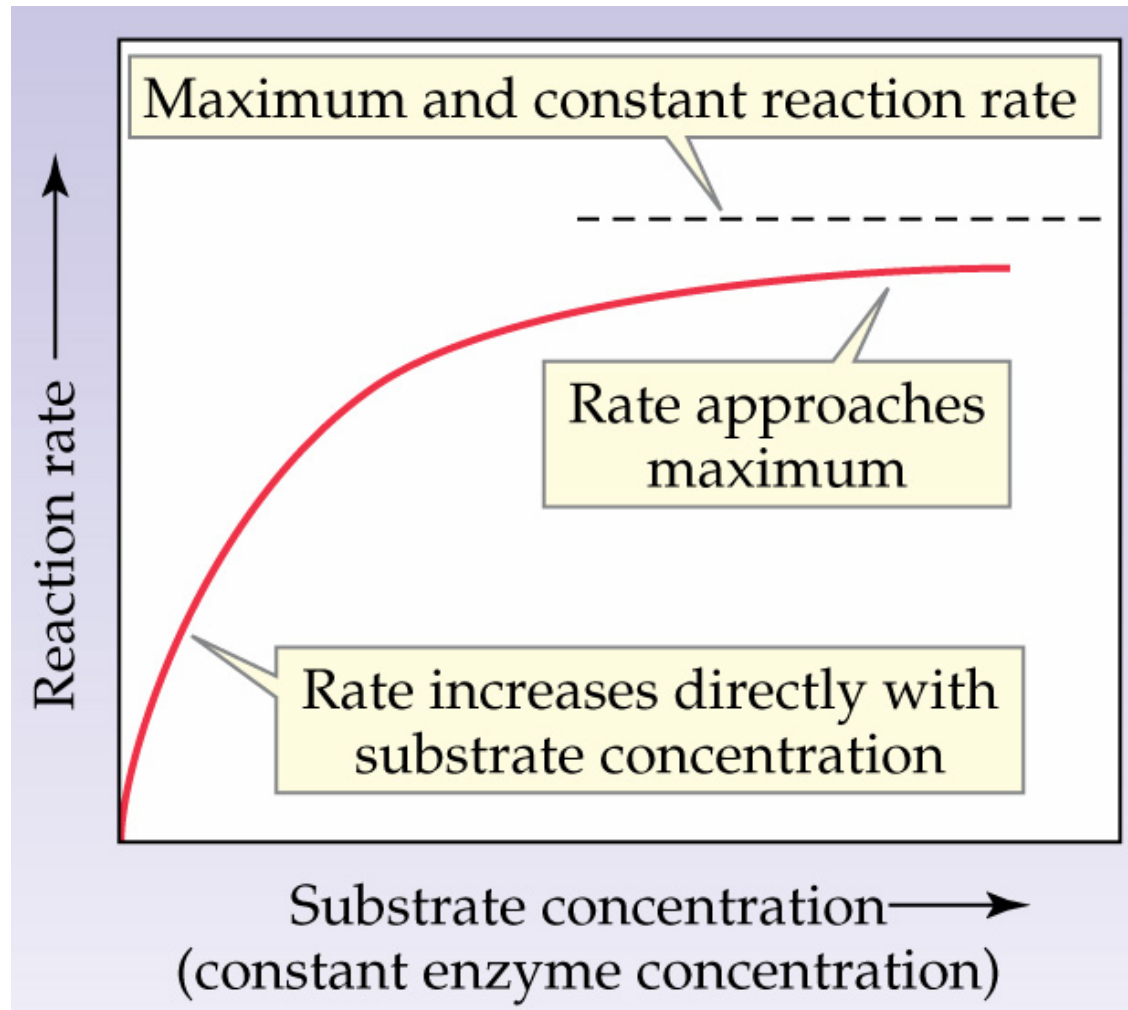
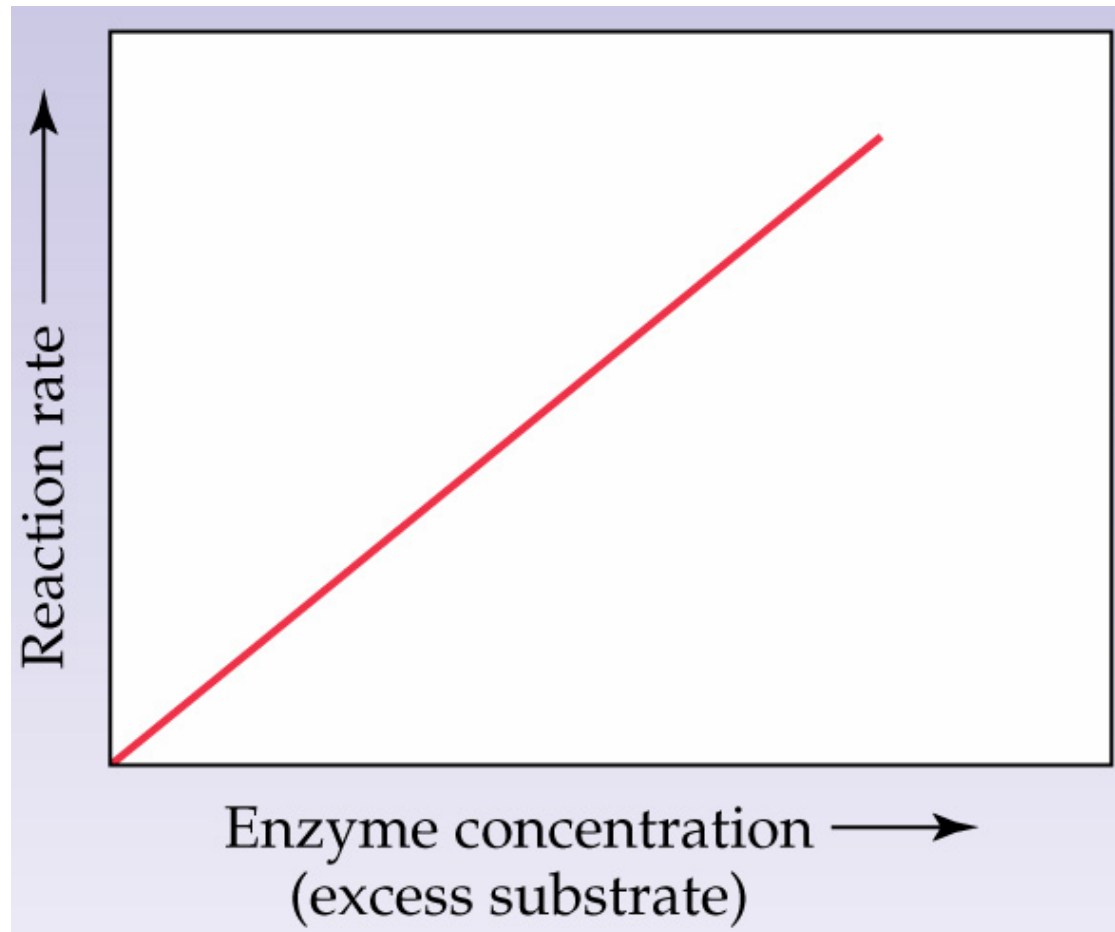


Fig 19.5 Change of reaction rate with substrate concentration when enzyme concentration is constant.



- *Enzyme concentration:* The reaction rate varies directly with the enzyme concentration as long as the substrate concentration does not become a limitation, Fig 19.6 below.



19.6 Effect of Temperature and pH on Enzyme Activity

- Enzymes maximum catalytic activity is highly dependent on temperature and pH.
- Increase in temperature increases the rate of enzyme catalyzed reactions. The rates reach a maximum and then begins to decrease. The decrease in rate at higher temperature is due to denaturation of enzymes.



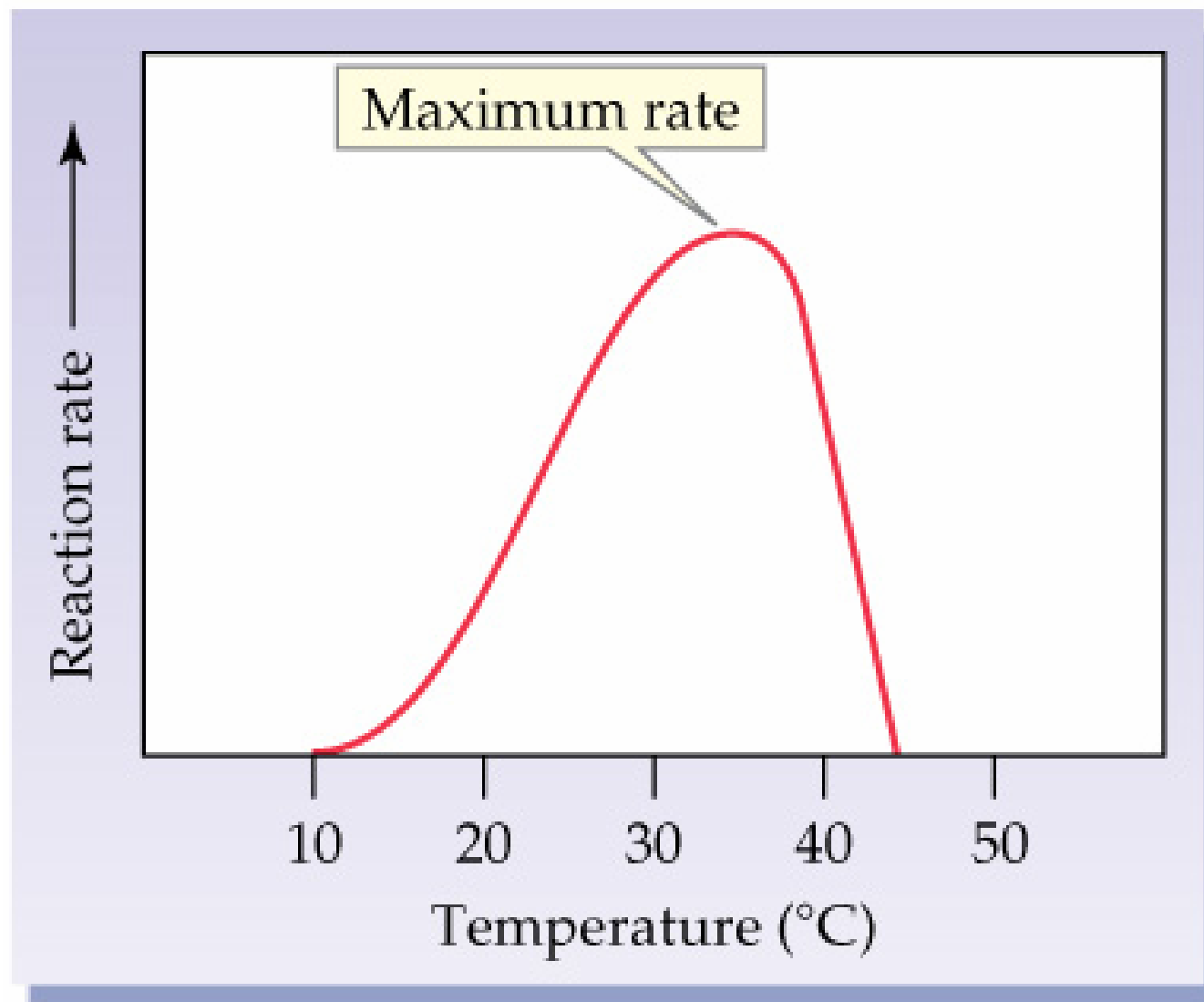
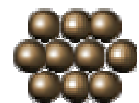
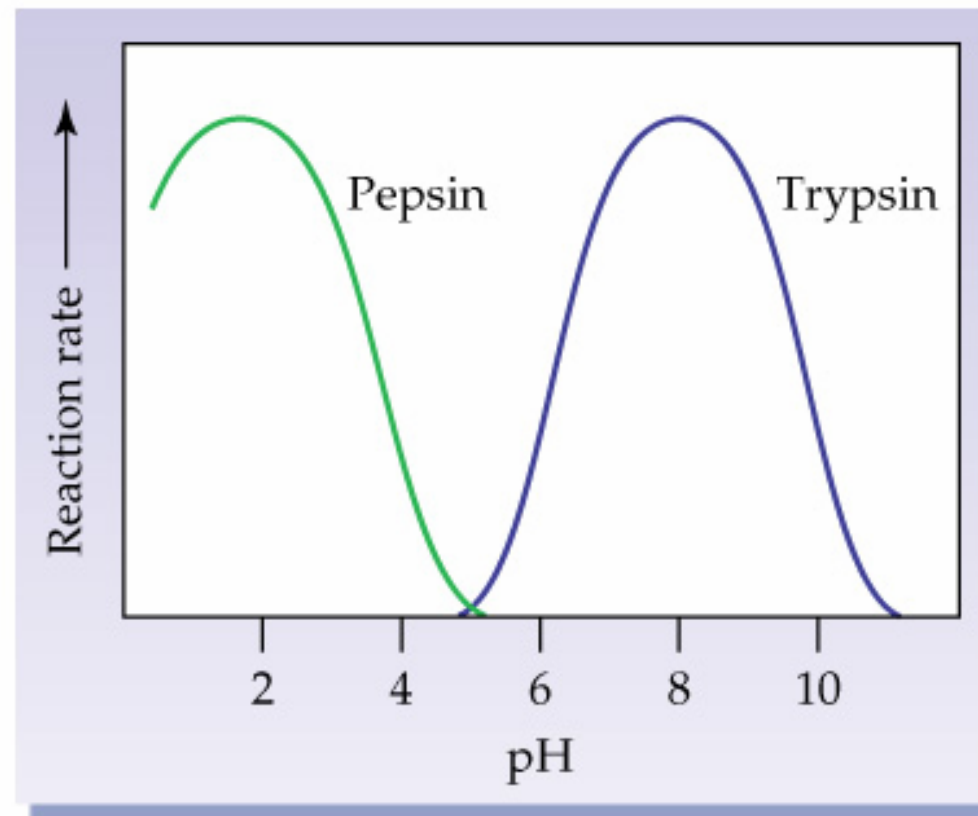


Fig 19.7 (a) Effect of temperature on reaction rate



- Effect of pH on Enzyme activity: The catalytic activity of enzymes depends on pH and usually has a well defined optimum point for maximum catalytic activity Fig 19.7 (b) below.



19.7 Enzyme Regulation: Feedback and Allosteric Control

- Concentration of thousands of different chemicals vary continuously in living organisms which requires regulation of enzyme activity.
- Any process that starts or increase the activity of an enzyme is ***activation***.
- Any process that stops or slows the activity of an enzyme is ***inhibition***.

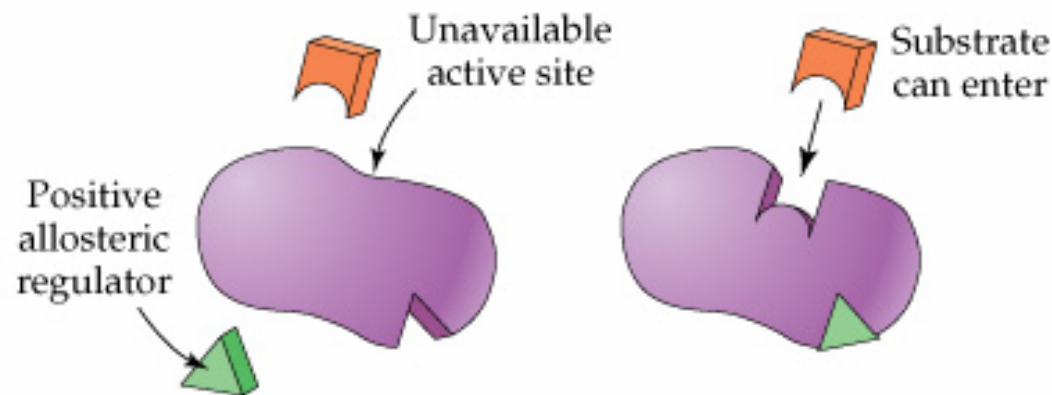


Two of the mechanism

- **Feedback control:** Regulation of an enzyme's activity by the product of a reaction later in a pathway.
- **Allosteric control:** Activity of an enzyme is controlled by the binding of an activator or inhibitor at a location other than the active site. Allosteric controls are further classified as positive or negative.
 - A positive regulator changes the activity site so that the enzyme becomes a better catalyst and rate accelerates.
 - A negative regulator changes the activity site so that the enzyme becomes less effective catalyst and rate slows down.

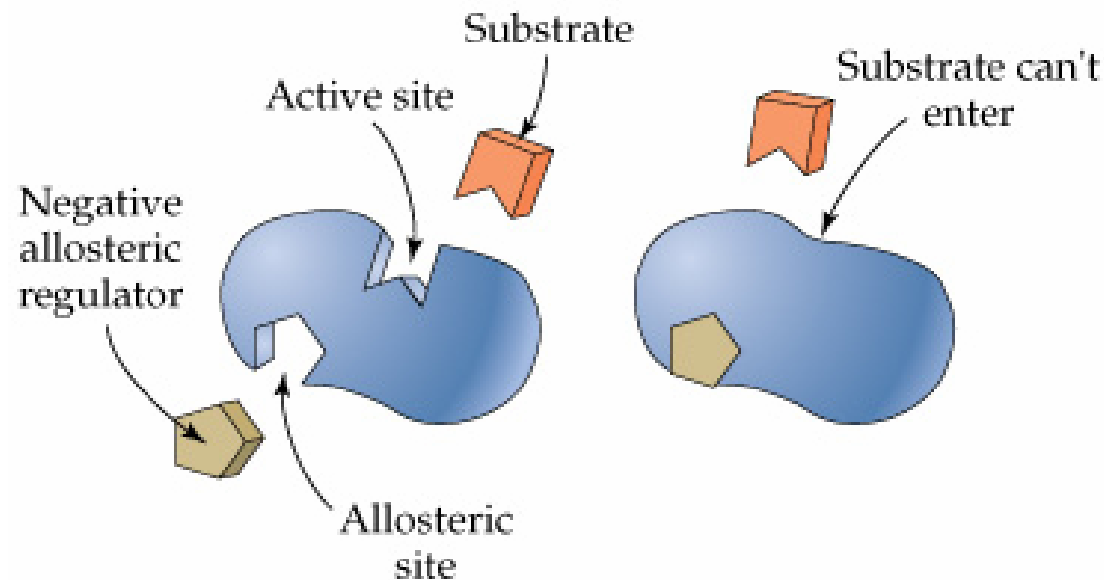


Positive allosteric control

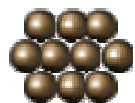


A positive regulator changes the activity site so that the enzyme becomes a better catalyst and rate accelerates.

Negative allosteric control



A negative regulator changes the activity site so that the enzyme becomes less effective catalyst and rate slows down.



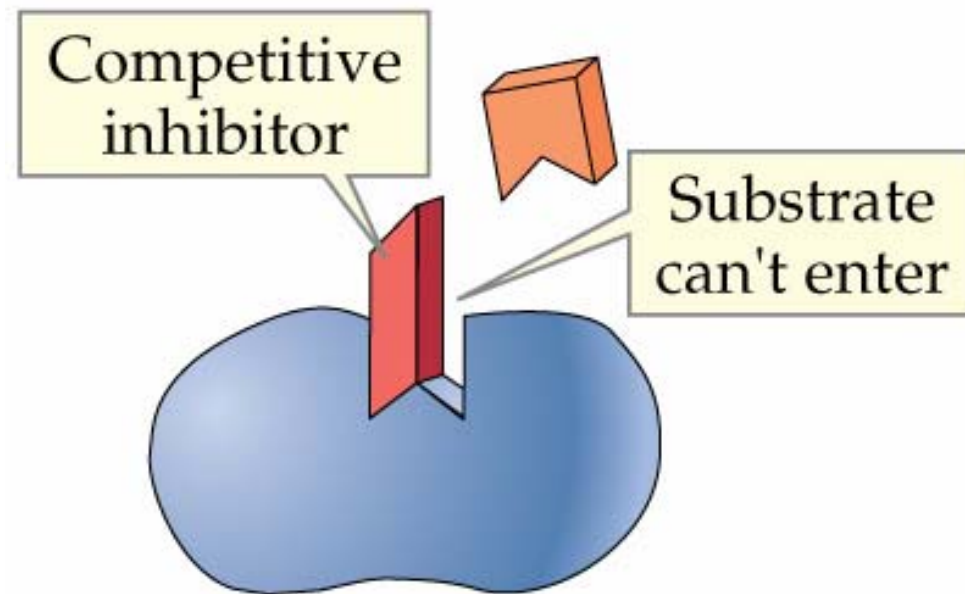
19.8 Enzyme Regulation: Inhibition

- The inhibition of an enzyme can be *reversible* or *irreversible*.
- In *reversible inhibition*, the inhibitor can leave, restoring the enzyme to its uninhibited level of activity.
- In *irreversible inhibition*, the inhibitor remains permanently bound to the enzyme and the enzyme is permanently inhibited.



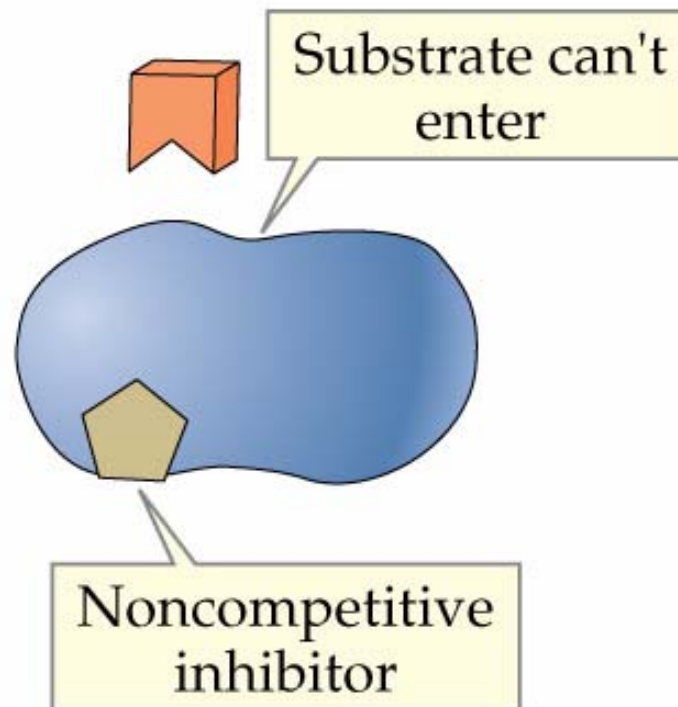
- Inhibitions are further classified as:
- *Competitive inhibition* if the inhibitor binds to the active site.

Competitive inhibition

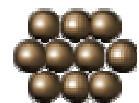
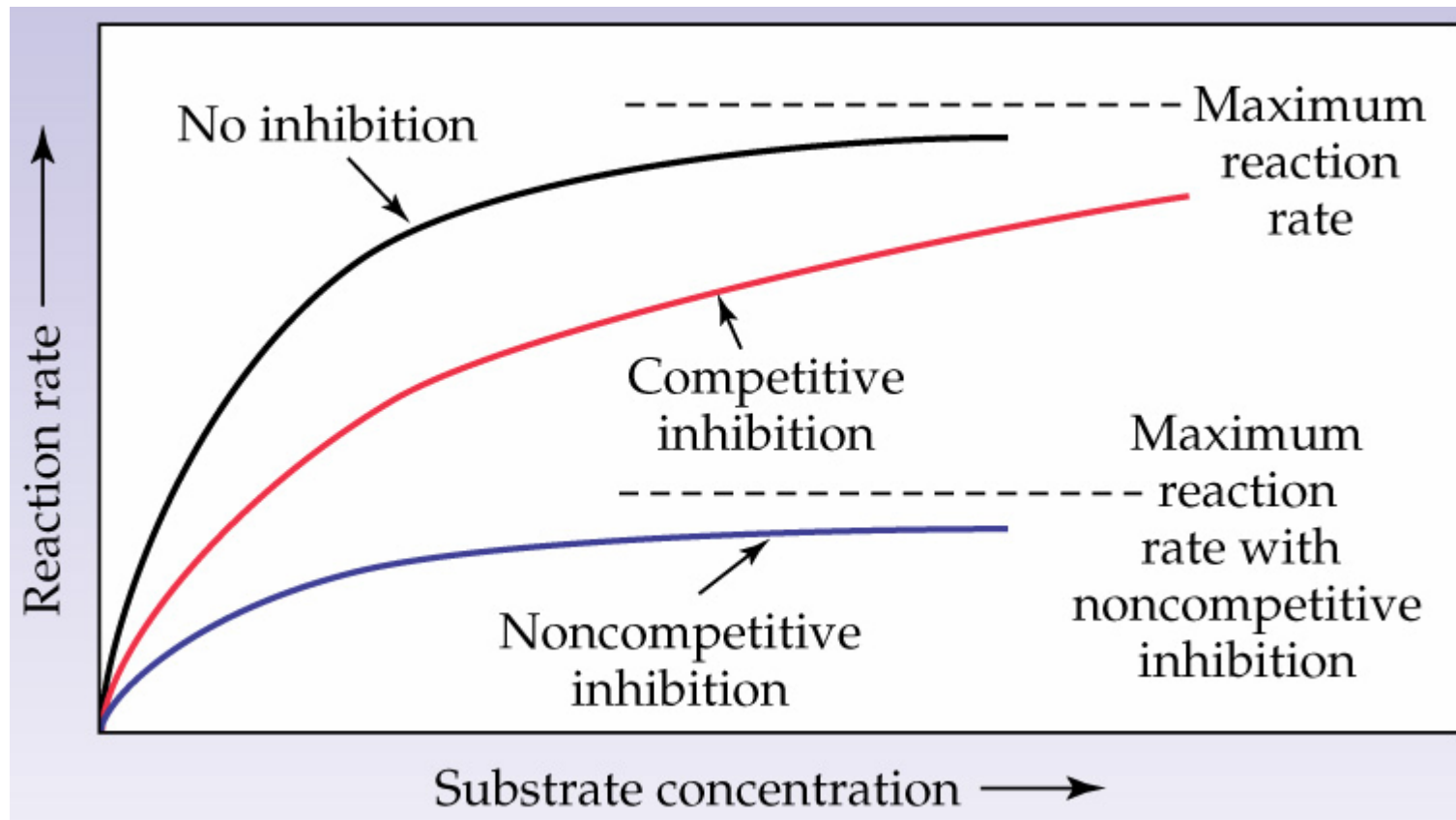


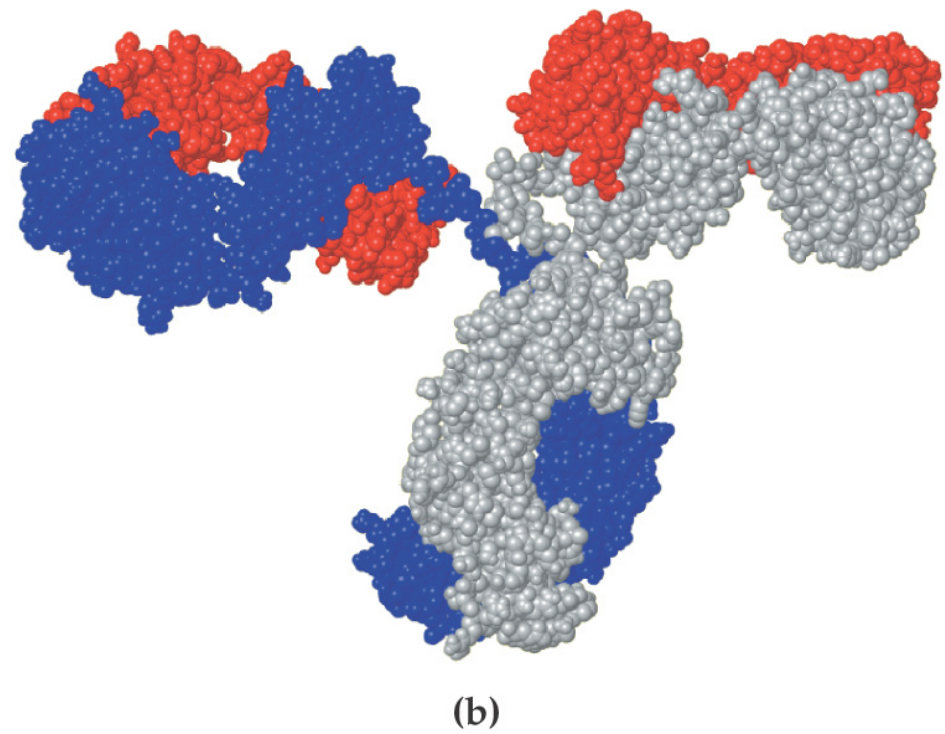
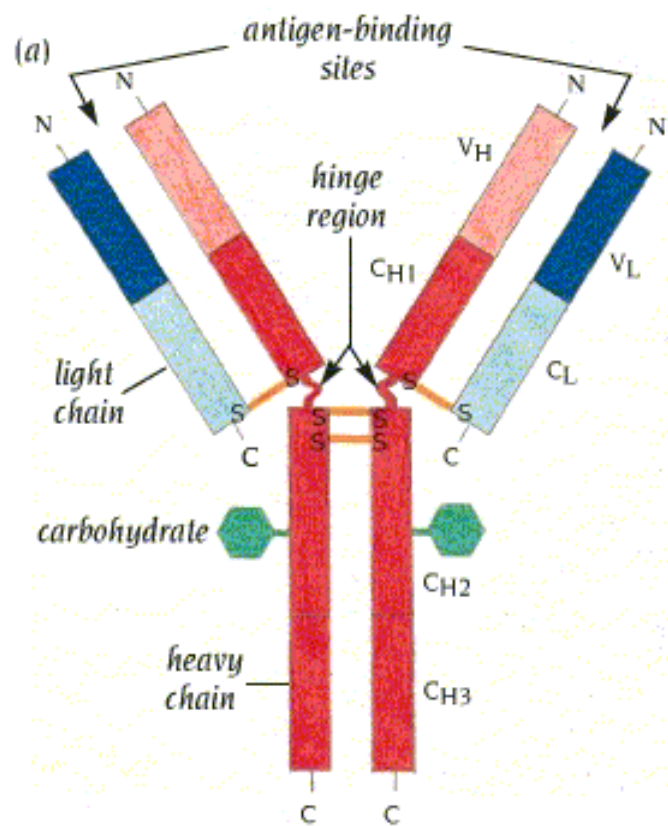
- *Noncompetitive inhibition*, if the inhibitor binds elsewhere and not to the active site.

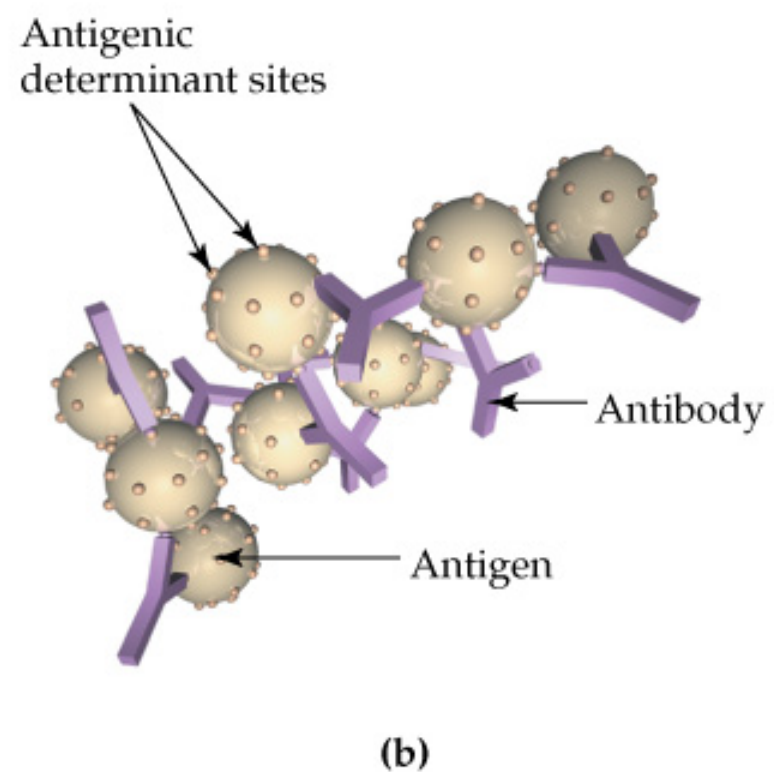
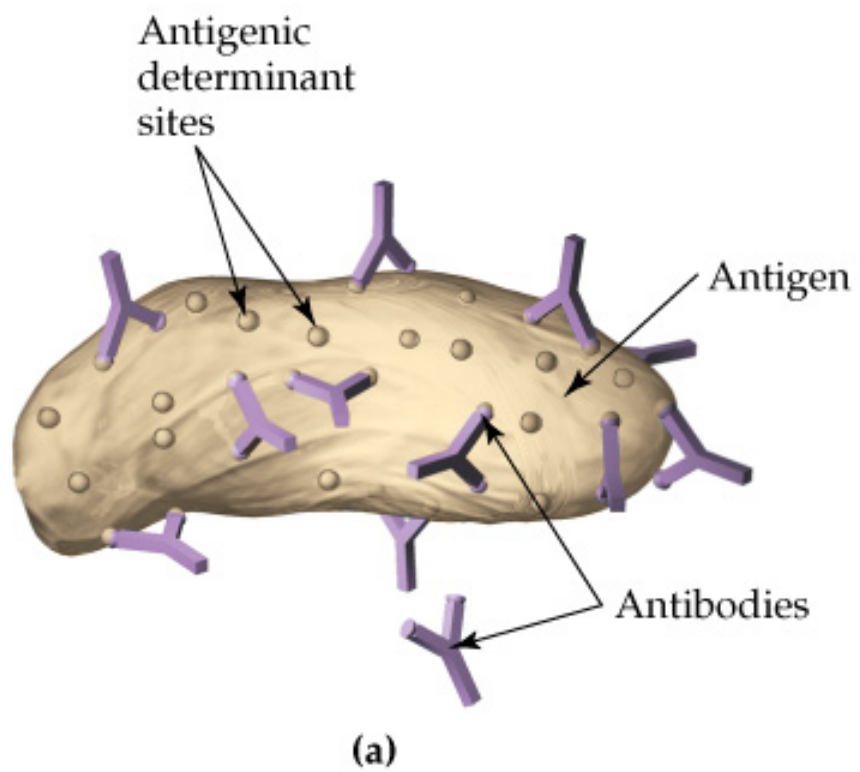
Noncompetitive inhibition



- The rates of enzyme catalyzed reactions with or without a competitive inhibitor are shown in the Fig 19.9 below.







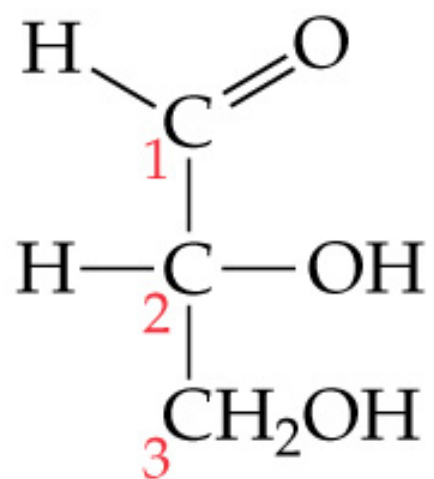
An Introduction to Carbohydrates

- *Carbohydrates* are a large class of naturally occurring polyhydroxy aldehydes and ketones.
- Monosaccharides also known as simple sugars, are the simplest carbohydrates containing 3-7 carbon atoms.
- sugar containing an aldehydes is known as an aldose.
- sugar containing a ketones is known as a ketose.

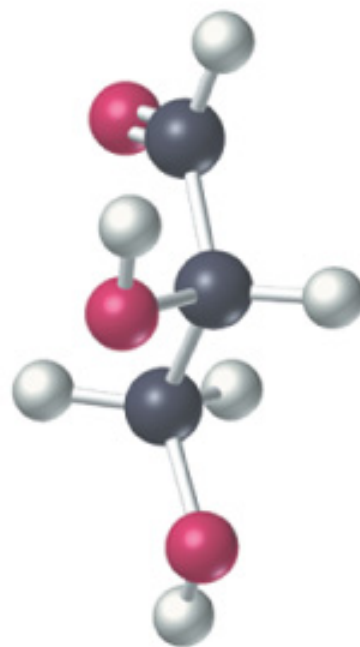
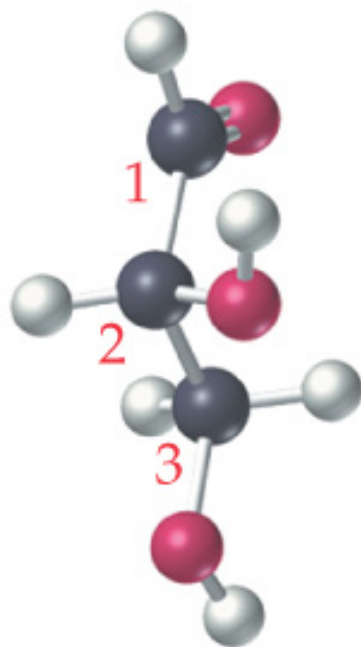


- The number of carbon atoms in an aldose or ketose may be specified as by tri, tetr, pent, hex, or hept. For example, glucose is aldohexose and fructose is ketohexose.
- Monosaccharides react with each other to form disaccharides and polysaccharides.
- Monosaccharides are chiral molecules and exist mainly in cyclic forms rather than the straight chain.

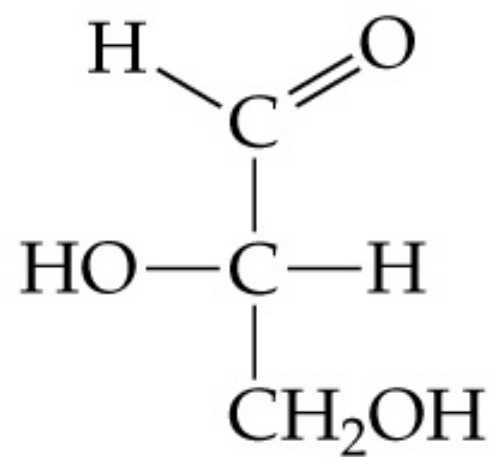


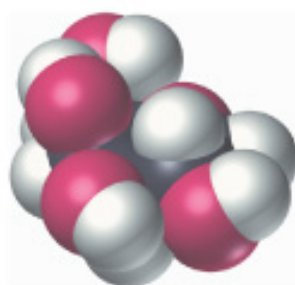
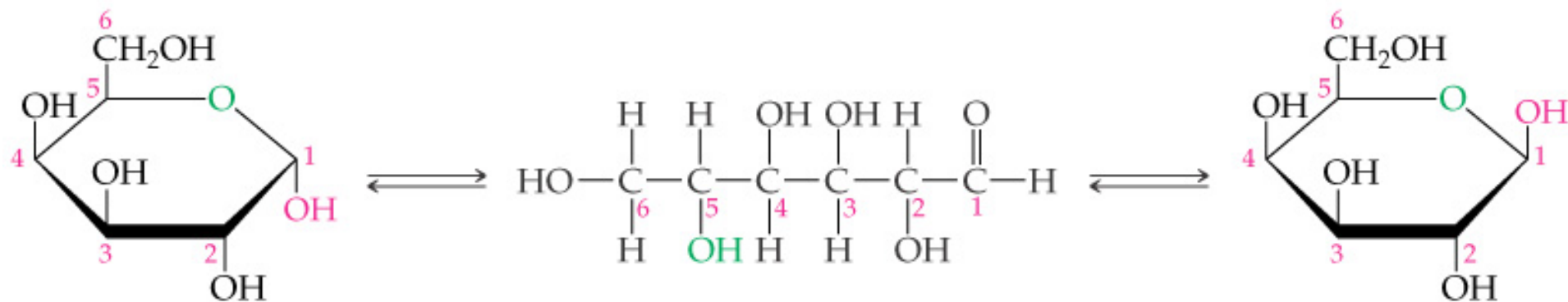


D-Glyceraldehyde
Right-handed

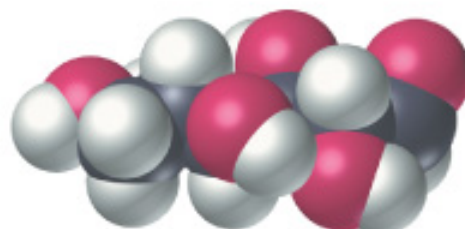


L-Glyceraldehyde
Left-handed

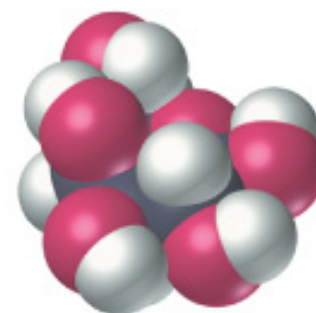




α -D-Galactose

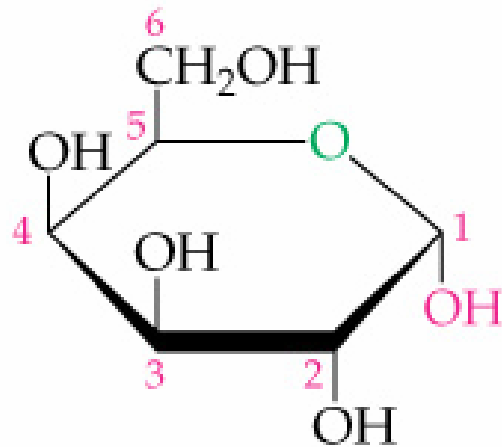


Open-chain galactose

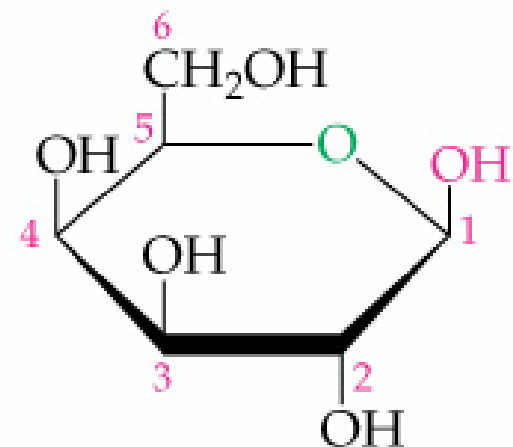


β -D-Galactose

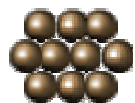
- *Anomers:* Cyclic sugars that differ only in positions of substituents at the hemiacetal carbon; the α -form has the -OH group on the opposite side from the $\text{-CH}_2\text{OH}$; the β -form has the -OH group on the same side as the $\text{-CH}_2\text{OH}$ group.



α -D-Galactose

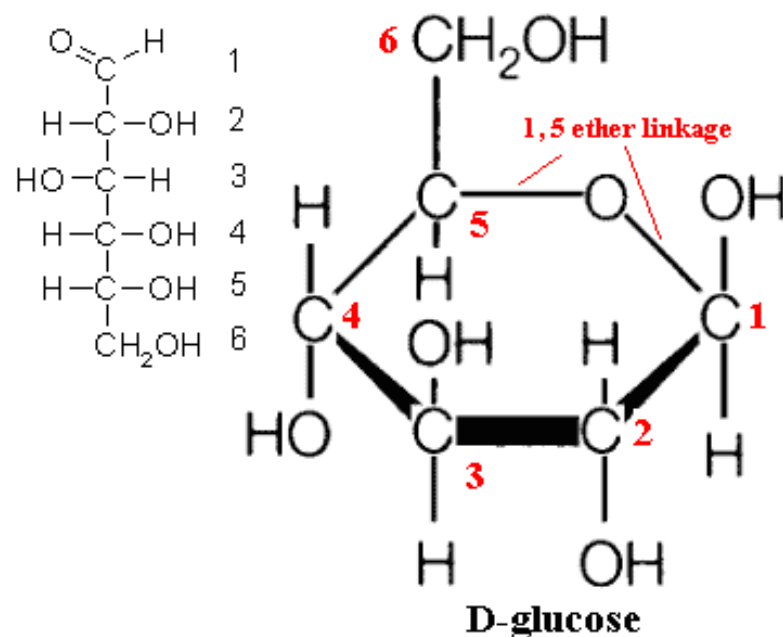


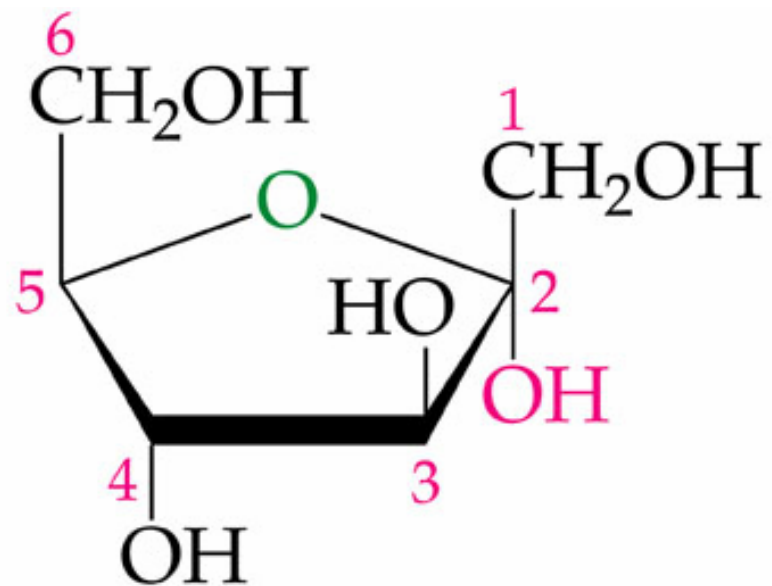
β -D-Galactose



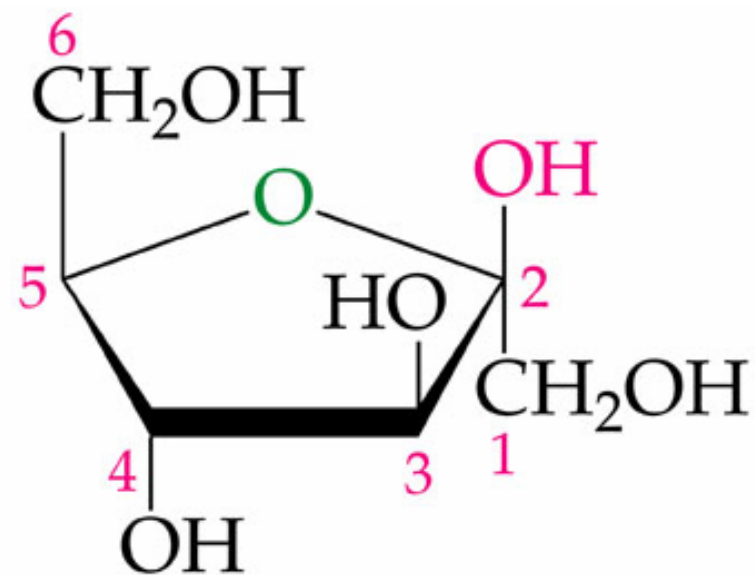
Some Important Monosaccharides

Monosaccharides are generally high-melting, white, crystalline solids that are soluble in water and insoluble in nonpolar solvents. Most monosaccharides are sweet tasting, digestible, and nontoxic.

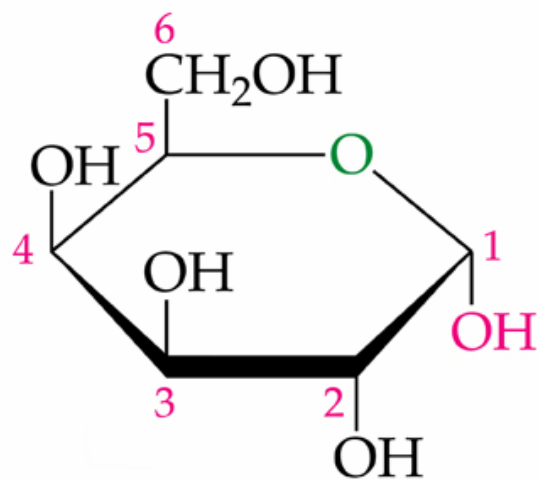




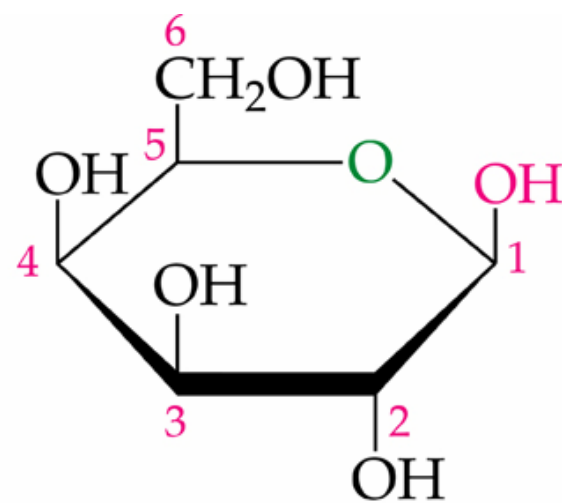
α -D-Fructose



β -D-Fructose



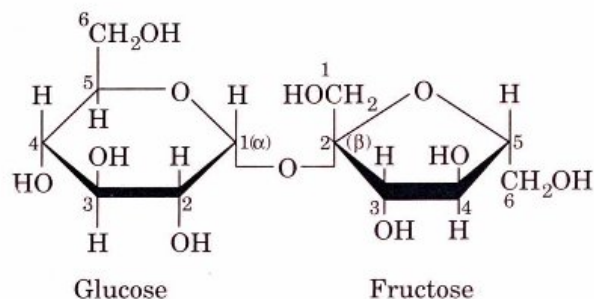
α -D-Galactose



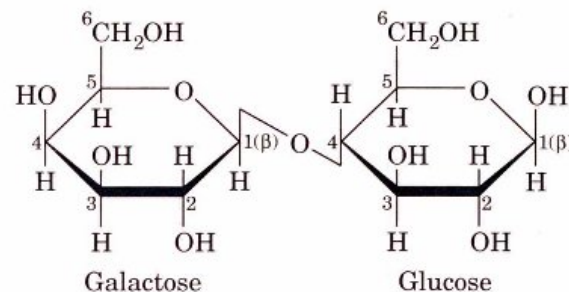
β -D-Galactose



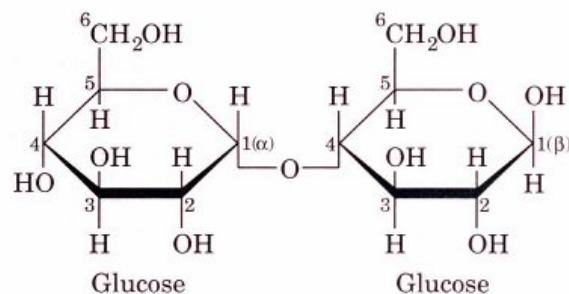
Some Common Disaccharides



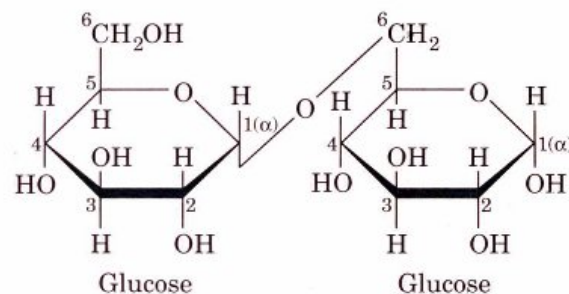
Sucrose



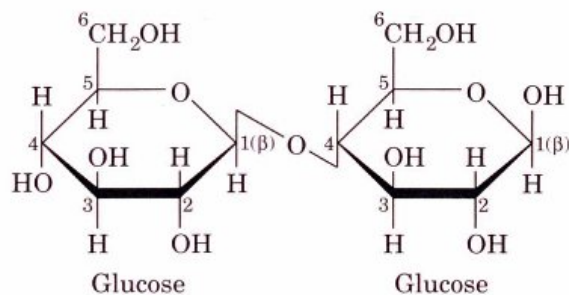
Lactose



Maltose



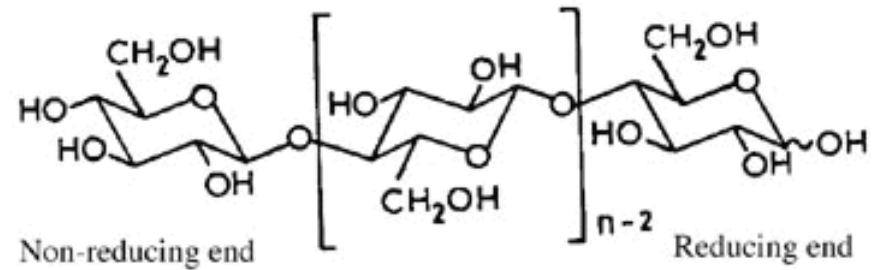
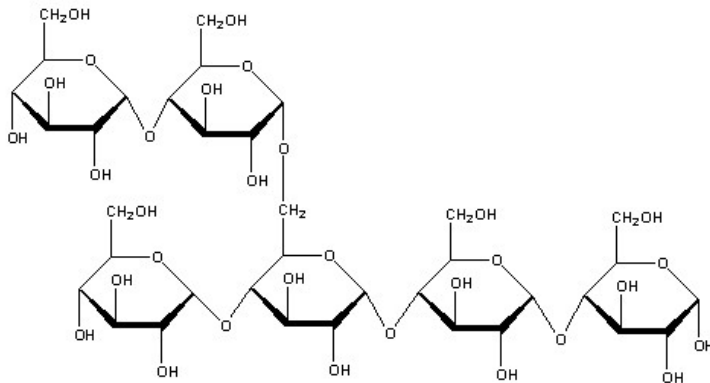
Isomaltose



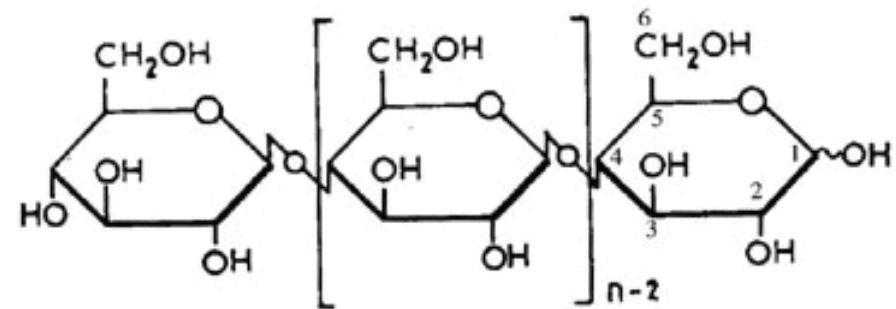
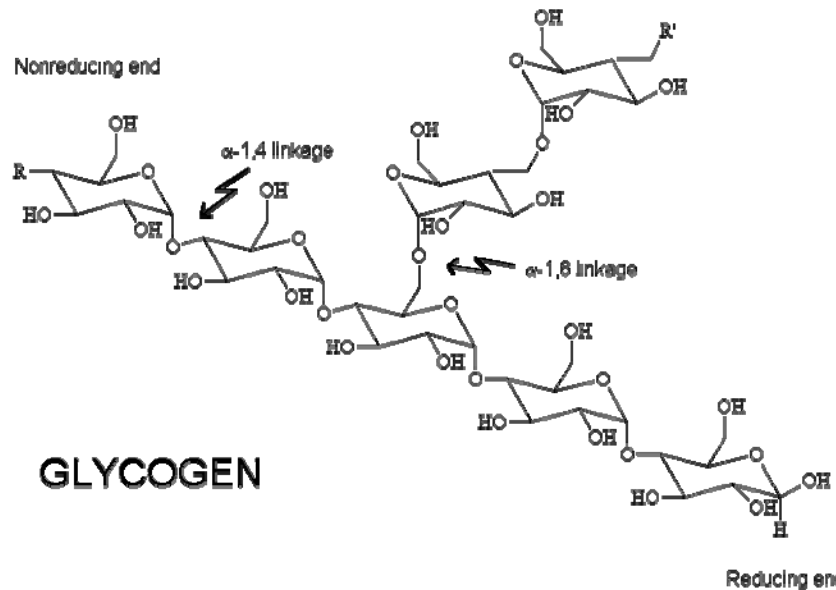
Cellobiose



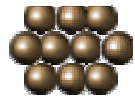
Polysaccharides



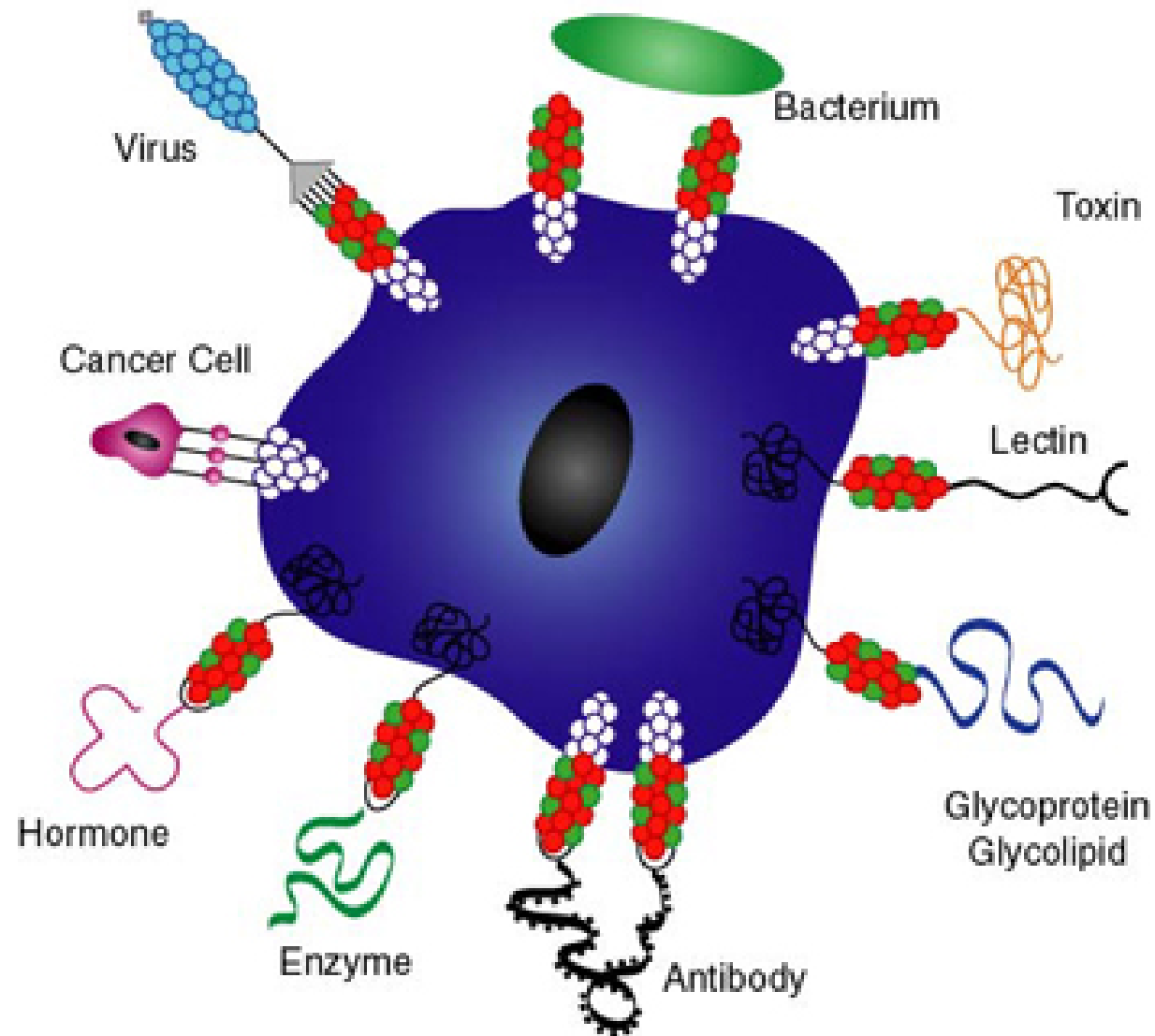
Sometimes shown as



Cellulose

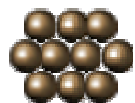
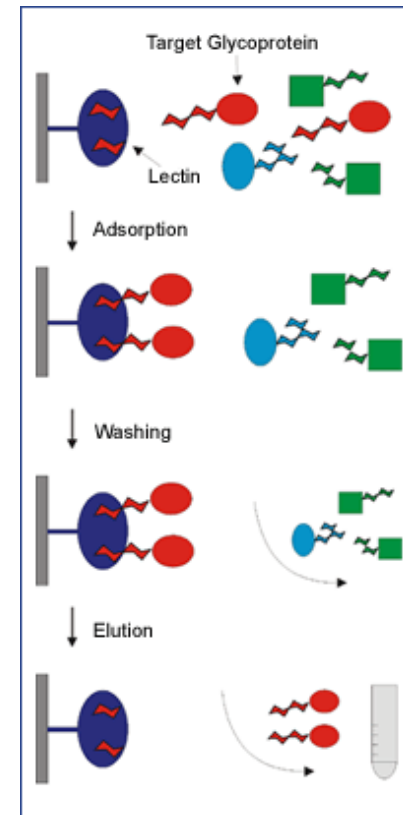
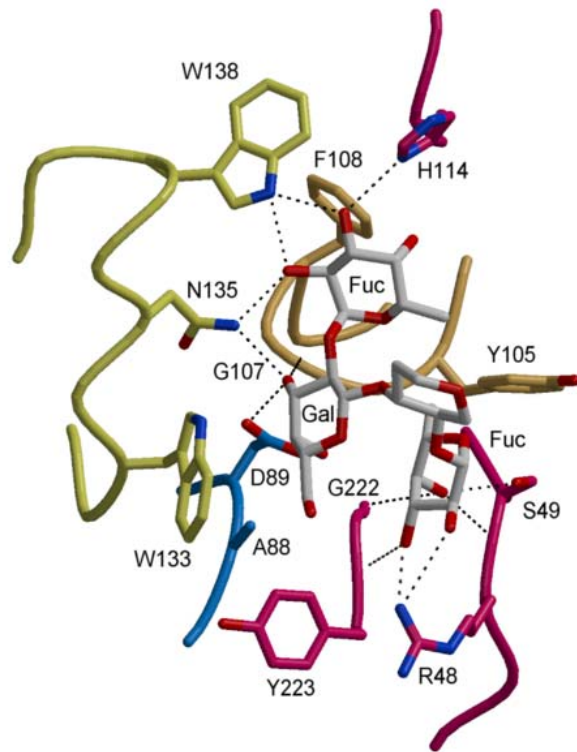


Cell-Surface Carbohydrates Involved in Molecular Recognition

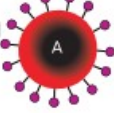
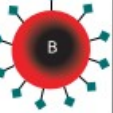
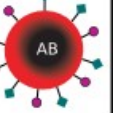
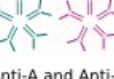


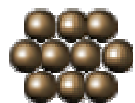
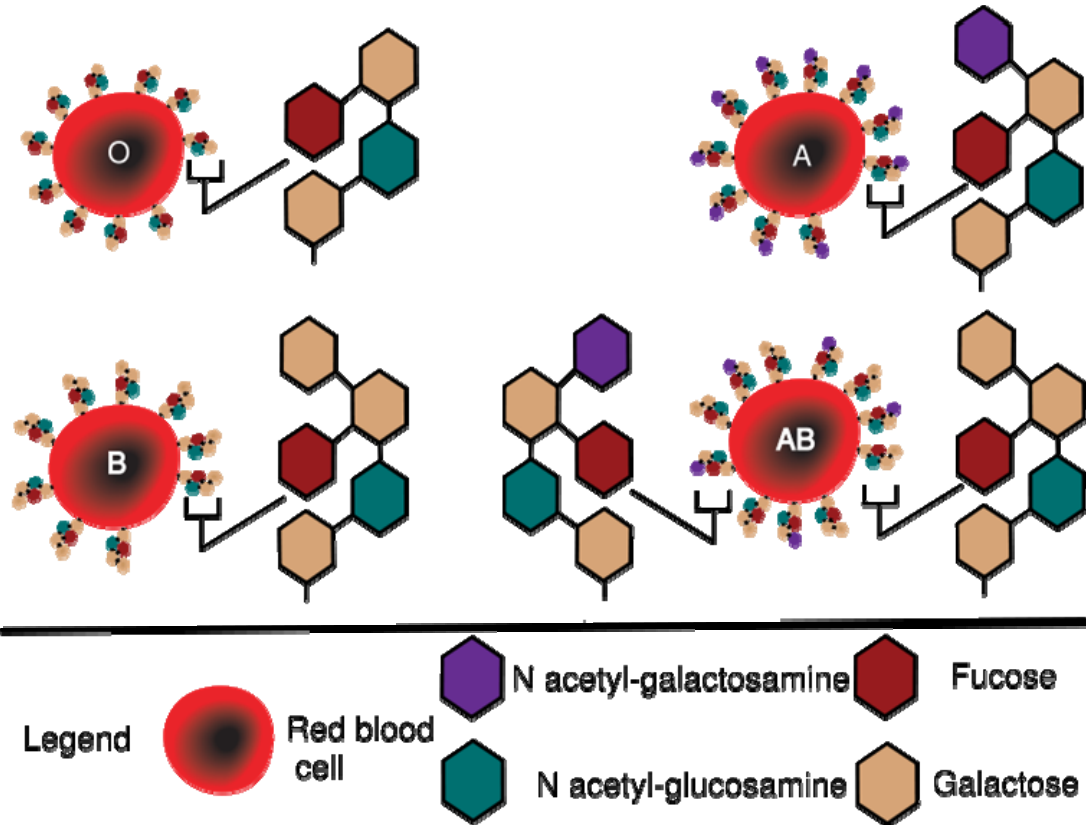
Lectin

Lectins are sugar-binding proteins which are highly specific for their sugar moieties. They typically play a role in biological recognition phenomena involving cells and proteins. For example, some bacteria use lectins to attach themselves to the cells of the host organism during infection.

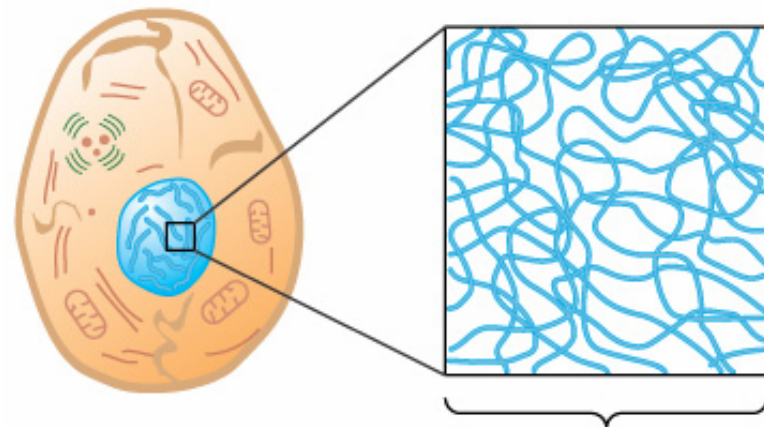


Blood Type

	Group A	Group B	Group AB	Group O
Red blood cell type				
Antibodies present	 Anti-B	 Anti-A	None	 Anti-A and Anti-B
Antigens present	A antigen 	B antigen 	A and B antigens  	No antigens

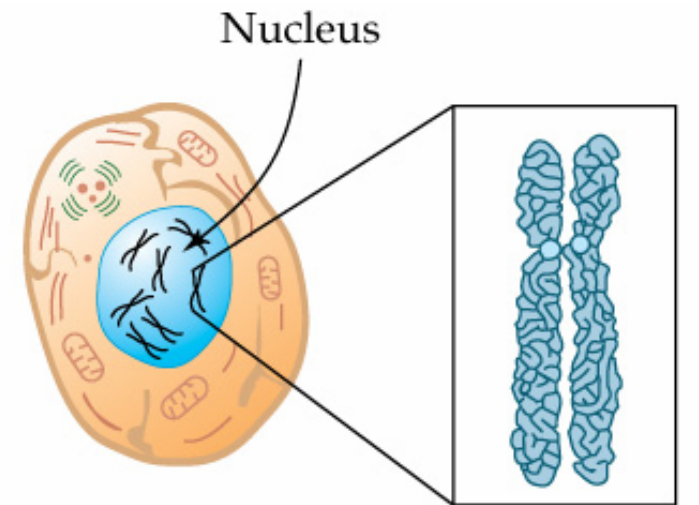


DNA



Nondividing
cell

Chromatin
in nucleus

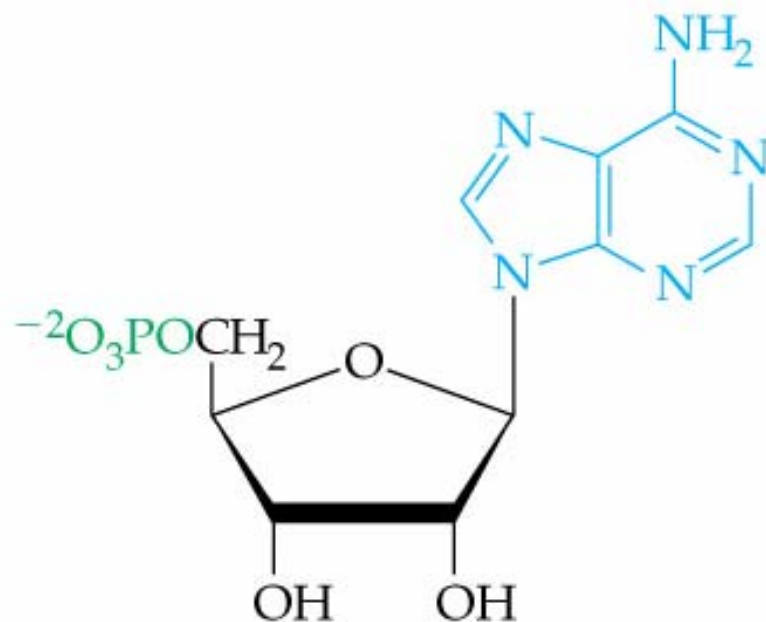


Cell prepared
for division

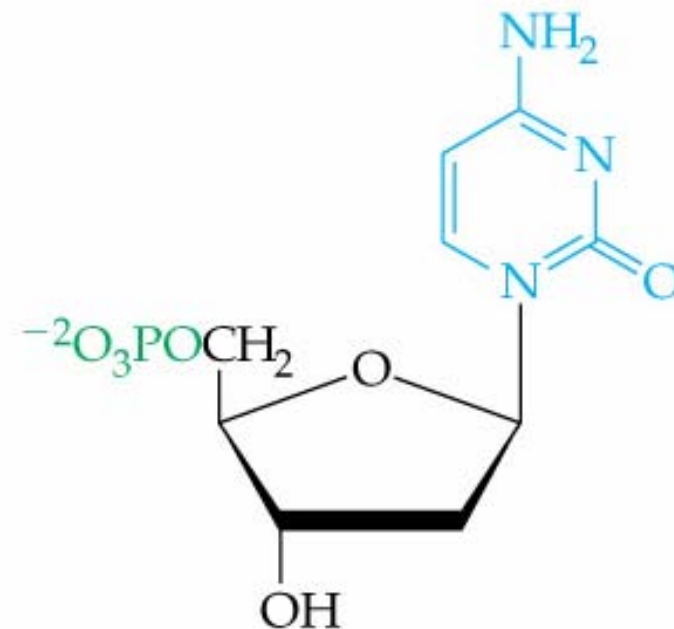
Visible
chromosome



- In RNA, the sugar is ribose.
- In DNA, the sugar is deoxyribose.



Adenosine 5'-monophosphate (AMP)
(a ribonucleotide)

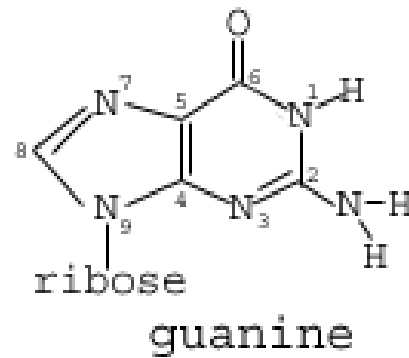
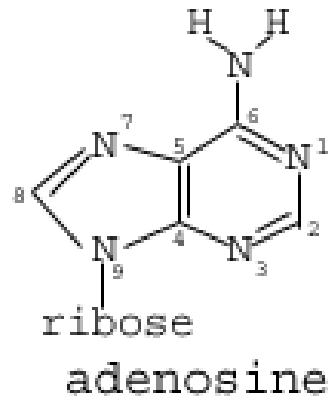


Deoxycytidine 5'-monophosphate (dCMP)
(a deoxyribonucleotide)

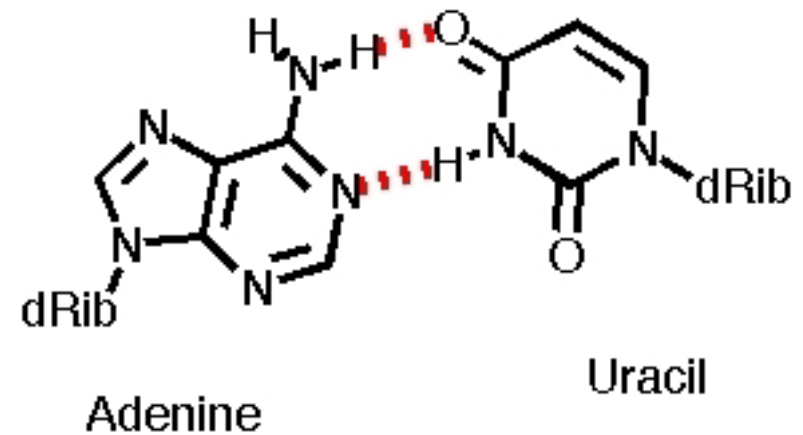
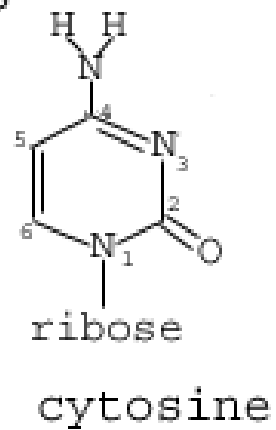
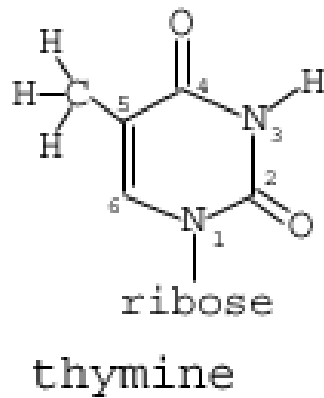


Base

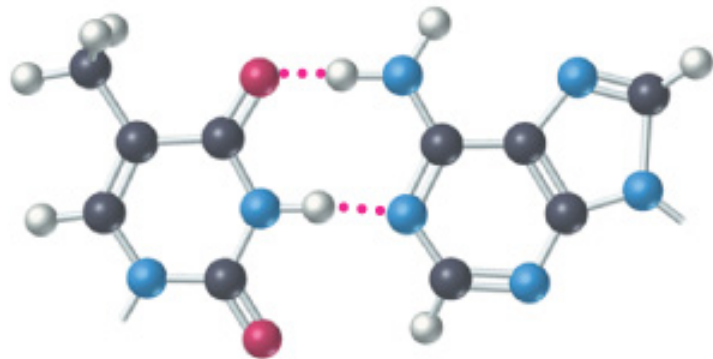
Purines



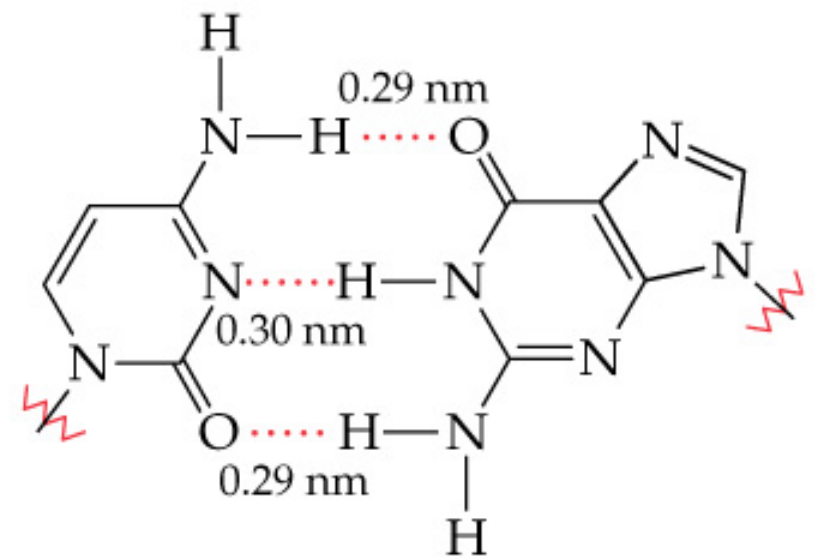
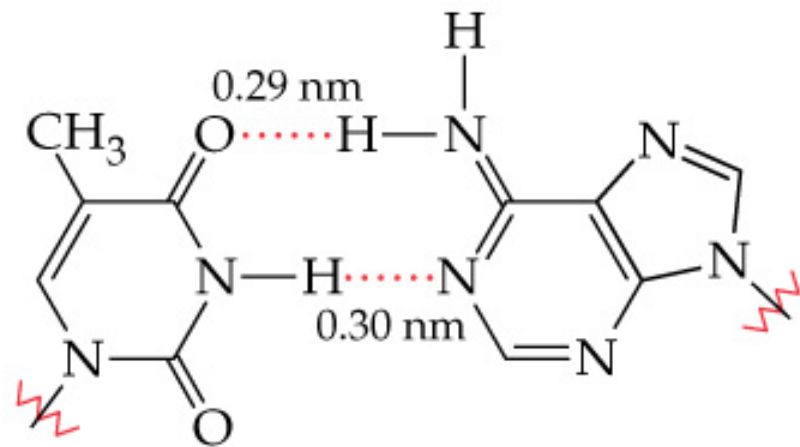
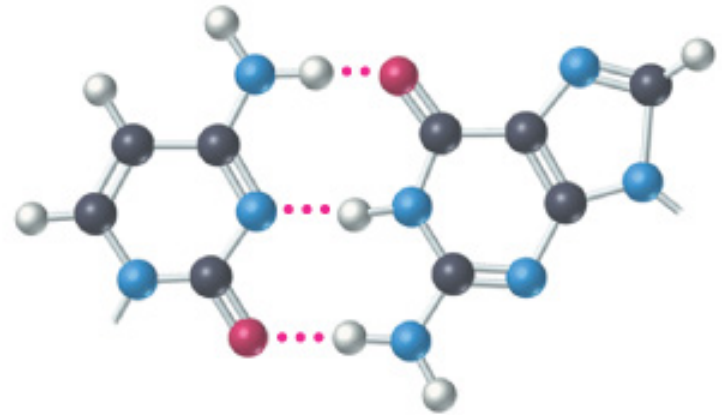
Pyrimidines

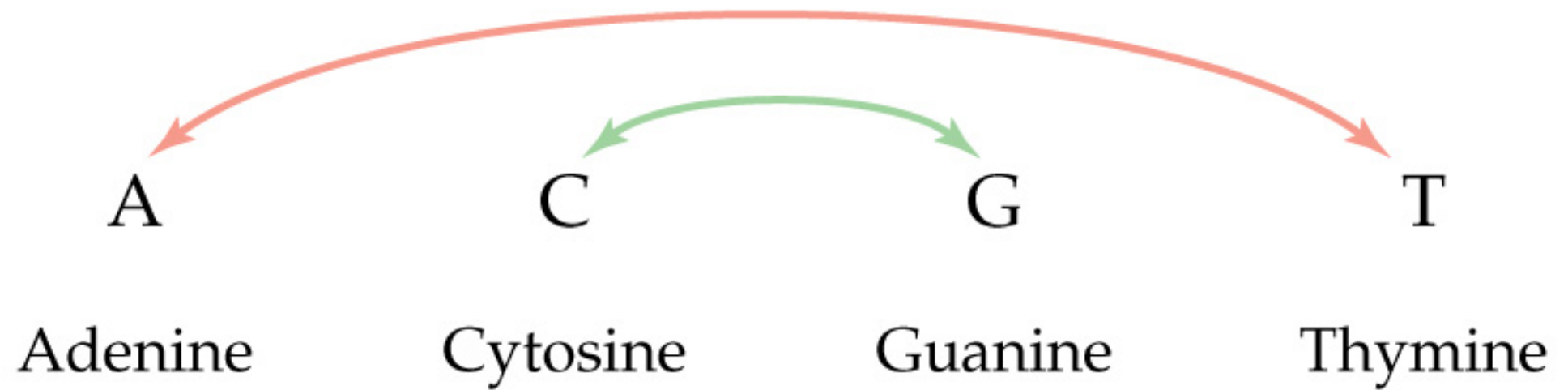


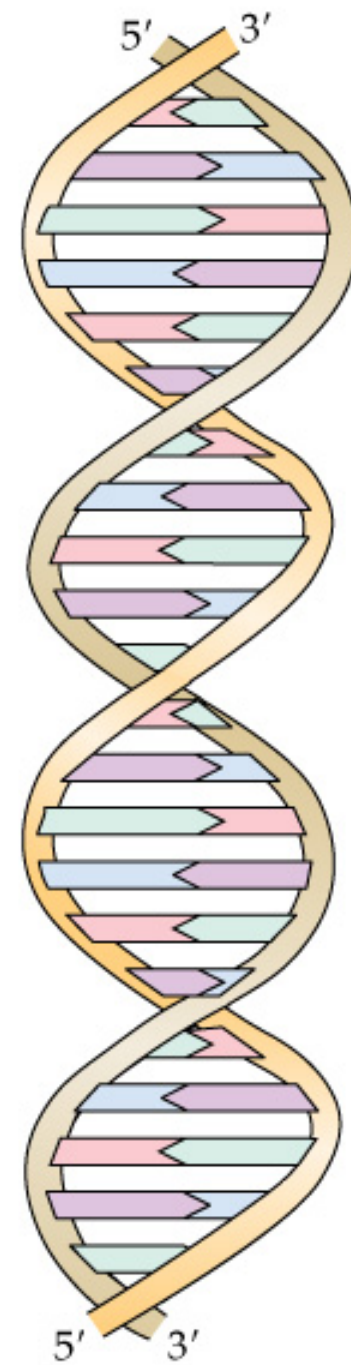
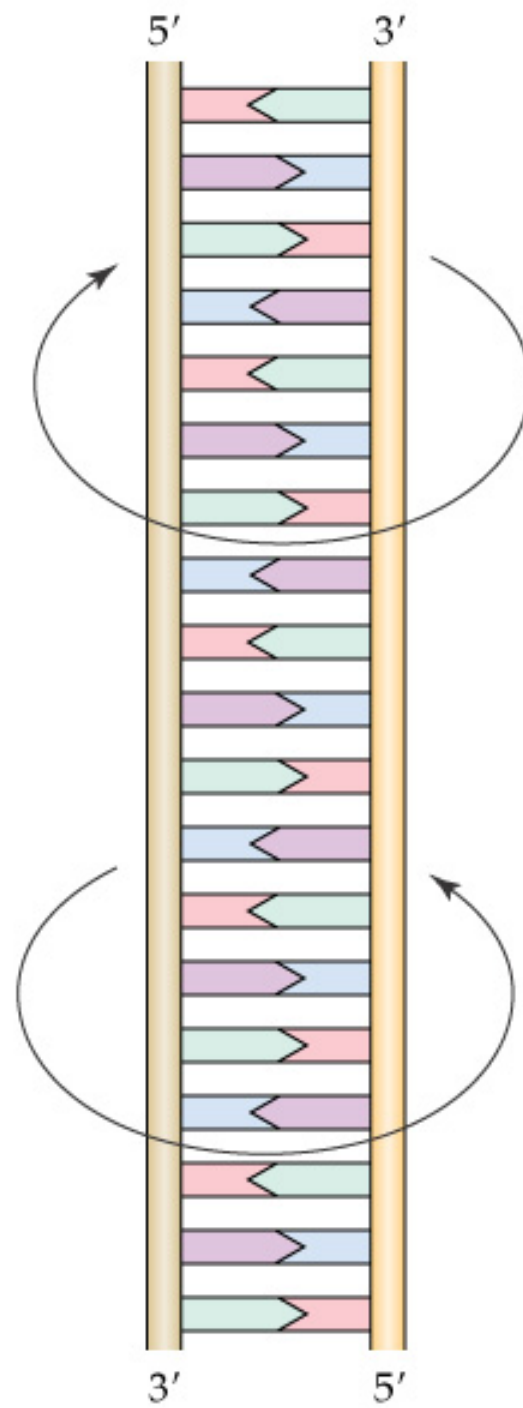
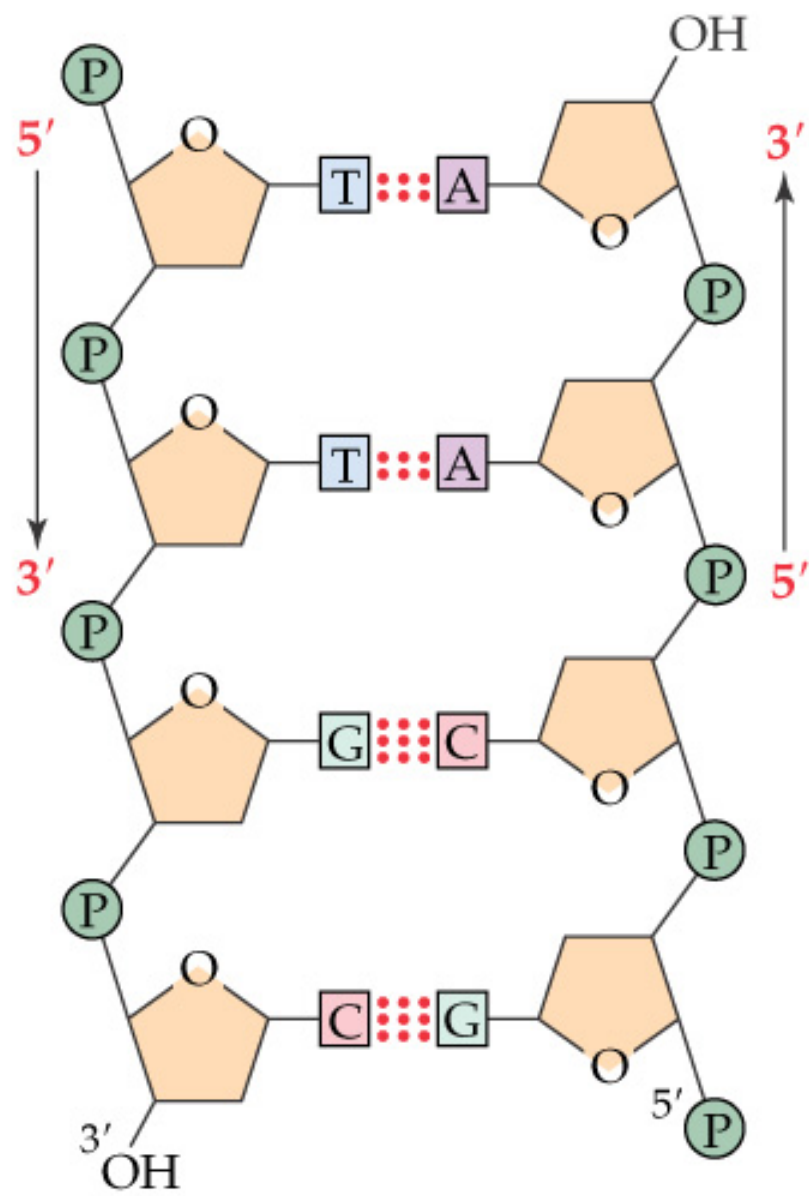
Thymine-Adenine

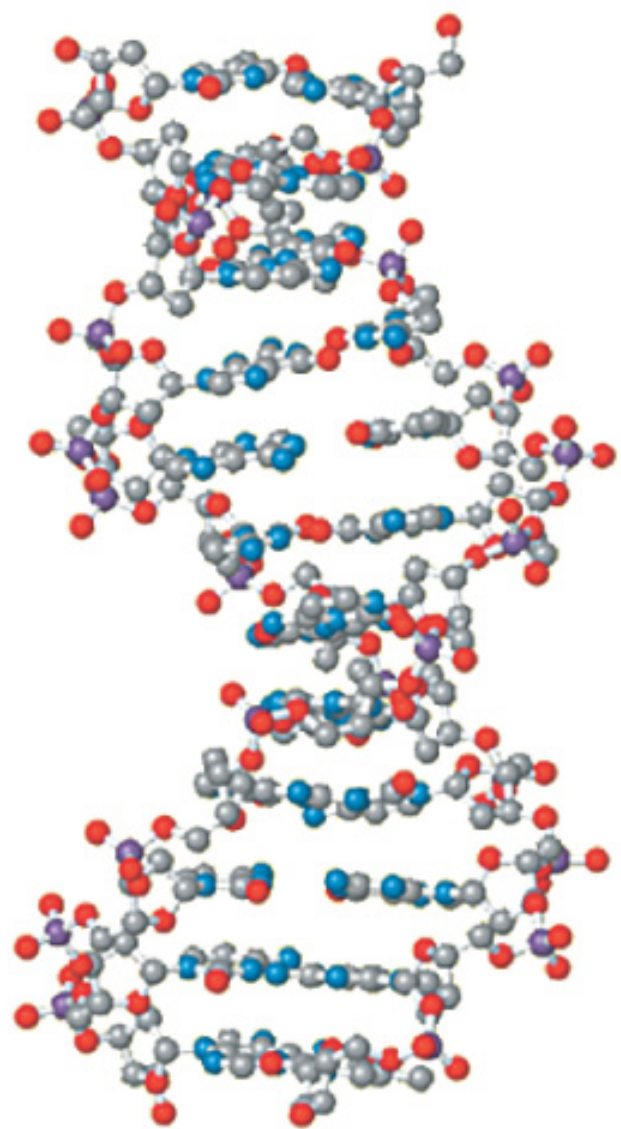


Cytosine-Guanine

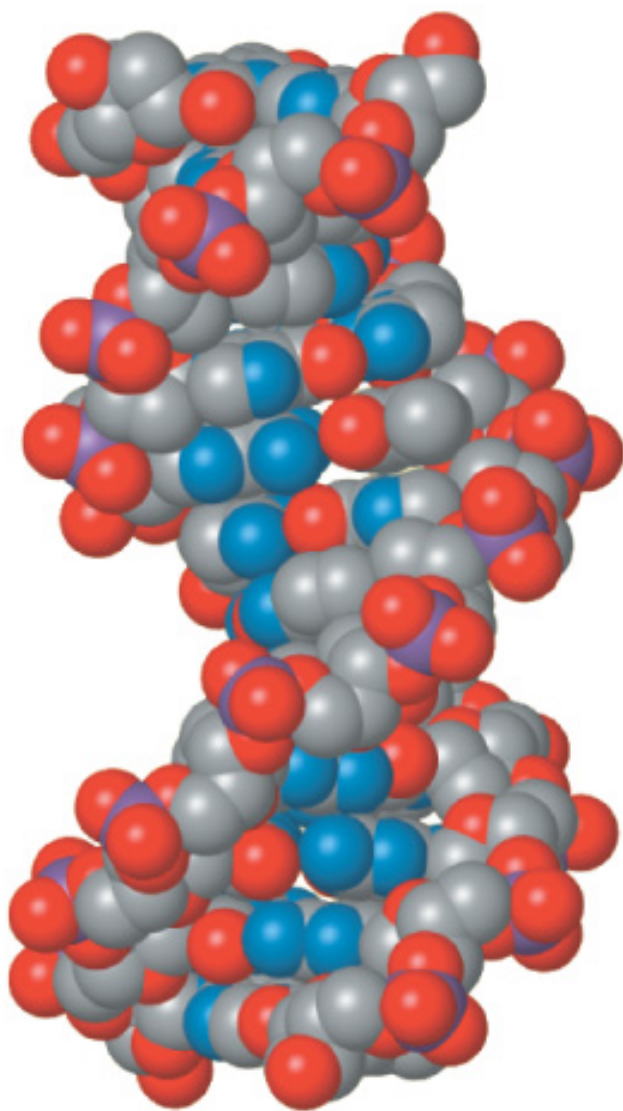








(a)

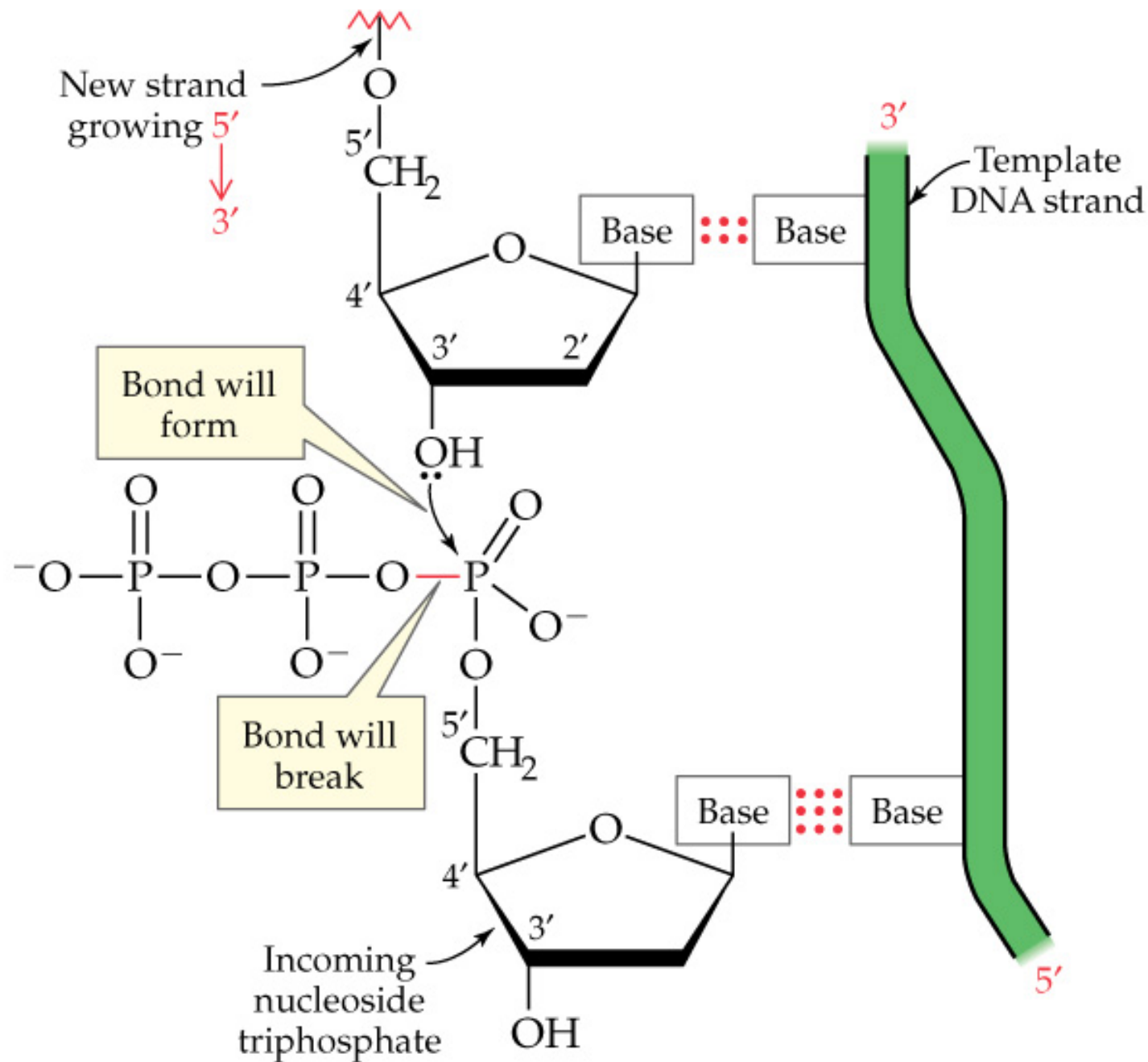


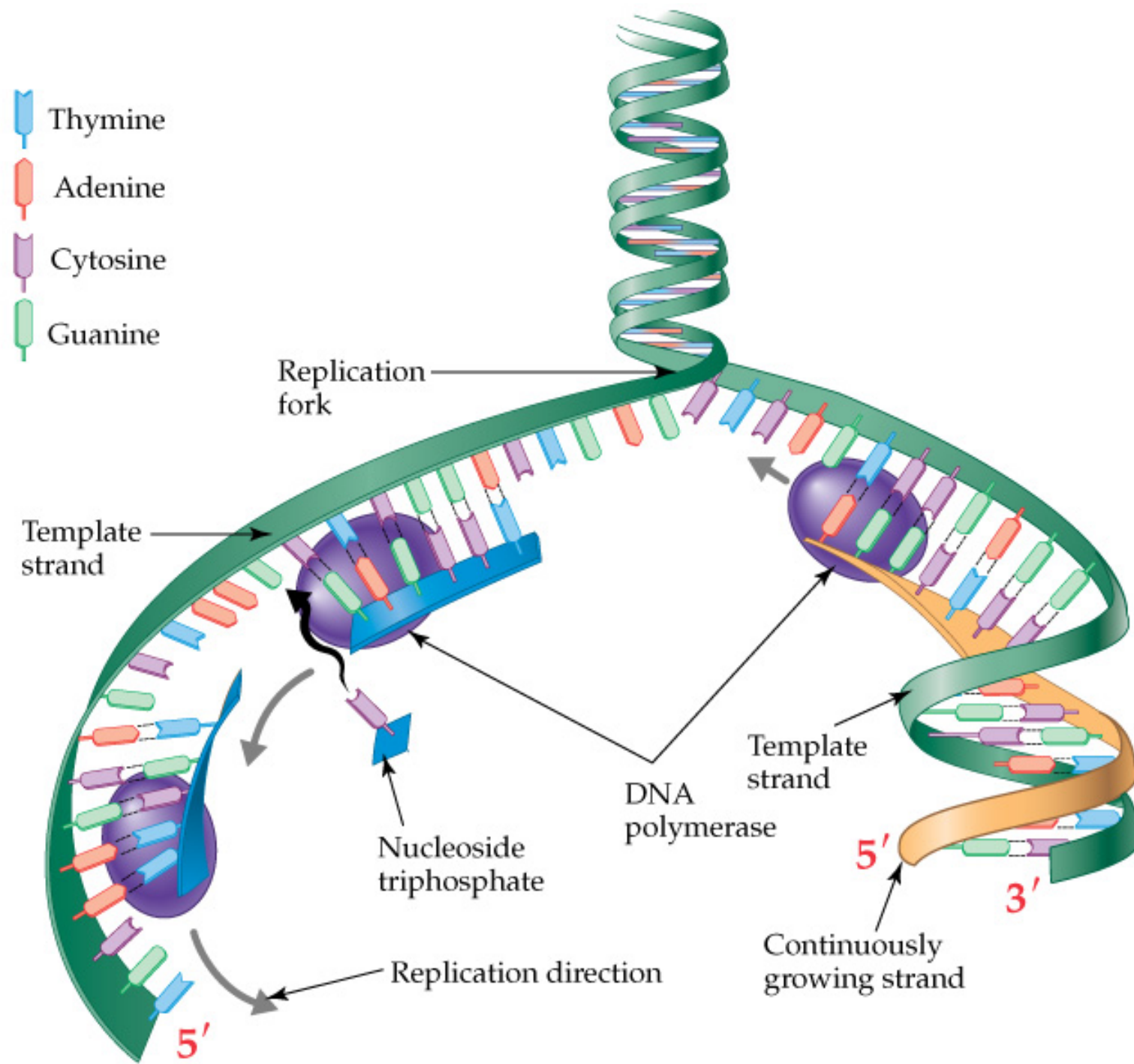
(b)

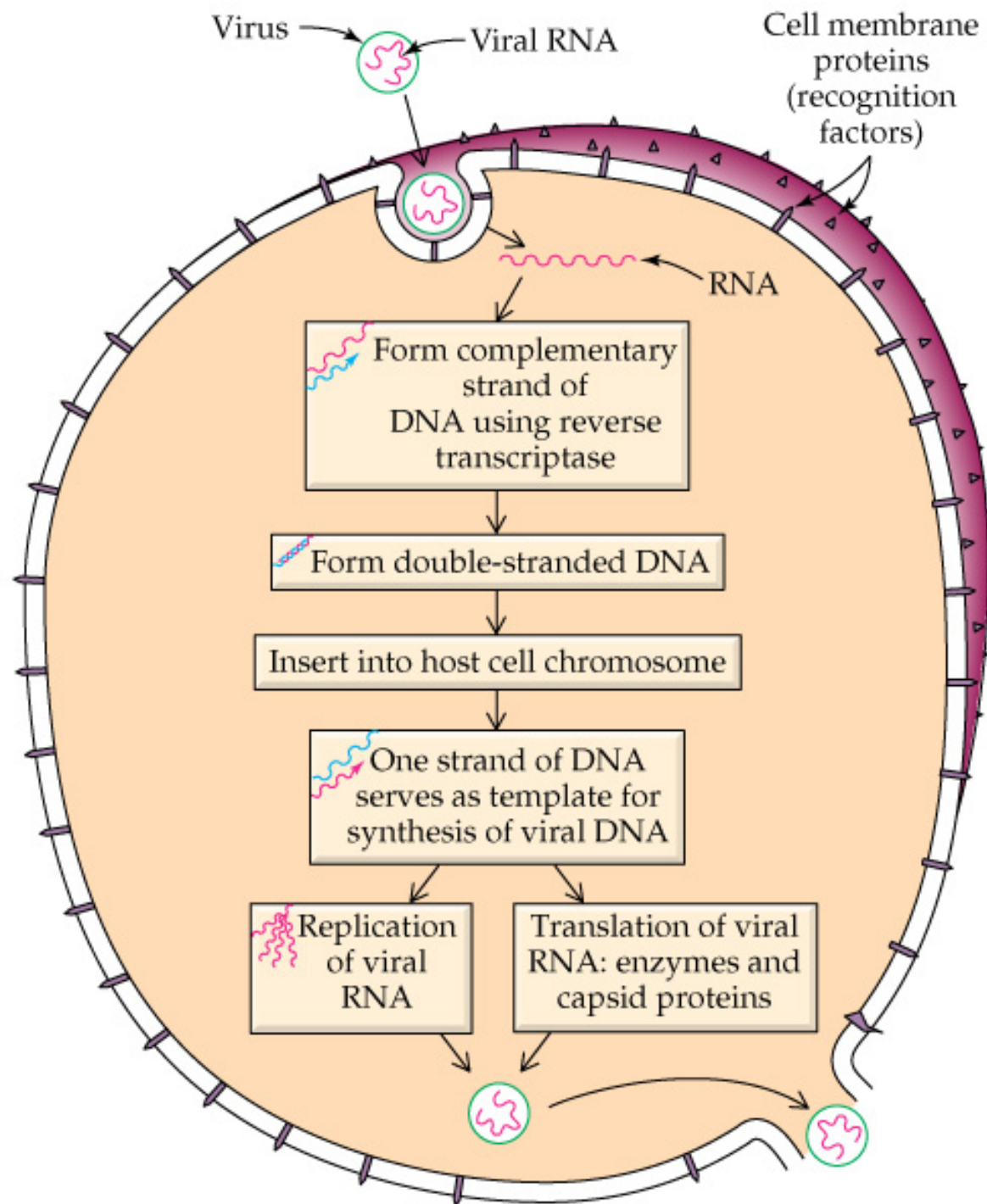


(c)

Bond formation in DNA replication







Cell nucleus



DNA

Transcription



mRNA

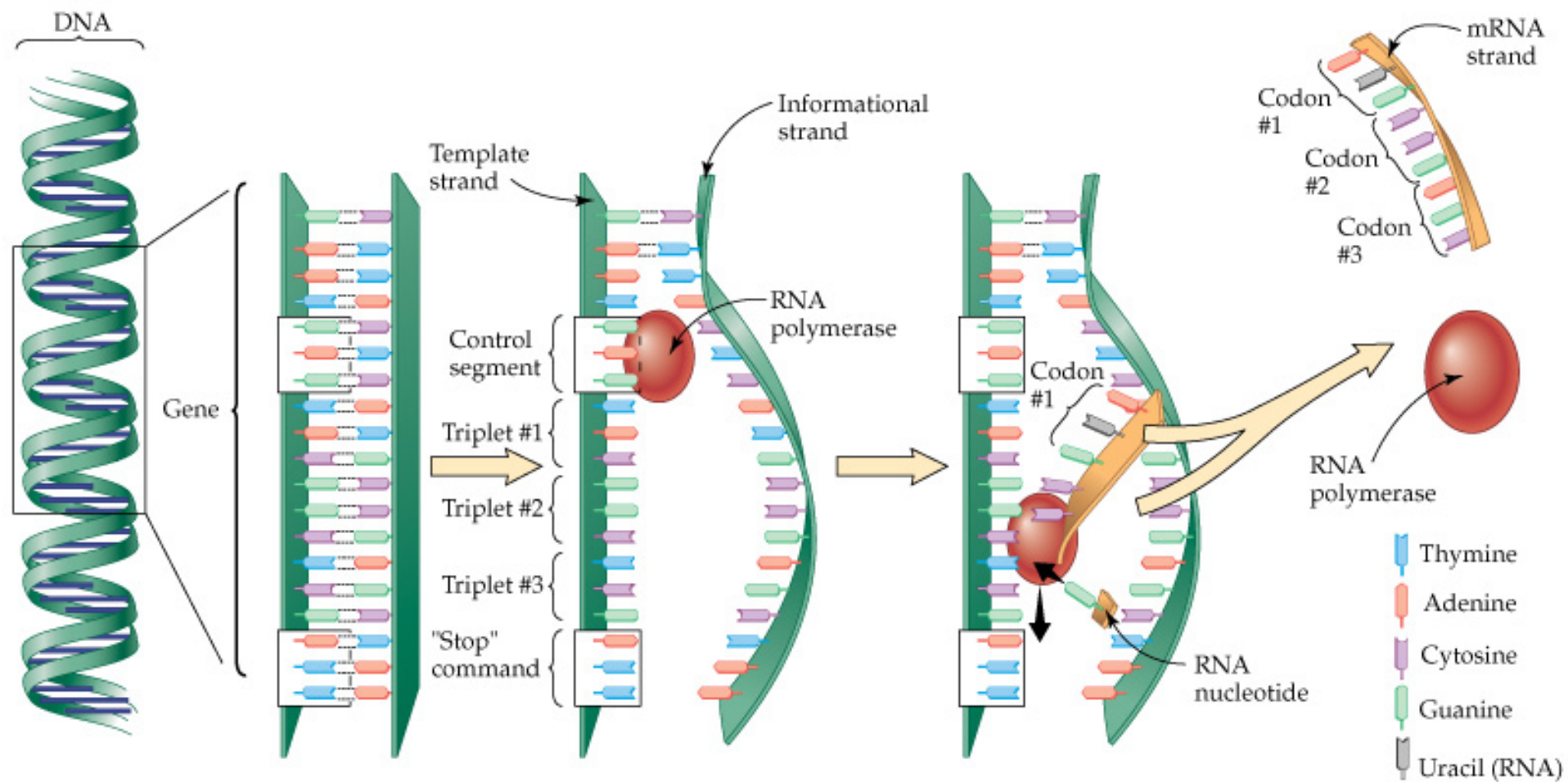
- The following three RNA make it possible for the encoded information carried by the DNA to be put to use in the synthesis of proteins.

- Ribosome RNA***: The granular organelles in the cell where protein synthesis takes place. These organelles are composed of protein and ribosomal RNA (rRNA).

- Messenger RNA (mRNA)***: The RNA that carries the code transcribed from DNA and directs protein synthesis.

- Transfer RNA (tRNA)***: The smaller RNA that delivers amino acids one by one to protein chains growing at ribosomes. Each tRNA recognizes and carries only one amino acid.





Initial mRNA



Cut out introns

Final mRNA



