

Review of General & Organic Chemistry



- Diameter of a nucleus is only about 10^{-15} m.
- Diameter of an atom is only about 10^{-10} m.

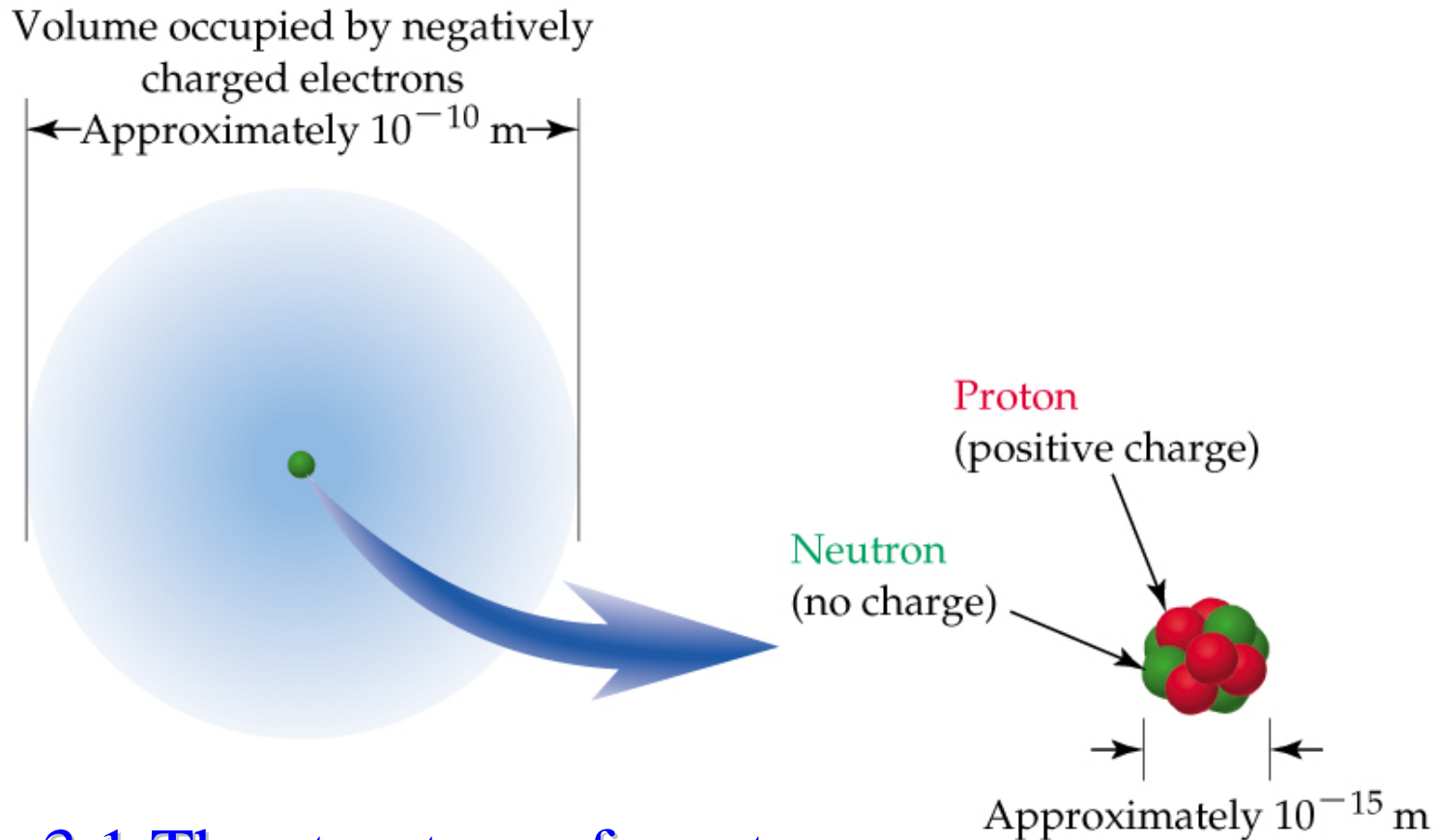


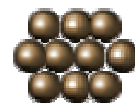
Fig 3.1 The structure of an atom



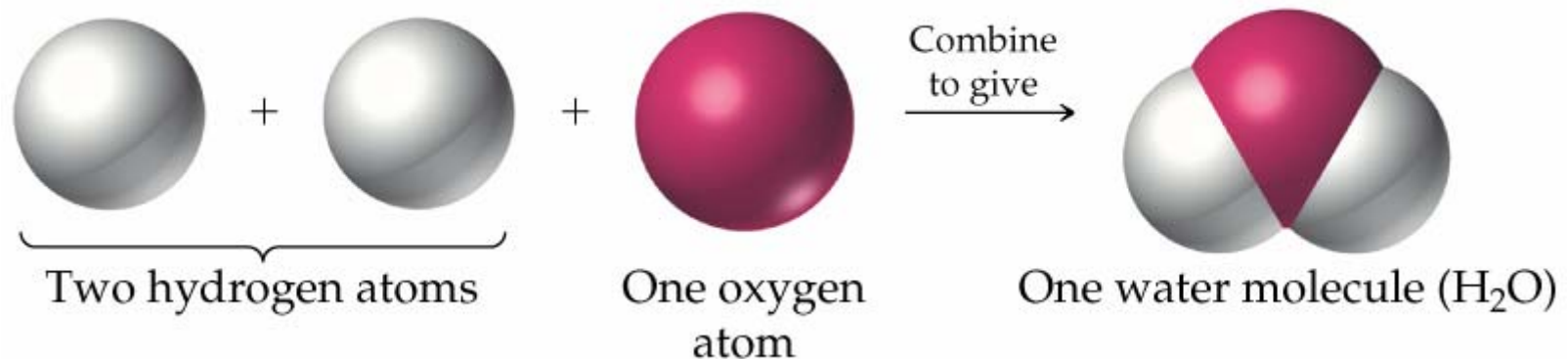
• **Periodic Table**, shown below, is a representation of 113 elements in a tabular

1A																		8A
1	2																	18
1 H 1.00794	2 He 4.00260																	
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797	
11 Na 22.98977	12 Mg 24.305	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	13 Al 26.98154	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948	
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.41	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.9045	54 Xe 131.29	
55 Cs 132.9054	56 Ba 137.33	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)	
87 Fr (223)	88 Ra 226.0254	89 †Ac 227.0278	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 (271)	111 (272)	112 (277)		114		116			

58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 PM (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.0399	92 U 238.0289	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)



- Water molecule results when two hydrogen atoms and one oxygen atom are covalently bonded in a way shown in the following picture:



A covalent bond between two hydrogen atoms is shown in this picture.

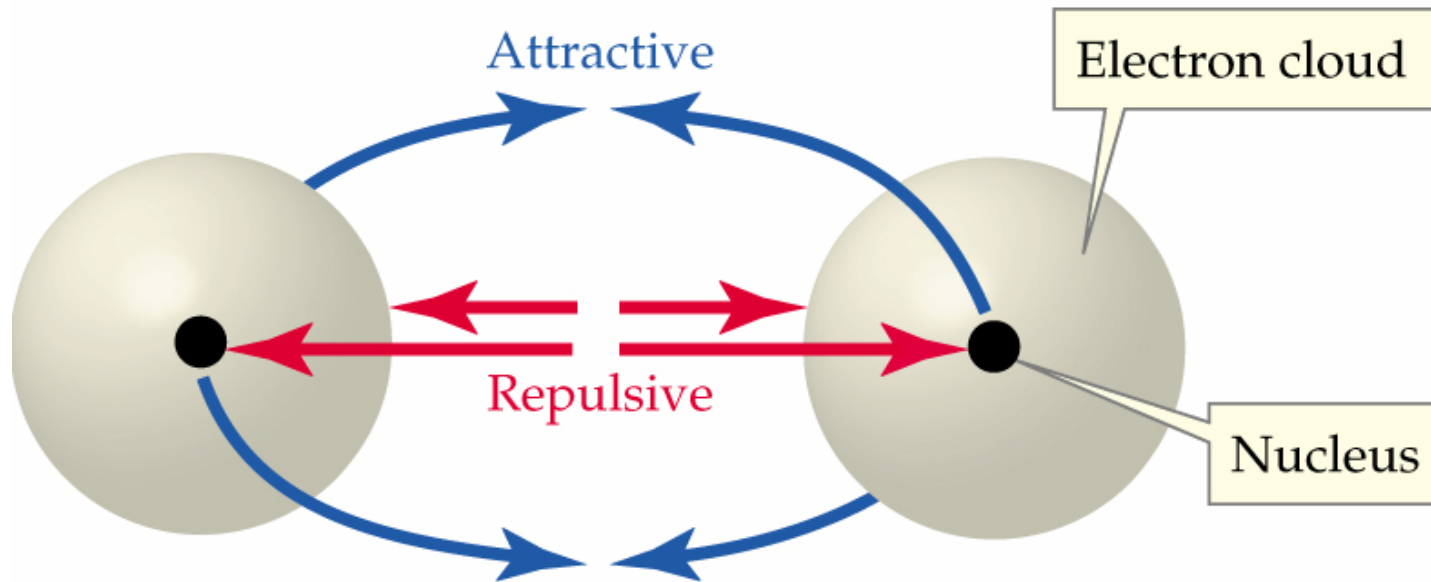
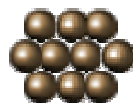


Fig 5.1 A covalent bond is the result of attractive and repulsive forces between atoms.



Free-energy change

$$\Delta G = \Delta H - T\Delta S$$

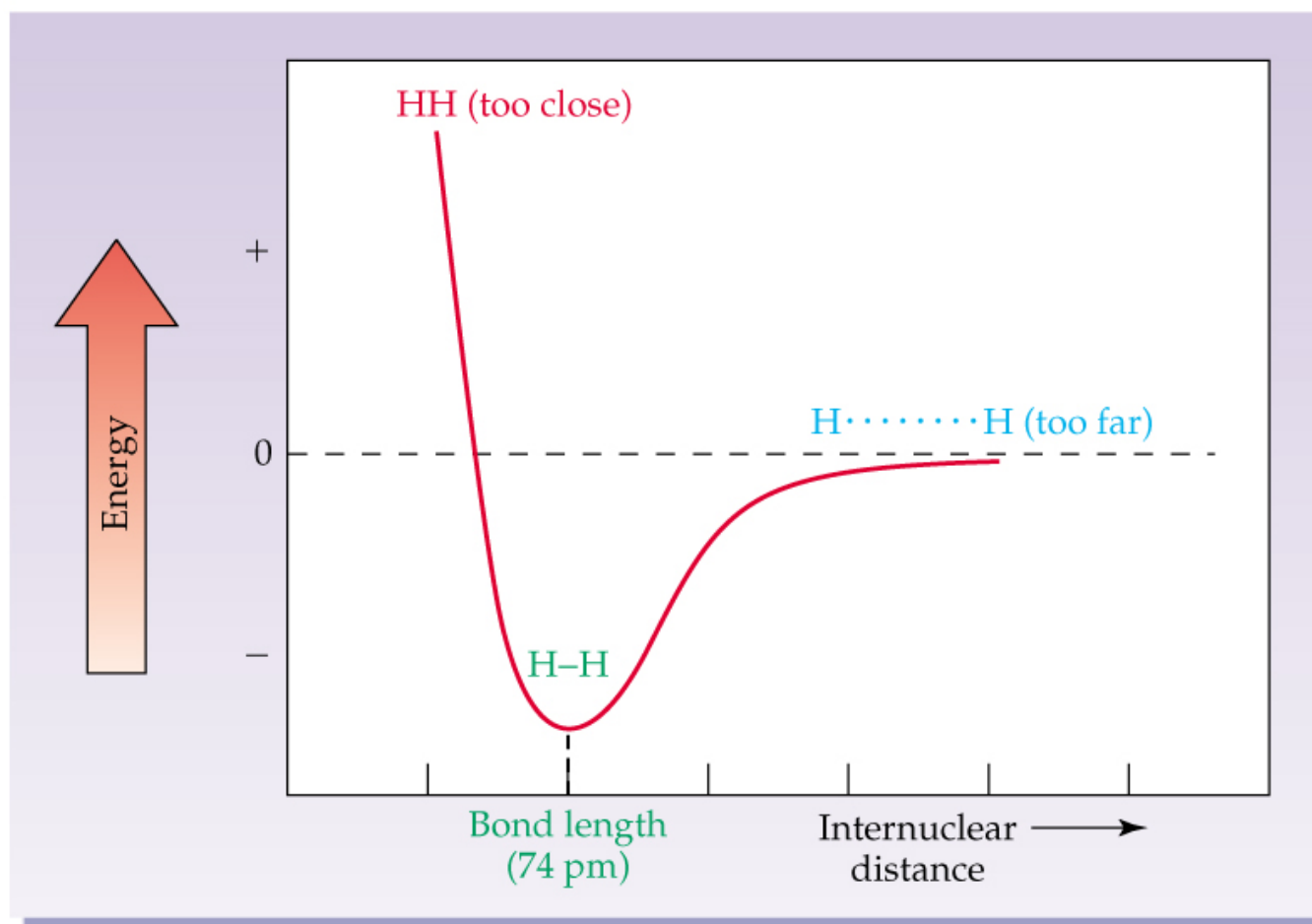
Heat of reaction

Temperature (in kelvins)

Entropy change

- The value of the free-energy change (ΔG) determines spontaneity.
- ΔG is negative; free energy is released; process is exothermic or exergonic.
- ΔG is positive; free energy is added; process is endothermic or endergonic.



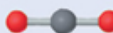

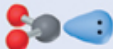
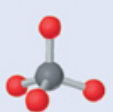




•Fig 5.2 A graph of potential energy versus internuclear distance for hydrogen.



- The shape depends on the number of charged clouds surrounding the atom as summarized in Table 5.1

TABLE 5.1 Molecular Geometry Around Atoms with 2, 3, and 4 Charge Clouds

Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
2	0	2	 Linear	$\text{O}=\text{C}=\text{O}$
$\begin{bmatrix} 3 \\ 2 \end{bmatrix}$	0	3	 Planar triangular	$\text{H}-\text{C}=\text{O}$
	1		 Bent	$\text{O}=\text{S}:$
$\begin{bmatrix} 4 \\ 3 \\ 2 \end{bmatrix}$	0	4	 Tetrahedral	$\text{H}-\text{C}-\text{H}$
	1		 Pyramidal	$\text{H}-\text{N}-\text{H}$
	2		 Bent	$\text{H}-\text{O}-\text{H}$



9.1 Mixtures and Solutions

- **Heterogeneous mixture:** A nonuniform mixture that has regions of different composition.
- **Homogeneous mixture:** A uniform mixture that has the same composition throughout.
- **Solution:** A homogeneous mixture that contains particles the size of a typical ion or small molecule.
- **Colloid:** A homogeneous mixture that contains particles in the range of 2-500 nm diameter.
- **Solute:** A substance dissolved in a liquid.
- **Solvent:** The liquid in which another substance is dissolved.



10.4 Water as Both an Acid and a Base

- Water is neither an acid nor a base according to Arrhenius acid-base theory since water does not contain appreciable amount of H_3O^+ or OH^- . However, according to Bronsted-Lowry acid-base theory, water is both an acid and a base.

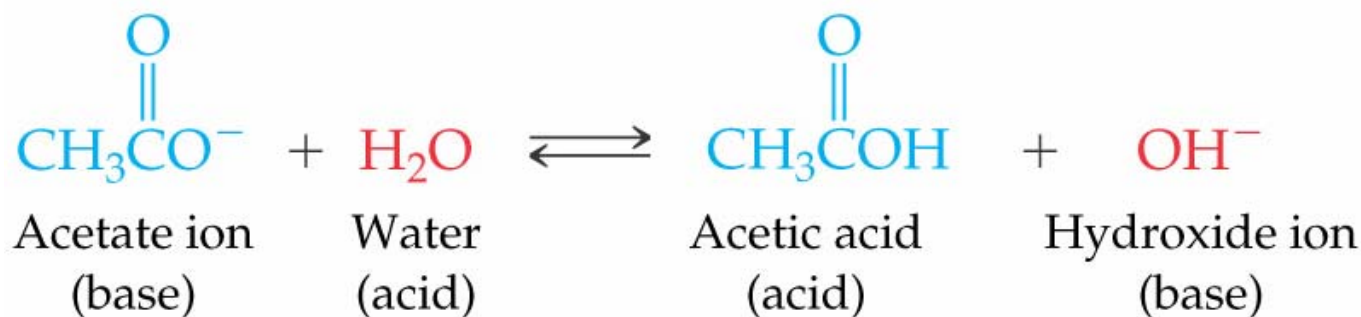



TABLE 10.1 Relative Strengths of Acids and Conjugate Bases

Acid		Conjugate Base		
Increasing acid strength 	Strong acids: 100% dissociated	Perchloric acid	HClO_4	ClO_4^- Perchlorate ion
		Sulfuric acid	H_2SO_4	HSO_4^- Hydrogen sulfate ion
		Hydriodic acid	HI	I^- Iodide ion
		Hydrobromic acid	HBr	Br^- Bromide ion
		Hydrochloric acid	HCl	Cl^- Chloride ion
	Weak acids	Nitric acid	HNO_3	NO_3^- Nitrate ion
		Hydronium ion	H_3O^+	H_2O Water
		Hydrogen sulfate ion	HSO_4^-	SO_4^{2-} Sulfate ion
		Phosphoric acid	H_3PO_4	H_2PO_4^- Dihydrogen phosphate ion
		Nitrous acid	HNO_2	NO_2^- Nitrite ion
	Very weak acids	Hydrofluoric acid	HF	F^- Fluoride ion
		Acetic acid	CH_3COOH	CH_3COO^- Acetate ion
		Carbonic acid	H_2CO_3	HCO_3^- Bicarbonate ion
		Dihydrogen phosphate ion	H_2PO_4^-	HPO_4^{2-} Hydrogen phosphate ion
		Ammonium ion	NH_4^+	NH_3 Ammonia
		Hydrocyanic acid	HCN	CN^- Cyanide ion
		Bicarbonate ion	HCO_3^-	CO_3^{2-} Carbonate ion
		Hydrogen phosphate ion	HPO_4^{2-}	PO_4^{3-} Phosphate ion
		Water	H_2O	OH^- Hydroxide ion

Little or no reaction as bases

Very weak bases

Weak bases

Strong base

Increasing base strength



Table 10.1 Relative strengths of acids and bases



10.8 Dissociation of Water

- Like all weak acids, water is slightly dissociated into H^+ and OH^- ions. The concentrations of the two ions are identical. At 25°C , concentration of each ion is 1.00×10^{-7} .
- Ion product constant for water, k_w :
 - $k_w = k_a[\text{H}_2\text{O}] = [\text{H}_3\text{O}^+][\text{OH}^-]$
 - $= [1.00 \times 10^{-7}][1.00 \times 10^{-7}]$
 - $= 1.00 \times 10^{-14}$ at 25°C .
- Product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ is a constant. Therefore, in an acidic solution where $[\text{H}_3\text{O}^+]$ is large and $[\text{OH}^-]$ must be small.



10.9 Measuring Acidity in Aqueous Solution: pH

- A pH value between 0 and 14 is used to indicate concentration of H_3O^+ or OH^- in solution. Mathematically, the pH of a solution is defined as the negative common logarithm of the H_3O^+ concentration:

- $\text{pH} = -\log [\text{H}_3\text{O}^+]$ or
- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
- Acidic solution: $\text{pH} < 7$ $[\text{H}_3\text{O}^+] > 1.00 \times 10^{-7} \text{ M}$
- Neutral solution: $\text{pH} = 7$ $[\text{H}_3\text{O}^+] = 1.00 \times 10^{-7} \text{ M}$
- Basic solution: $\text{pH} > 7$ $[\text{H}_3\text{O}^+] < 1.00 \times 10^{-7} \text{ M}$



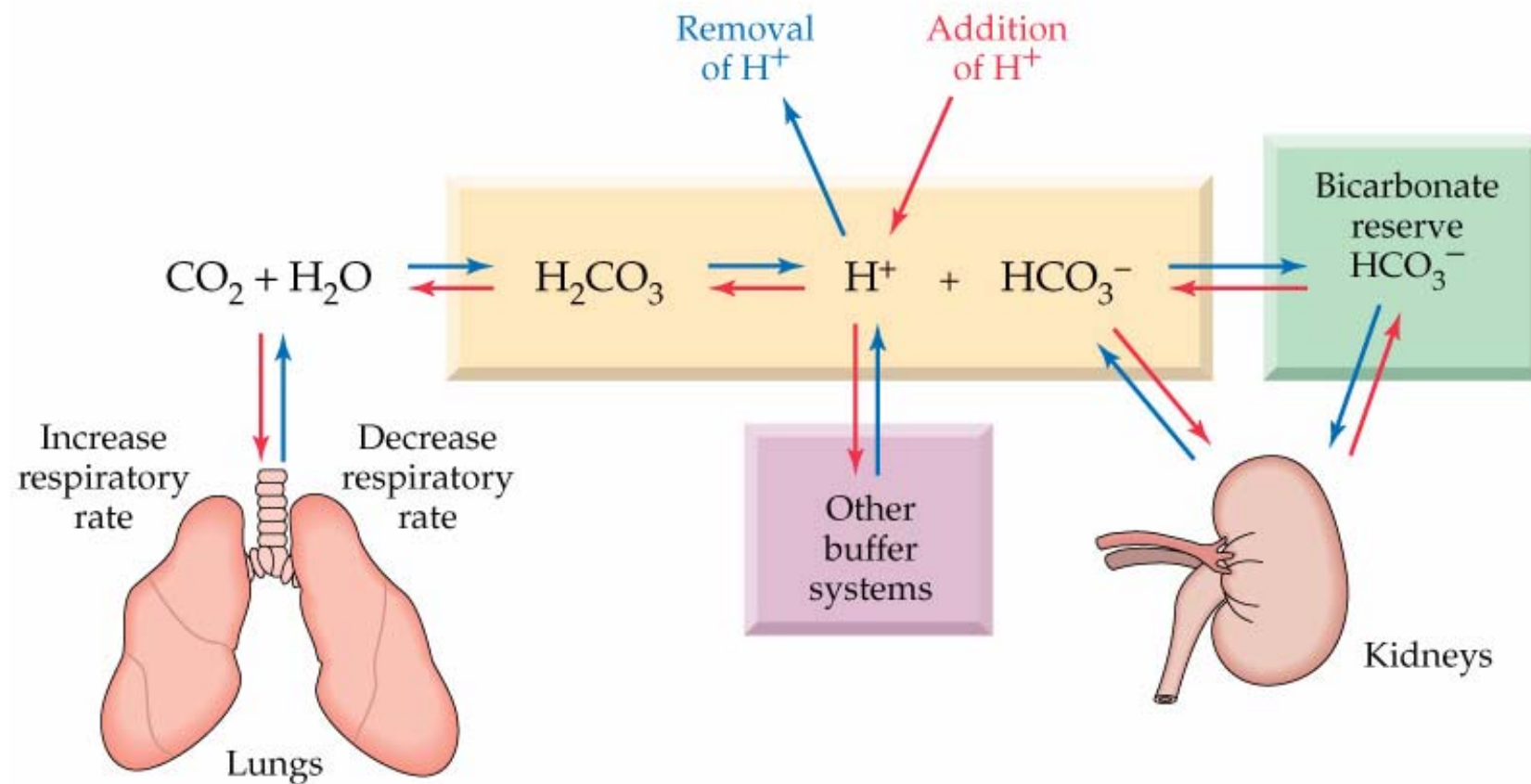
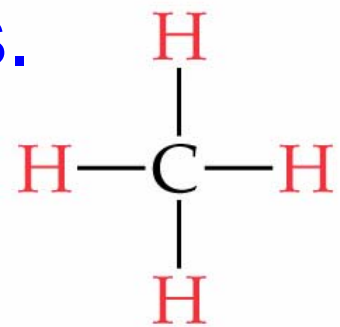


Fig 10.7 Lungs and kidneys relation with the bicarbonate buffer system

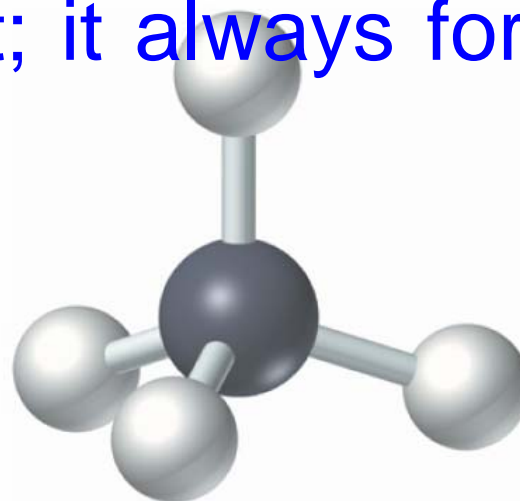


12.1 The Nature of Organic molecules

- **Organic chemistry:** The chemistry of carbon compounds.
- Carbon is tetravalent; it always form four bonds.



Methane, CH₄



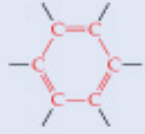
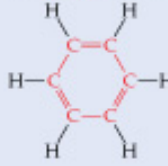




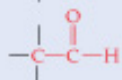
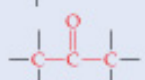
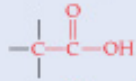
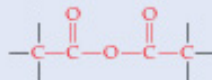
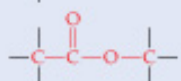
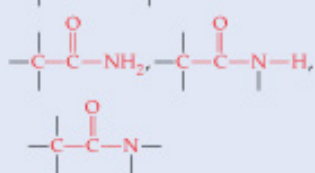


Organic molecules

- CH
- CHO, CHS
- CHN
- C=O
- COO
- CON



TABLE 12.1 Some Important Families of Organic Molecules

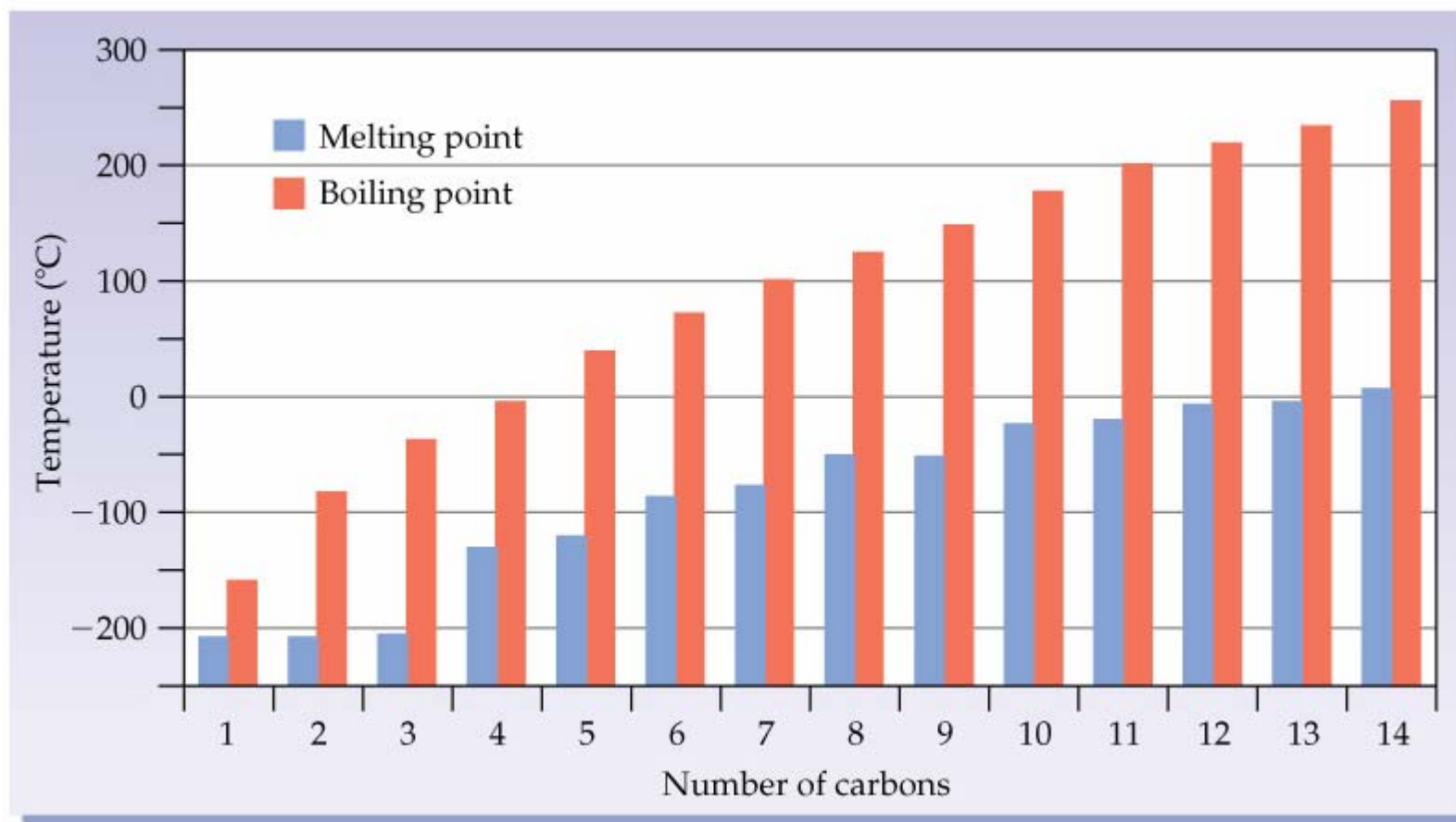
Family Name	Functional Group Structure*	Simple Example	Name Ending
Alkane	Contains only C—H and C—C single bonds	CH ₃ CH ₃ Ethane	-ane
Alkene		H ₂ C=CH ₂ Ethylene	-ene
Alkyne		H—C≡C—H Acetylene (Ethyne)	-yne
Aromatic		 Benzene	None
Alkyl halide	 (X = F, Cl, Br, I)	CH ₃ —Cl Methyl chloride	None
Alcohol		CH ₃ —OH Methyl alcohol (Methanol)	-ol
Ether		CH ₃ —O—CH ₃ Dimethyl ether	None
Amine		CH ₃ —NH ₂ Methylamine	-amine
Aldehyde		CH ₃ —C(=O)—H Acetaldehyde (Ethanal)	-al
Ketone		CH ₃ —C(=O)—CH ₃ Acetone	-one
Carboxylic acid		CH ₃ —C(=O)—OH Acetic acid	-ic acid
Anhydride		CH ₃ —C(=O)—O—C(=O)—CH ₃ Acetic anhydride	None
Ester		CH ₃ —C(=O)—O—CH ₃ Methyl acetate	-ate
Amide		CH ₃ —C(=O)—NH ₂ Acetamide	-amide

* The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

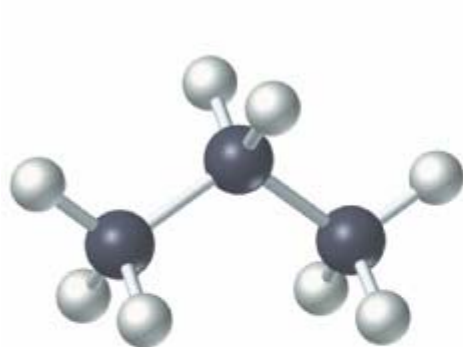


12.7 Properties of Alkanes

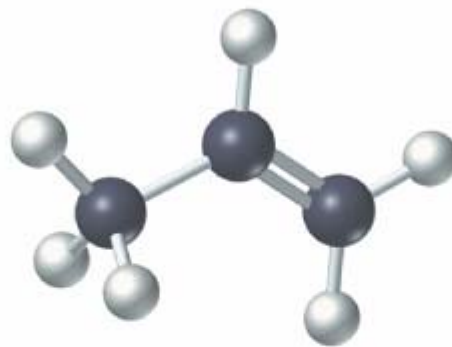
- Melting points and boiling points of straight chain alkanes increases with molecular size.



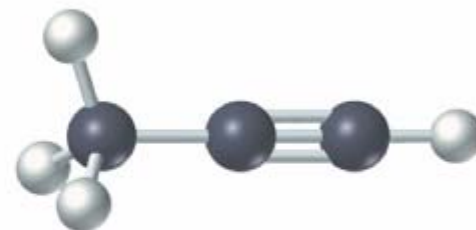
- Alkenes are hydrocarbons that contain carbon-carbon double bonds.
- Alkynes are hydrocarbons that contain carbon-carbon triple bonds.



$\text{CH}_3\text{CH}_2\text{CH}_3$
Propane—an alkane
(saturated)



$\text{CH}_3\text{CH}=\text{CH}_2$
Propene—an alkene
(unsaturated)



$\text{CH}_3\text{C}\equiv\text{CH}$
Propyne—an alkyne
(unsaturated)

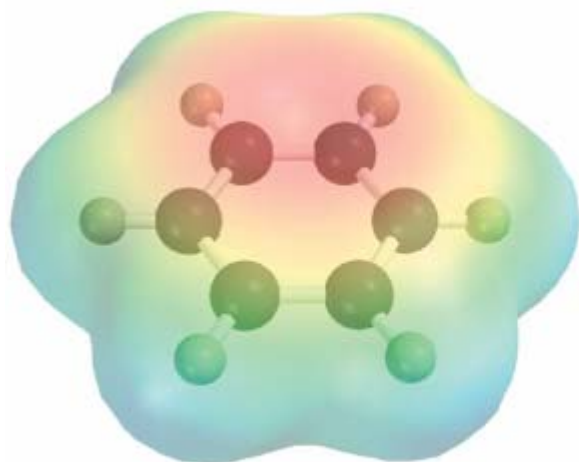


13.4 Properties of Alkenes and Alkynes

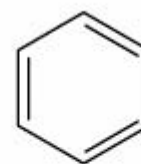
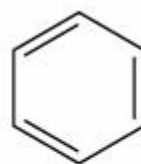
- Nonpolar, insoluble in water, soluble in nonpolar organic solvents.
- Less dense than water as a result floats on water.
- Flammable
- Nontoxic
- Alkenes display cis-trans isomerism whereas alkynes do not.
- Both alkenes and alkynes are chemically reactive.



- Unlike alkenes, benzene does not undergo addition reactions.
- Benzene's relatively lack of chemical reactivity is due to its structure.
- There are two possible structures with alternating double and single bonds.



(a)



Two equivalent structures, which differ in the position of their double-bond electrons. Neither structure is correct by itself.

(b)



(c)

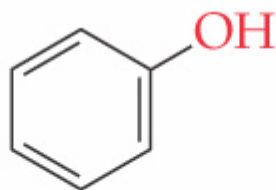


14.1 Alcohols, Phenols, and Ethers

- Alcohol: A compound that has an –OH group bonded to a saturated, alkane like carbon atom, R-OH.
- Phenol: A compound that has an –OH group bonded to an aromatic, benzene like ring, Ar-OH.
- Ether**: A compound that has an oxygen bonded to two organic groups, R-O-R.



Ethyl alcohol



Phenol

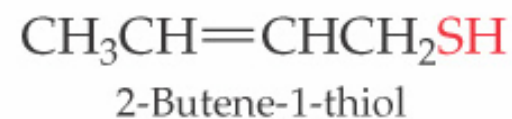


Diethyl ether



14.9 Thiols and Disulfides

- Thiols (R-SH) are sulfur analog of alcohols (R-OH).
- The systematic name of a thiol is formed by adding -thiol to the parent hydrocarbon



- Thiols have characteristic foul smell.

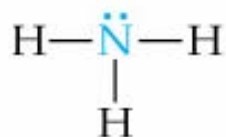


- Thiols (R-SH) react with mild oxidizing agents such as Br_2 in water to yield disulfide (R-S-S-R).
- The reverse reaction ($\text{RS-SR} \rightarrow 2\text{RSH}$) occurs when a disulfide is treated with a reducing agent.
- S-S bonds between two amino acid cysteines gives protein molecules their required shapes in order to function.
- Hair protein is rich in S-S and $-\text{SH}$ groups. When hair is 'permed' some of the disulfide bonds are broken and new ones are formed giving hairs a different shape.

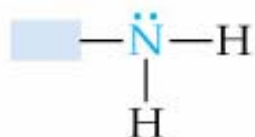


15.1 Amines

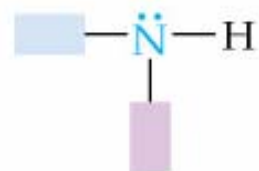
- Amines are compounds that contain one or more organic groups bonded to nitrogen. They are classified as primary, secondary, and tertiary according to how many organic groups are bonded to the nitrogen atom.



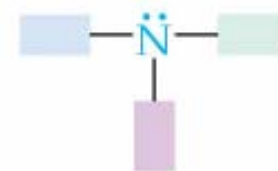
Ammonia



A primary amine
(RNH_2)



A secondary amine
(R_2NH)

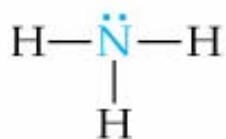


A tertiary amine
(R_3N)

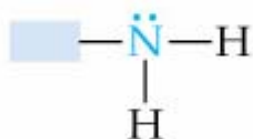


15.1 Amines

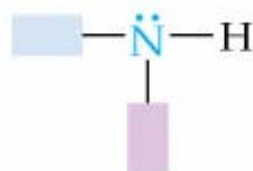
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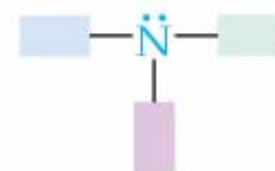
Ammonia



A primary amine
(RNH_2)



A secondary amine
(R_2NH)



A tertiary amine
(R_3N)



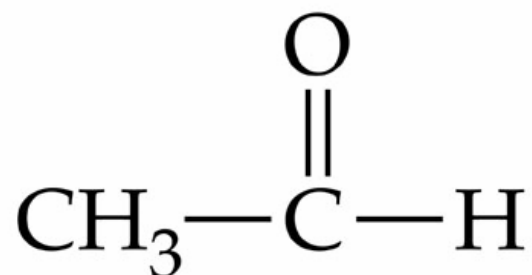
TABLE 16.1 Some Kinds of Carbonyl Compounds

Family Name	Structure	Example	
Aldehyde	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Acetaldehyde
Ketone	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Acetone
Carboxylic acid	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$	Acetic acid
Ester	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_3$	Methyl acetate
Amide	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N} \begin{array}{l} \diagup \\ \diagdown \end{array}$	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	Acetamide

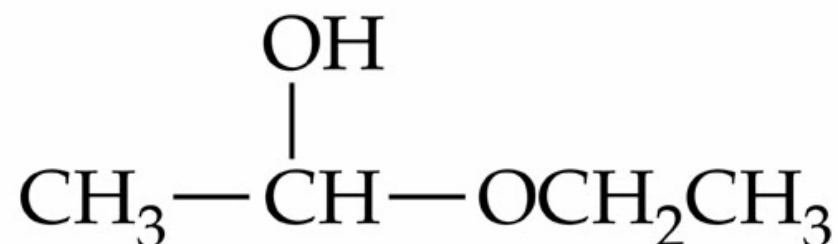


- The reaction is reversible. Hemiacetals rapidly revert back to aldehydes or ketones by loss of alcohol.
- **Acetal Formation**
- In the presence of a small amount of acid catalyst, hemiacetals are converted to acetals. Acetals have two –OR groups attached to what was the original carbonyl carbon.

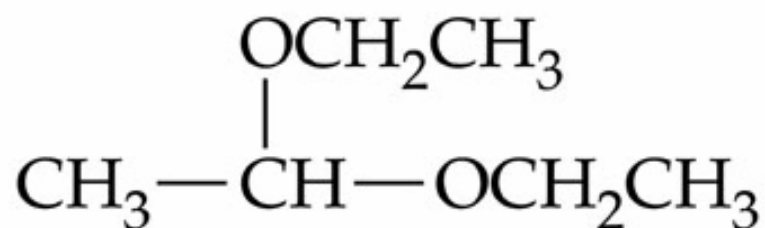




Acetaldehyde



Acetaldehyde hemiacetal
with ethanol



Acetaldehyde acetal
with ethanol

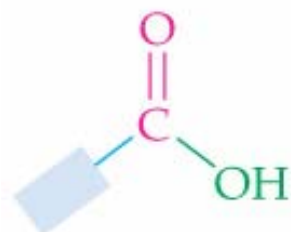
- Fig 16.3 Acetaldehyde and its hemiacetal and acetal



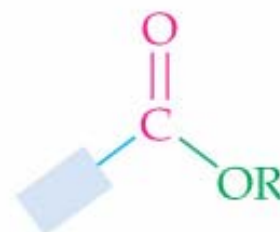
17.1 Carboxylic Acids and Their Derivatives: Properties and Names

- Carboxylic acids have an –OH group bonded to a carbonyl group. In their derivatives, OH is substituted by other group. Such as,
- Esters have a –OR group bonded to a carbonyl group.

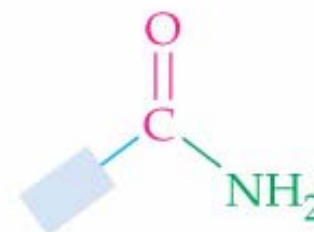
- Amides
- carbonyl



Carboxylic acid



Ester



Amide

a

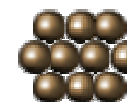


TABLE 18.1 Functional Groups of Importance in Biochemical Molecules

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	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH}, \quad \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}^- \end{array} \end{array}$	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-	$\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)- \\ \end{array}$	ATP and many metabolism intermediates (Sections 17.8, 21.5, and throughout metabolism sections)
	$\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)- \\ \end{array}$	
	$\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)- \\ \end{array}$	
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)



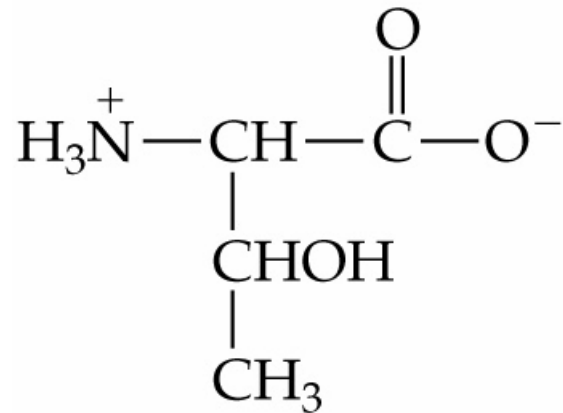
Biochemical Building Block

- Protein ---- Amino Acid
- Lipid ----- fatty acid
- Carbohydrate ----- sugar



- 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.





Threonine—zwitterion

• Because they are zwitterion, amino acids have many properties that are common for salts. Such as

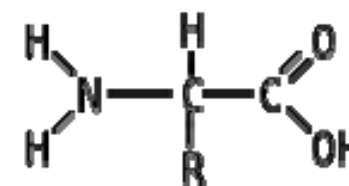
- amino acids crystalline
- amino acids have high melting points
- amino acids are water soluble.



- The charge of an amino acid molecule at any given moment depends on the identity of the amino acid and pH of the medium.
- The pH at which the net positive and negative charges are evenly balanced is the amino acid's *isoelectric point*- the overall charges is zero.



20 Amino Acids



Amino Acids with Aliphatic R-Groups

			pK1	pK2
Glycine	Gly - G	$\text{H}-\text{CH}-\text{COOH}$ NH_2	2.4	9.8
Alanine	Ala - A	$\text{CH}_3-\text{CH}-\text{COOH}$ NH_2	2.4	9.9
Valine	Val - V	$\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{CH}-\text{CH}-\text{COOH}$ NH_2	2.2	9.7
Leucine	Leu - L	$\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{CH}-\text{CH}_2-\text{CH}-\text{COOH}$ NH_2	2.3	9.7
Isoleucine	Ile - I	$\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_3\text{C} \end{array} \text{CH}_2-\text{CH}-\text{CH}-\text{COOH}$ NH_2	2.3	9.8



20 Amino Acids

Non-Aromatic Amino Acids with Hydroxyl R-Groups

Serine	Ser - S	$\text{HO}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	2.2	9.2	~13
Threonine	Thr - T	$\text{H}_3\text{C}-\underset{\text{HO}}{\text{CH}}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	2.1	9.1	~13

Amino Acids with Sulfur-Containing R-Groups

Cysteine	Cys - C	$\text{HS}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	1.9	10.8	8.3
Methionine	Met-M	$\text{H}_3\text{C}-\text{S}-(\text{CH}_2)_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	2.1	9.3	



20 Amino Acids

Acidic Amino Acids and their Amides

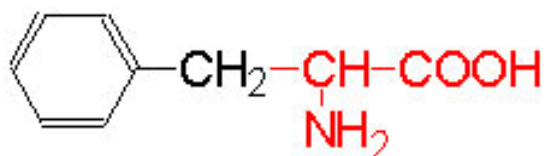
Aspartic Acid	Asp - D	$\text{HOOC}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	2.0	9.9	3.9
Asparagine	Asn - N	$\text{H}_2\text{N}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	2.1	8.8	
Glutamic Acid	Glu - E	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	2.1	9.5	4.1
Glutamine	Gln - Q	$\text{H}_2\text{N}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$	2.2	9.1	



20 Amino Acids

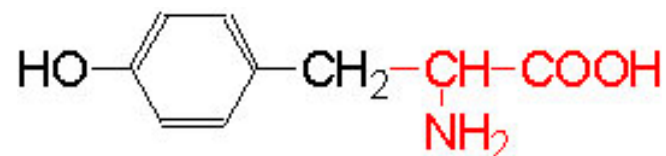
Amino Acids with Aromatic Rings

Phenylalanine Phe - F



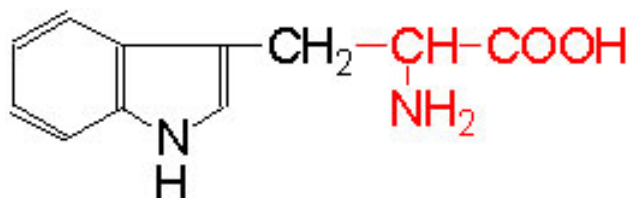
2.2 9.2

Tyrosine Tyr - Y



2.2 9.1 10.1

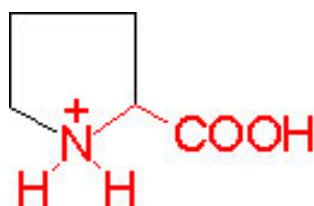
Tryptophan Trp - W



2.4 9.4

Imino Acids

Proline Pro - P



2.0 10.6



20 Amino Acids

Basic Amino Acids

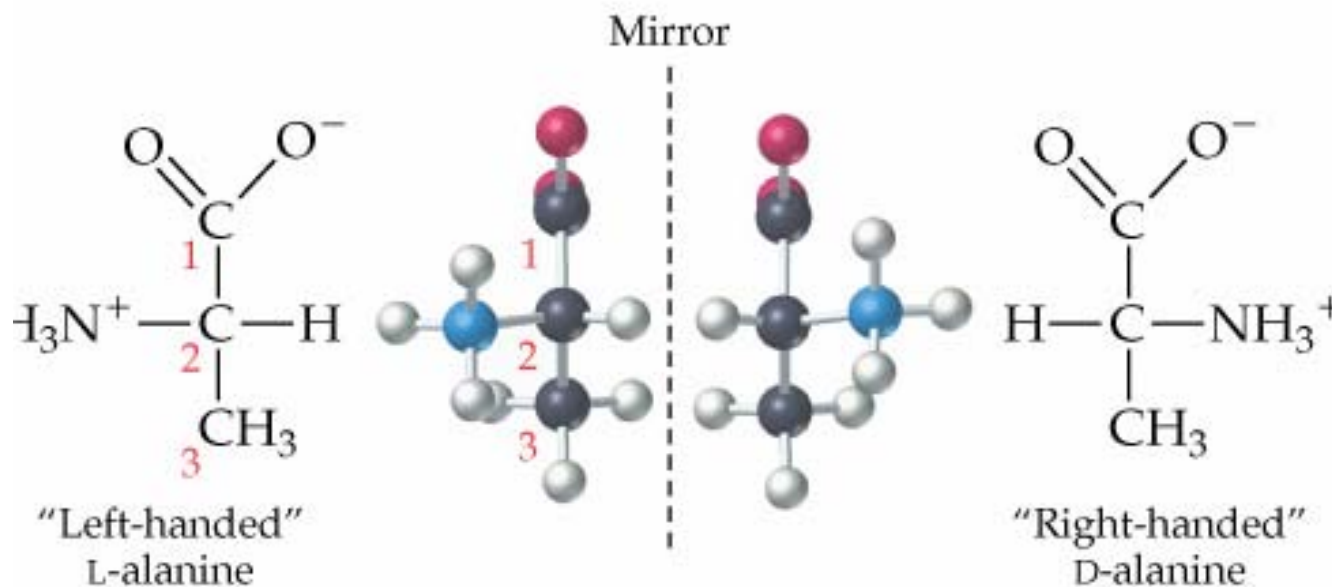
Arginine	Arg - R	$ \begin{array}{c} \text{HN}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{COOH} \\ \qquad \qquad \qquad \\ \text{C}=\text{NH} \qquad \qquad \text{NH}_2 \\ \\ \text{NH}_2 \end{array} $	1.8	9.0	12.5
Lysine	Lys - K	$ \begin{array}{c} \text{H}_2\text{N}-(\text{CH}_2)_4-\text{CH}-\text{COOH} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{NH}_2 \end{array} $	2.2	9.2	10.8
Histidine	His - H	$ \begin{array}{c} \text{Imidazole ring}-\text{CH}_2-\text{CH}-\text{COOH} \\ \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{NH}_2 \end{array} $	1.8	9.2	6.0



18.6 Molecular Handedness and Amino Acids

- Like objects, organic molecules can also have handedness, that is they can be ch

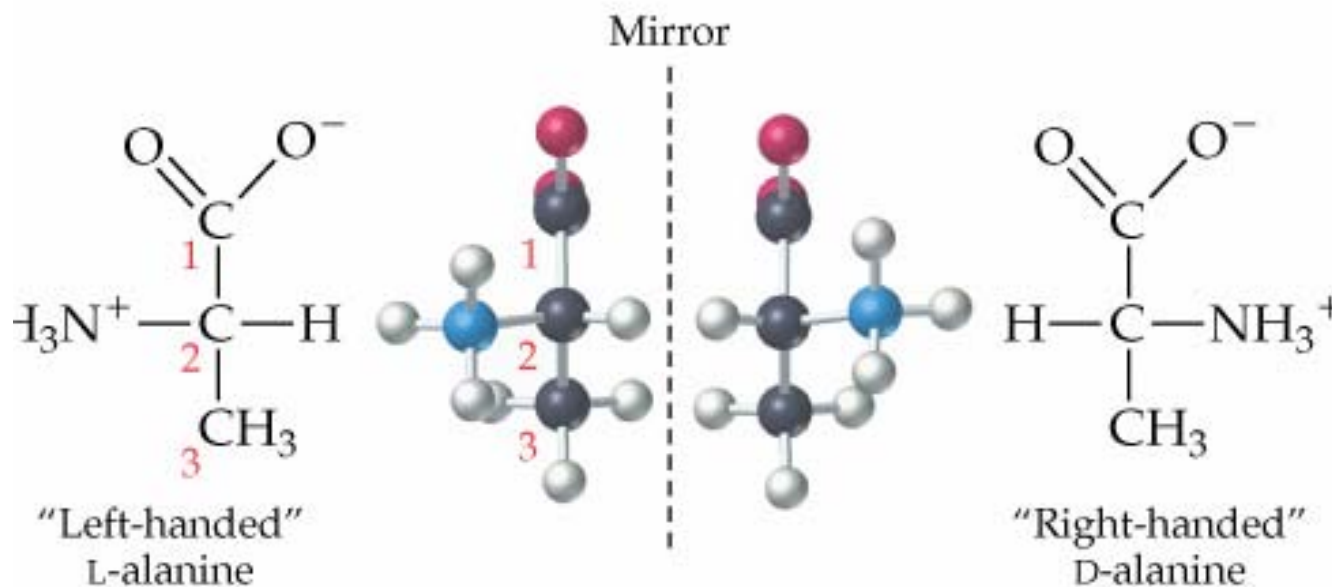
Alanine, a chiral molecule



18.6 Molecular Handedness and Amino Acids

- Like objects, organic molecules can also have handedness, that is they can be ch

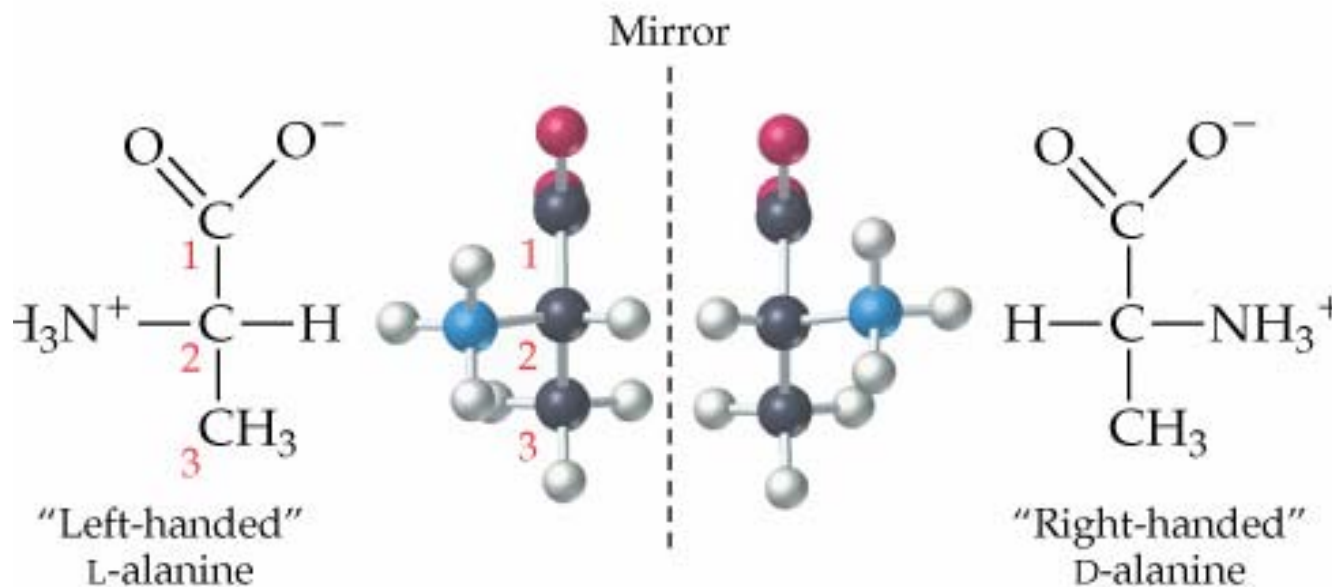
Alanine, a chiral molecule



18.6 Molecular Handedness and Amino Acids

- Like objects, organic molecules can also have handedness, that is they can be ch

Alanine, a chiral molecule



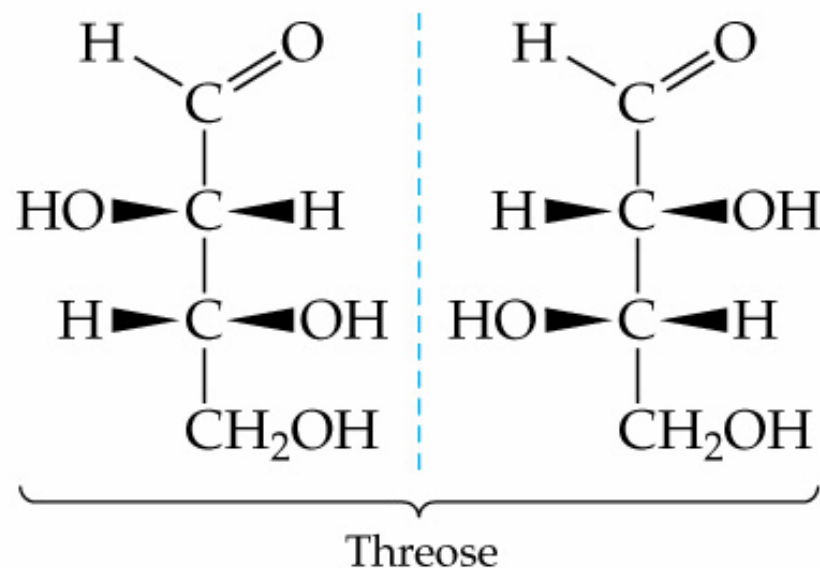
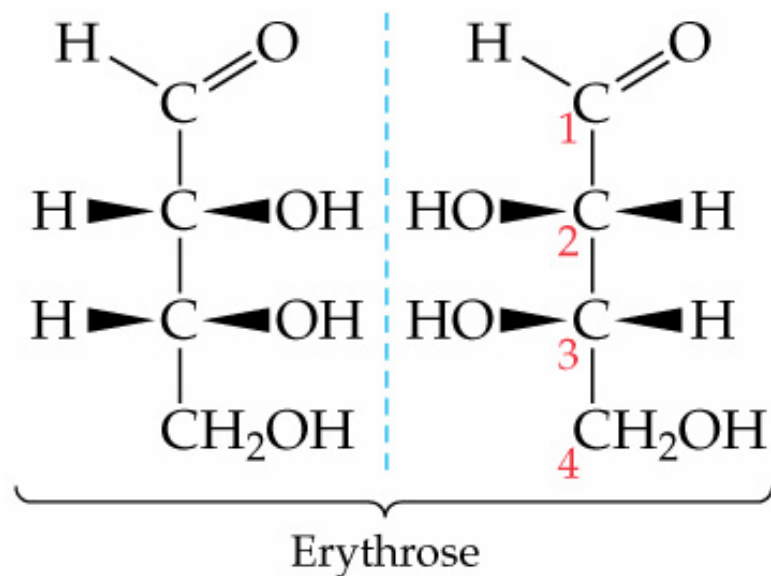
22.1 An Introduction to Carbohydrates

- *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.

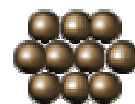


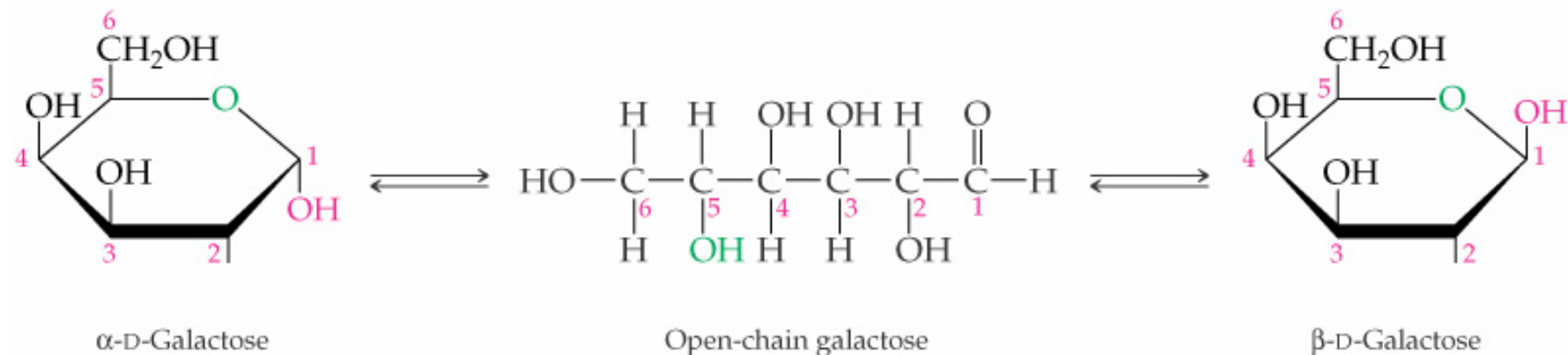
- *Carbohydrates* are a large class of naturally occurring polyhydroxy aldehydes and ketones.
- Monosaccharides also known as simple sugars, are the simplest carbohydrates containing 3-7 carbon atoms.
- sugar containing an aldehydes is known as an aldose.
- sugar containing a ketones is known as a ketose.
- The family name ending -ose indicates a carbohydrate.
- Simple sugars are known by common names such as glucose, ribose, fructose, etc.





- Fig 22.2 Two pairs of enantiomers. The four isomeric aldotetroses, 2,3,4-trihydroxybutanals.





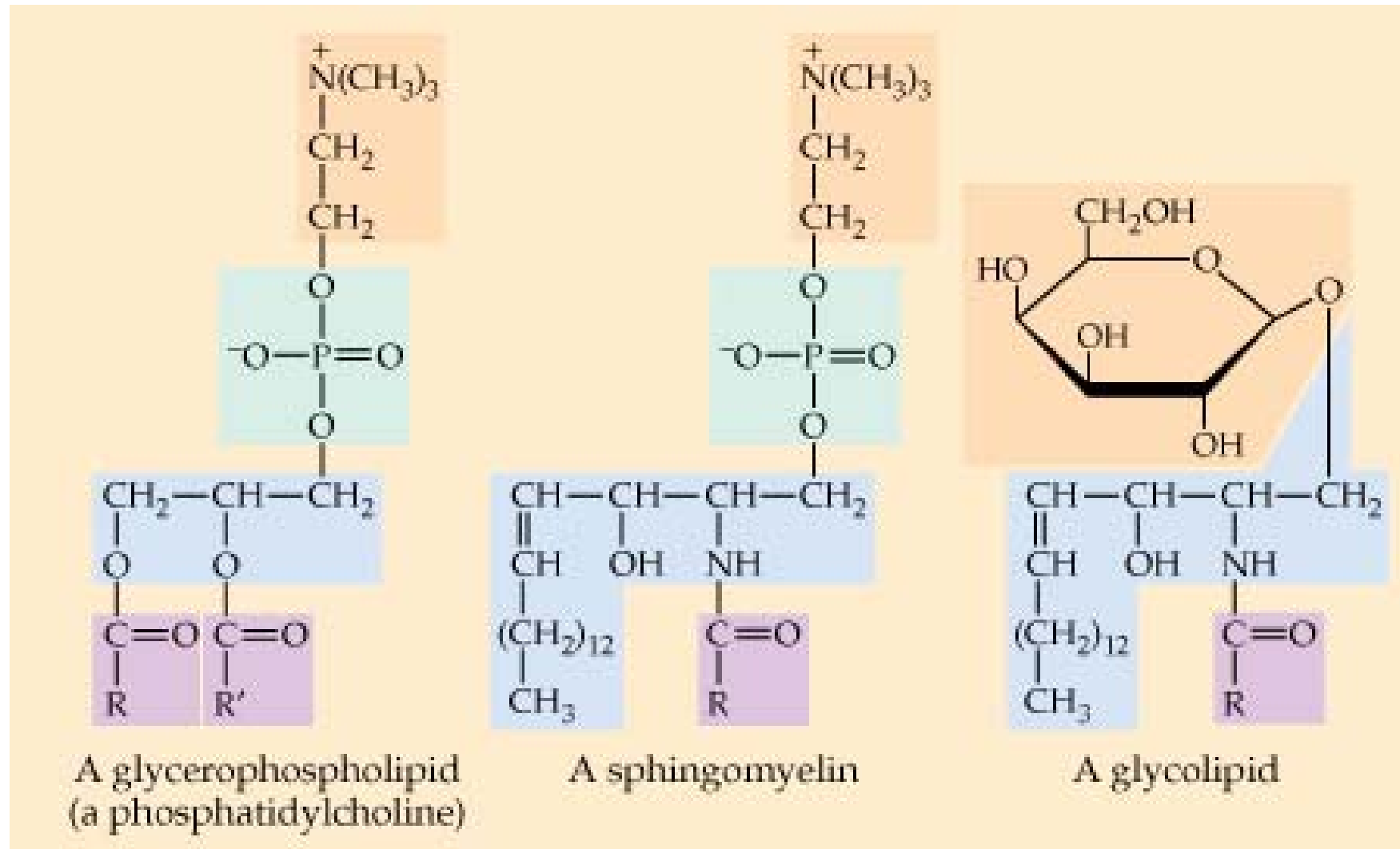
- The structure of D-galactose: The molecule can exist as an open chain hydroxy aldehyde or as a pair of cyclic hemiacetals.



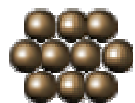
24.1 Structure and Classification of Lipids

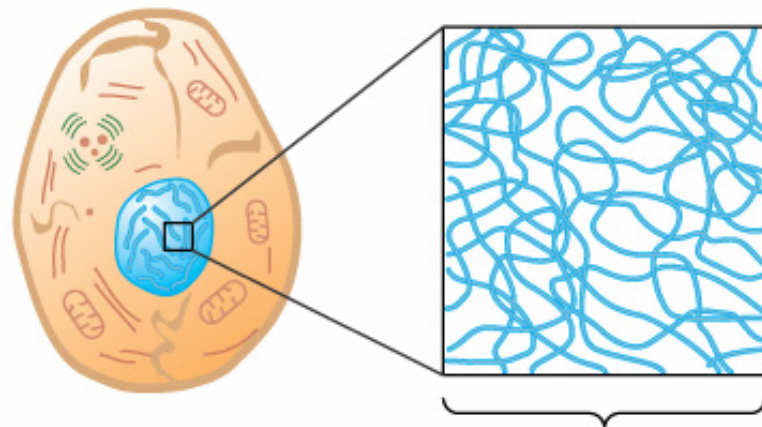
- *Lipids* are naturally occurring molecules from plants or animals that are soluble in nonpolar organic solvents.
- Lipid molecules contain large hydrocarbon portion and not many polar functional group, which accounts for their solubility behavior.





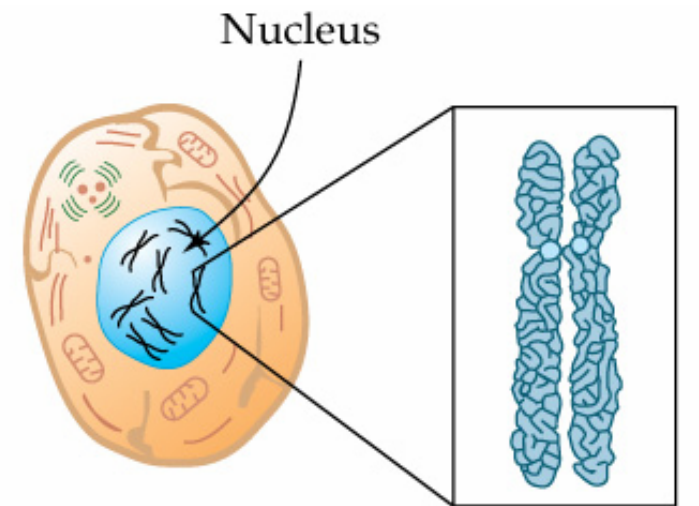
• Fig 24.4 Membrane lipids





Nondividing
cell

Chromatin
in nucleus

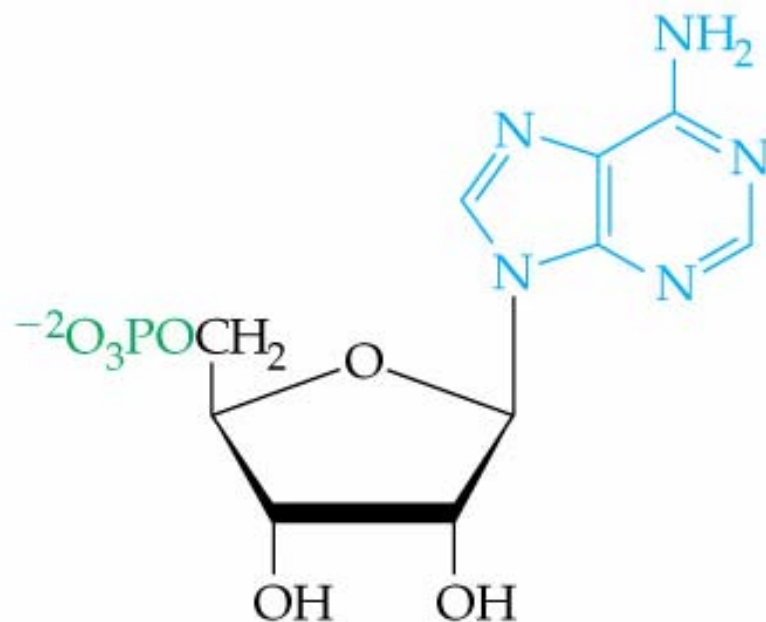


Cell prepared
for division

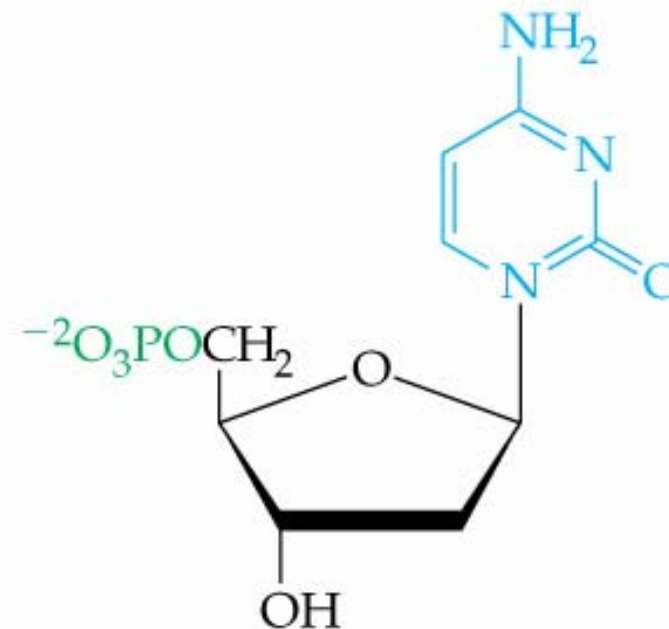
Visible
chromosome



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



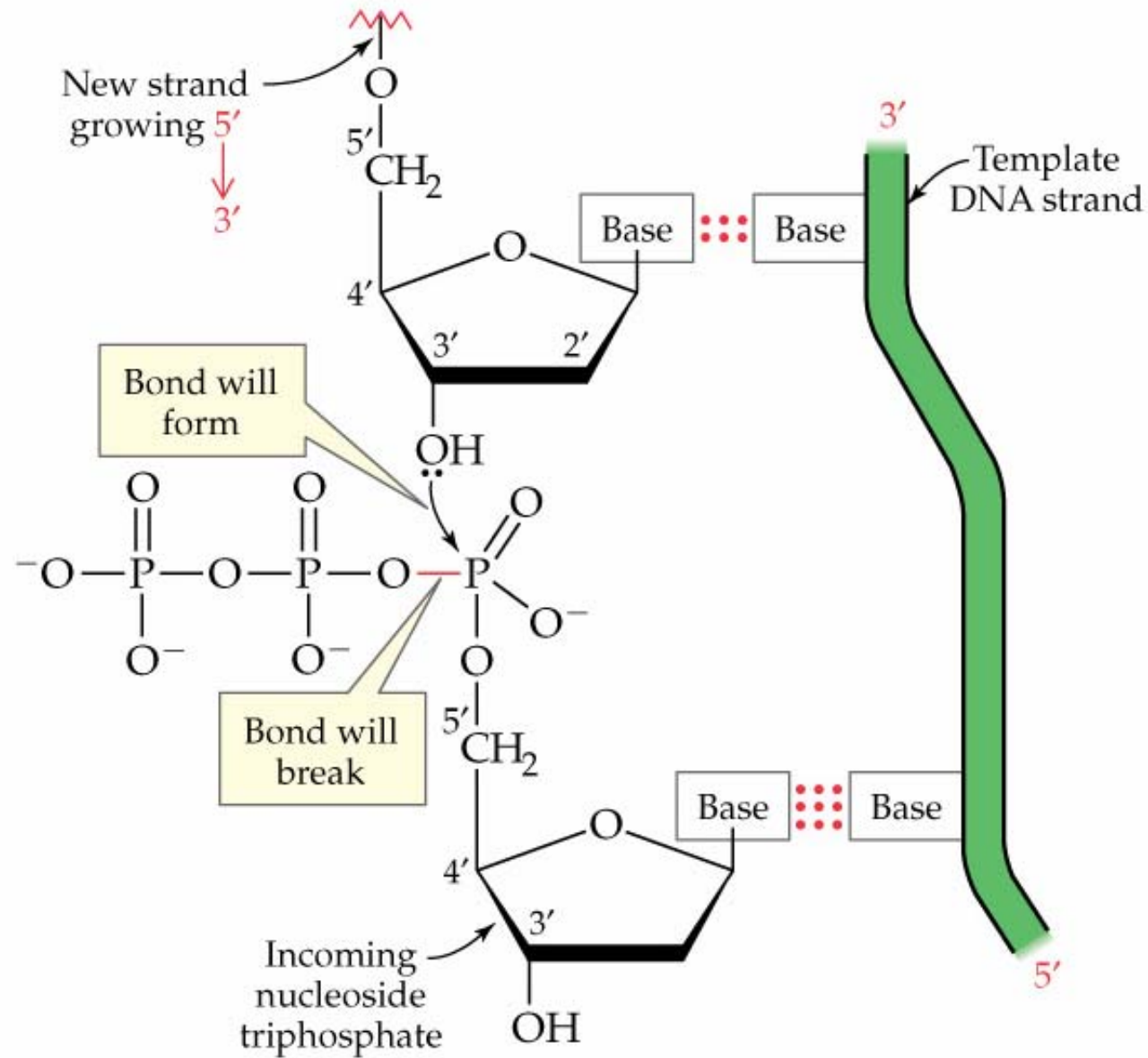
Adenosine 5'-monophosphate (AMP)
(a ribonucleotide)



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



Bond formation in DNA replication



18.1 An Introduction to Biochemistry

• **Biochemistry** - chemical basis of life. Biochemical reactions are involved in such areas as breaking down food molecules, generate and store energy, buildup new biomolecules, and eliminate waste. Some biomolecules are small and have only a few functional groups others are huge and contains a large number of functional groups. The principal classes of biomolecules are: *Proteins, lipids, and nucleic acids.*



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	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH}, -\text{C}-\text{O}^- \end{array}$	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-	$\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)- \\ \end{array}$ $\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)- \\ \end{array}$ $\begin{array}{c} \\ \\ -\text{C}-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)-\text{O}-\text{P}(=\text{O})(\text{O}^-)- \\ \end{array}$	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)



18.2 Protein Structure and Function: An Overview

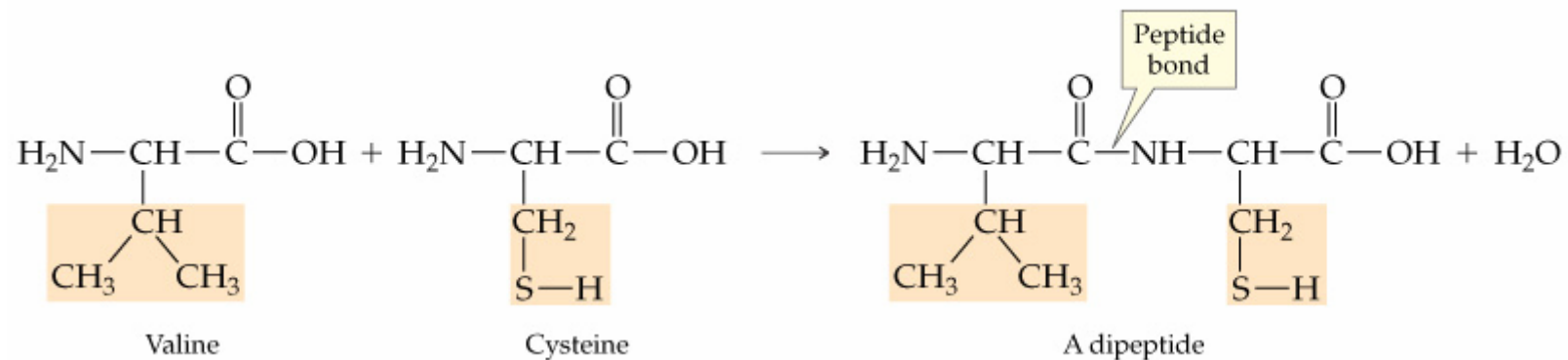
- Proteins are **polymers** of amino acids.
- Each amino acids in a protein contains a amino group, -NH_2 , a carboxyl group, -COOH , and an R group, all bonded to the central carbon atom. The R group may be a hydrocarbon or they may contain functional group.



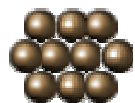
- All amino acids present in a proteins are *α -amino acids* in which the amino group is bonded to the carbon next to the carboxyl group.
- Two or more amino acids can join together by forming amide bond, which is known as a **peptide bond** when they occur in proteins.



- A dipeptide results when two amino acids combine together by forming a peptide bond using amino group of one amino acid and carboxyl group of another amino acid.



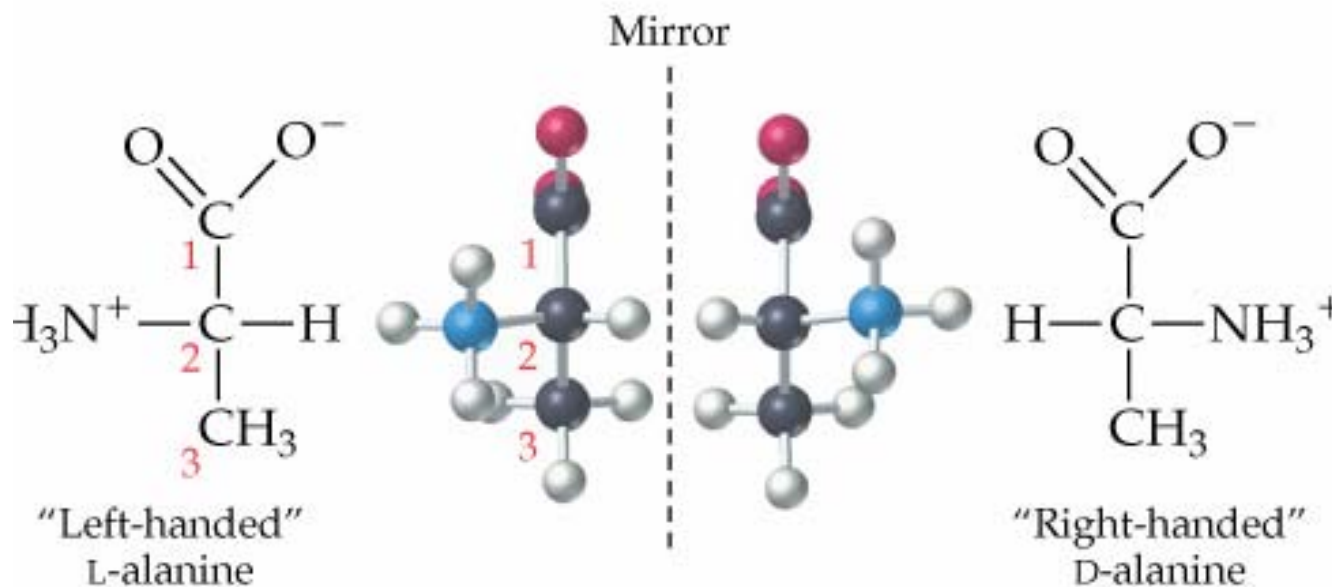
- A *tripeptide* results when three amino acids combine together by forming two peptide bonds, and so on. Any number of amino acids can link together and form a linear chain like polymer – *polypeptide*.



18.6 Molecular Handedness and Amino Acids

- Like objects, organic molecules can also have handedness, that is they can be ch

Alanine, a chiral molecule



- A molecule is a chiral molecule if four different atoms or groups are attached to a **carbon**. The carbon carrying four different groups called a chiral carbon. Chiral molecules has no plane of symmetry.
- The two mirror image forms of a chiral molecule like alanine are called *enantiomers or optical isomers*.
- Enantiomers have the same formula but different arrangements of their atoms.

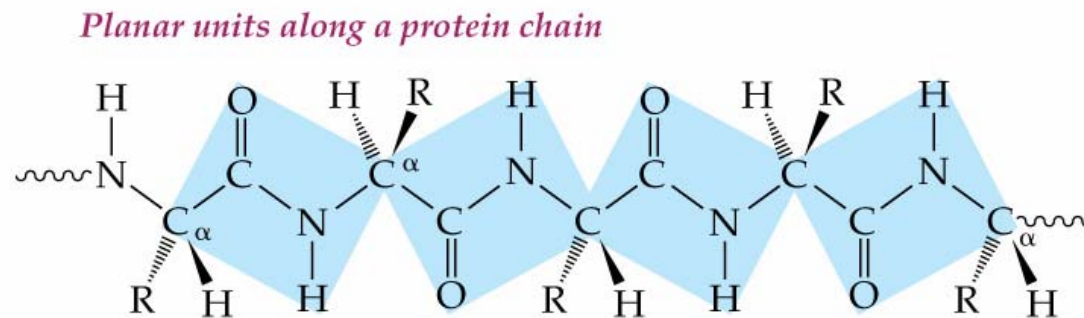


- 19 out of 20 natural amino acids are chiral – they have four different groups on the α -carbon. Only glycine is achiral.
- Nature uses only one isomer out of a pair of enantiomers for each amino acid to build the proteins.
- The naturally occurring amino acids are classified as left-handed or L-amino acids.

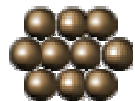
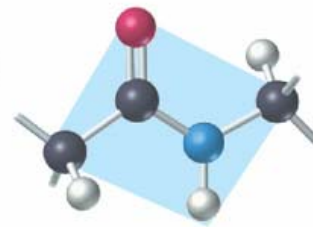


18.7 Primary Protein Structure

- 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.



18.8 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.
- The kinds of interaction that determine the shape protein molecules are shown in Fig 18.4.



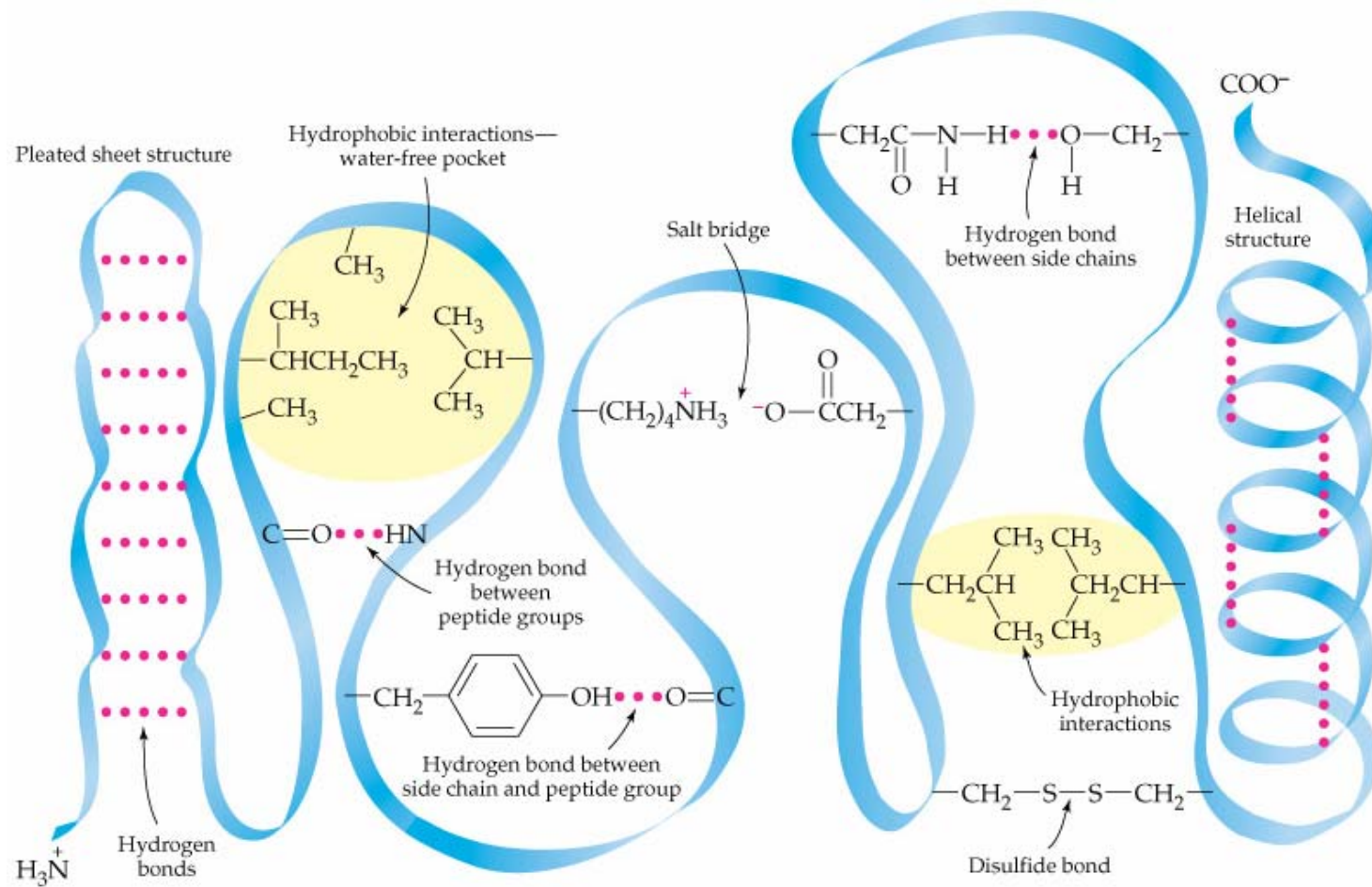
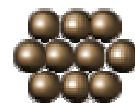


Fig 18.4 Interactions that determine protein shape



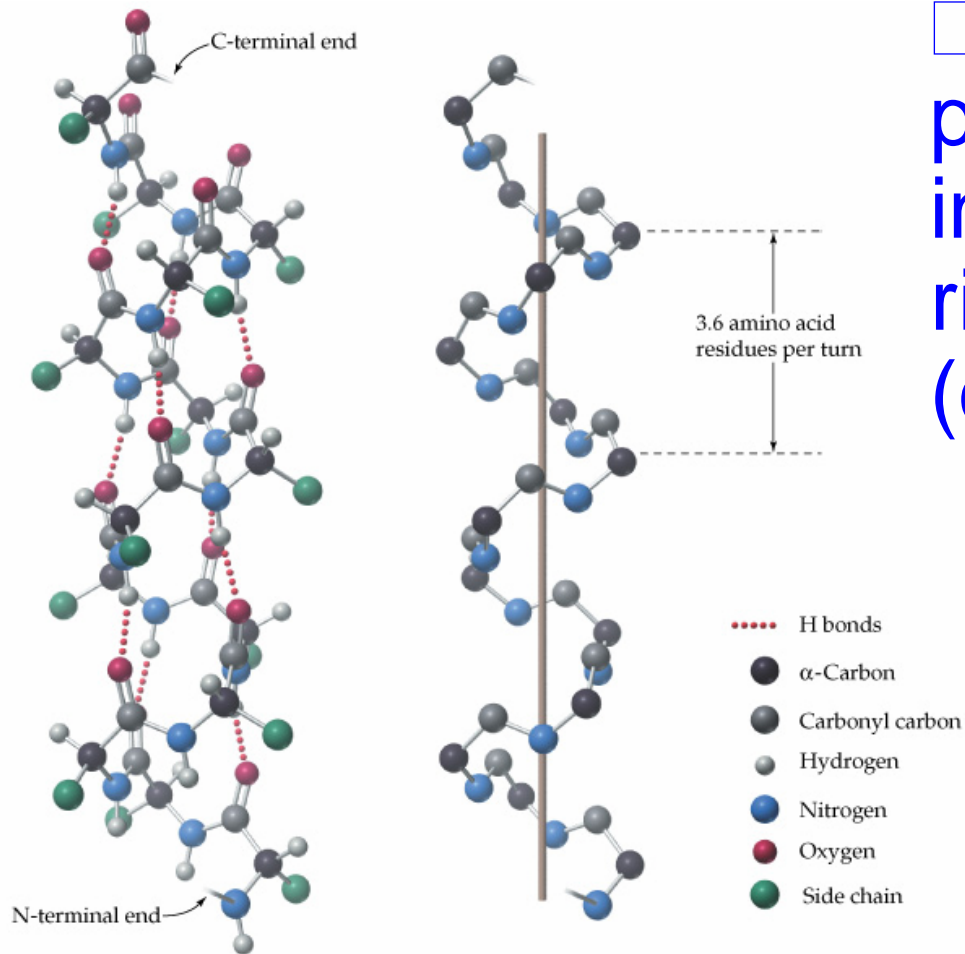
- Protein shape determining interactions are summarized below:
- **Hydrogen bond** between neighboring backbone segments.
- Hydrogen bonds of side chains with each other or with backbone atoms.
- **Ionic attractions** between side chain groups or salt bridge.
- **Hydrophobic** interactions between side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



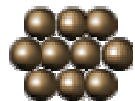
18.9 Secondary Protein Structure

- 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.

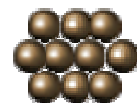
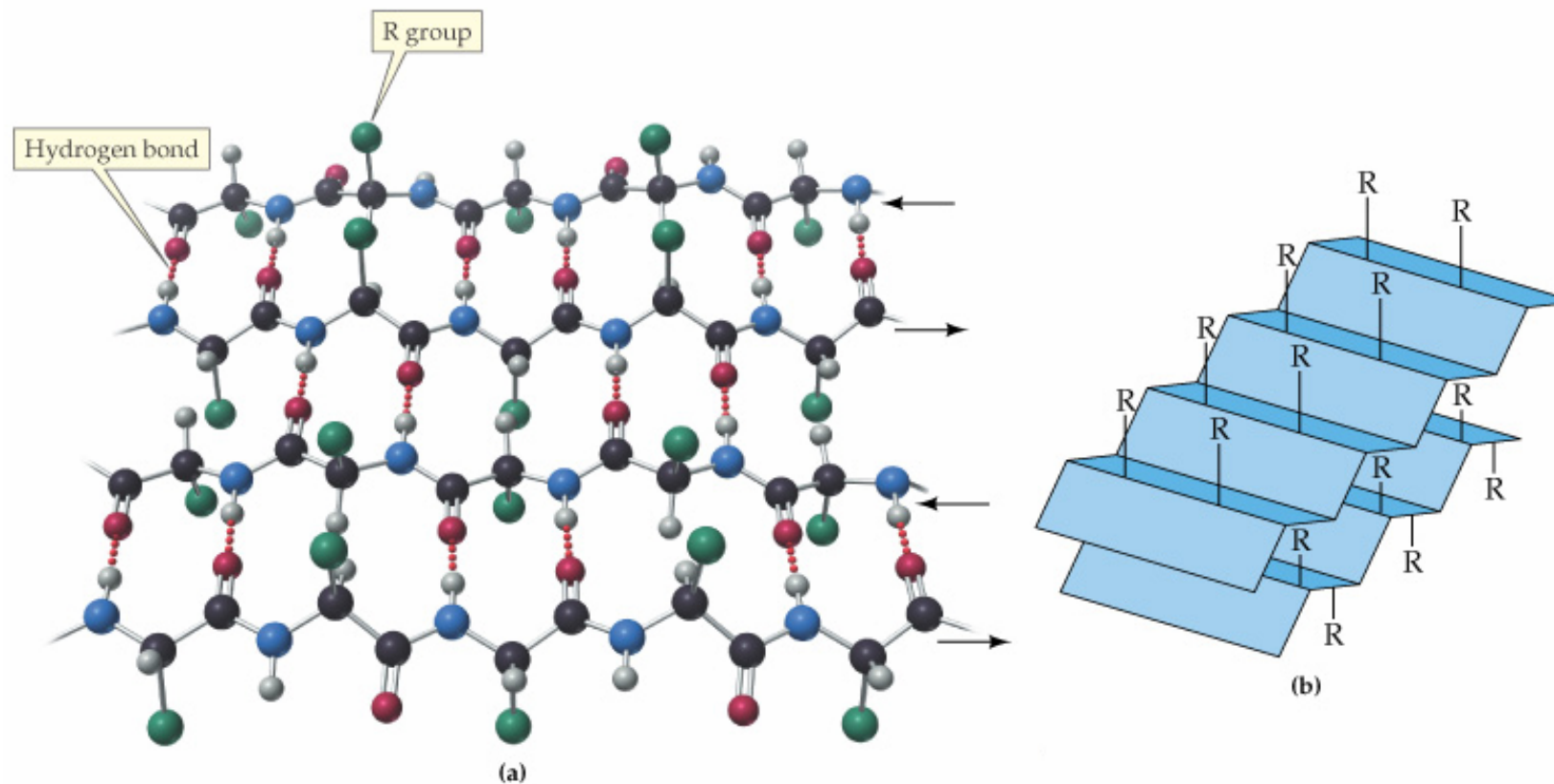




□ **α -Helix:** A single protein chain coiled in a spiral with a right-handed (clockwise) twist.



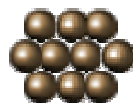
□ **β -Sheet:** The polypeptide chain is held in place by hydrogen bonds between pairs of peptide units along neighboring backbone segments.



- **Fibrous and Globular proteins:** one of the several classifications of proteins.

- *Fibrous protein:* Tough and **insoluble** protein in which the chain form **long fibers or sheet**. Secondary structure is responsible for the shape of fibrous proteins. Wool, hair, and finger nails are made of fibrous proteins.

- *Globular protein:* water **soluble** proteins whose chains are folded into compact, **globular shape** with hydrophilic groups on the outside.



18.10 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



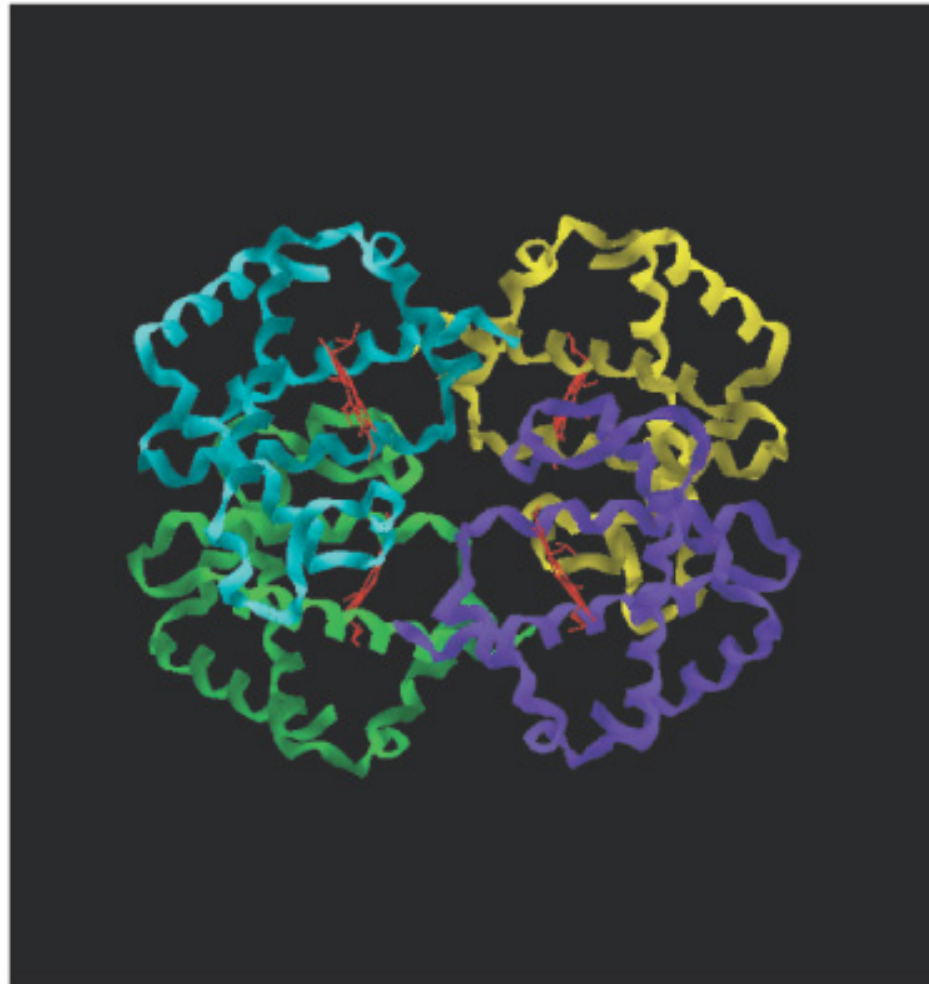
- ***Simple protein***: A protein composed of only amino acid residues.
- ***Conjugated protein***: A protein that incorporates one or more non-amino acid units in its structure.



18.11 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.





•Fig 18.8(b) Hemoglobin, a protein with quaternary structure

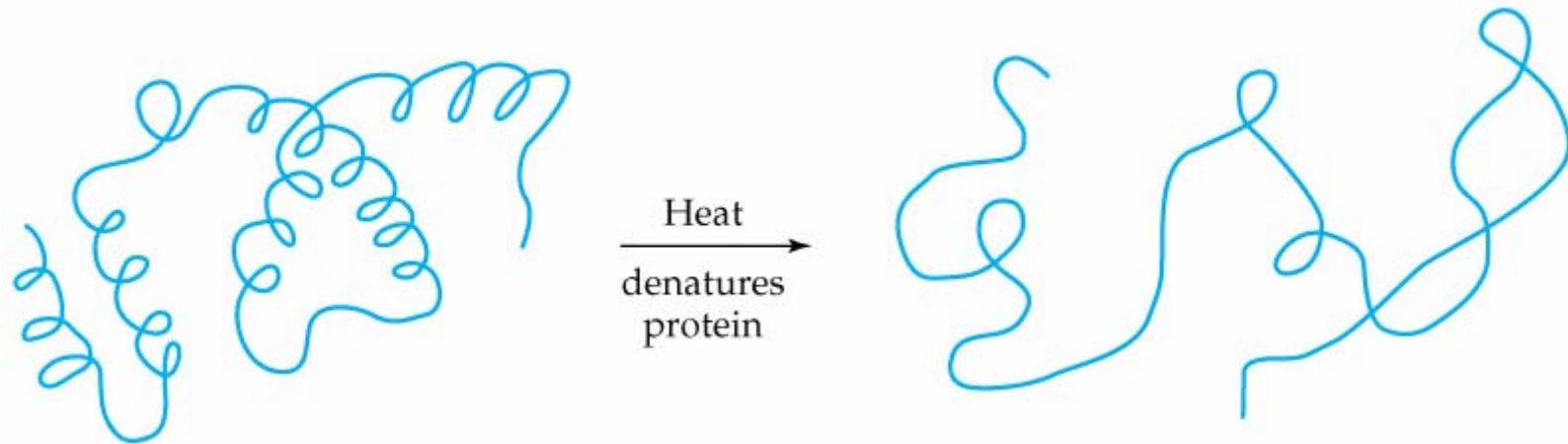


18.12 Chemical Properties of Proteins

- *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



19.1 Catalysis by Enzymes

- **Enzyme** A protein that acts as a catalyst for a biochemical reaction.
- **Active site** A pocket in an enzyme with the specific shape and chemical makeup necessary to bind a substrate and where the reaction takes place.
- **Substrate** A reactant in an enzyme catalyzed reaction.



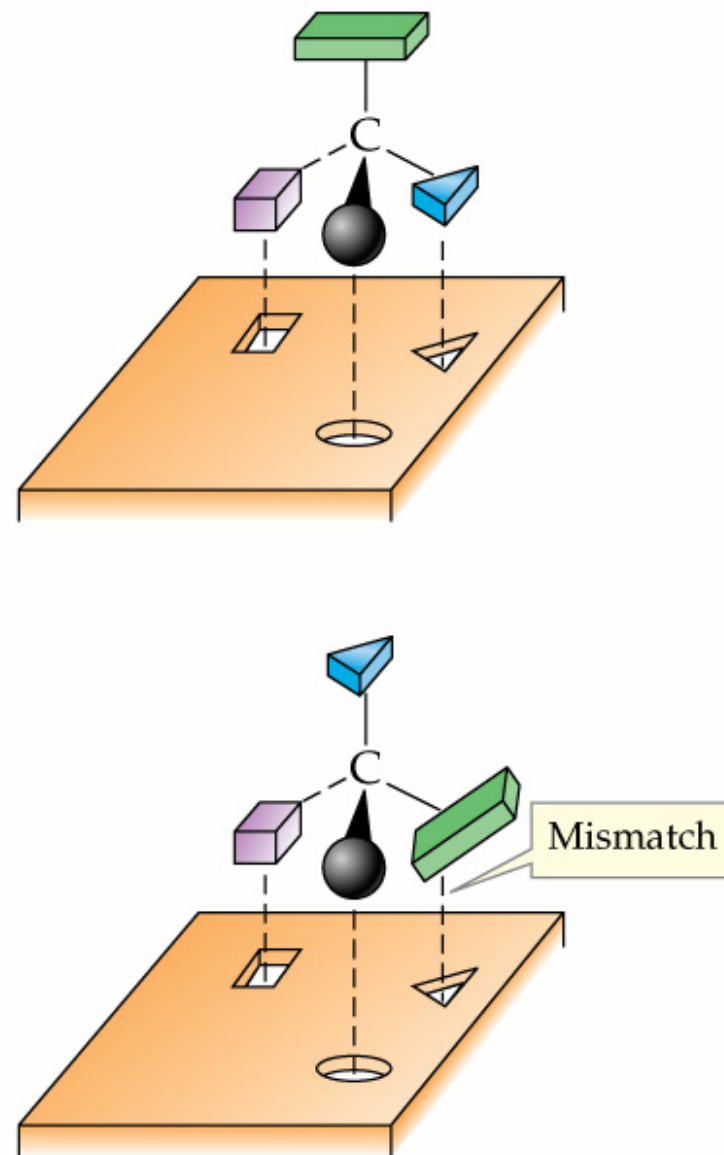
- Enzymes activity is limited to a certain substrate and a certain type of reaction, is referred as the ***specificity*** of the enzyme.
- Enzymes differs greatly in their specificity. Catalase, for example, is almost completely specific for one reaction – decomposition of hydrogen peroxide, a necessary reaction that destroys hydrogen peroxide before it damages biomolecules by oxidizing them.



- Enzymes are specific with respect to stereochemistry – catalyze reaction of only one of the pair of enantiomers. For example, the enzyme lactate dehydrogenase catalyzes the removal of hydrogen from L-lactate but not from D-lactate.



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.



19.2 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.



- 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.



19.3 Enzyme Classification

- Enzymes are divided into **six** main classes according to the general kind of reaction they catalyze, and each class is further subdivided.
- *Oxidoreductases*: Catalyze oxidation-reduction reactions, most commonly addition or removal of oxygen or hydrogen.
- *Transferases*: Catalyze transfer of a group from one molecule to another.



- *Hydrolases*: Catalyze the hydrolysis of substrate – the breaking of bond with addition of water.
- *Isomerases*: Catalyze the isomerization (rearrangement of atoms) of a substrate in reactions that have one substrate and one product.
- *Lyases*: Catalyze the addition of a molecule such as H_2O , CO_2 , or NH_3 to a double bond or reverse reaction in which a molecule is eliminated to create a double bond.
- *Lygases* Catalyze the bonding of two substrate molecules.

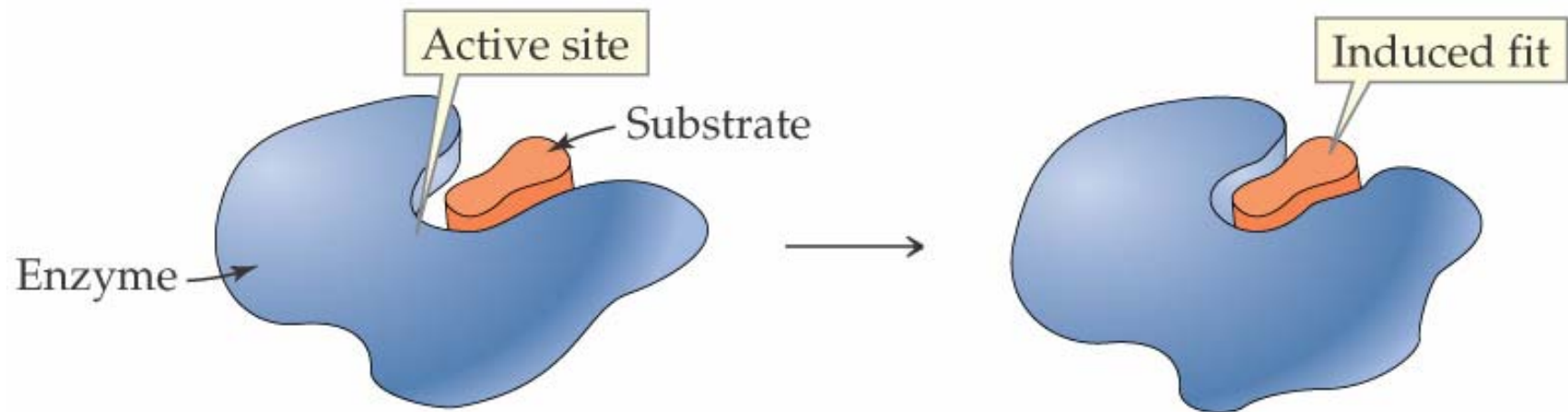


19.4 How Enzyme Work

- 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.



- In enzyme catalyzed reactions, substrates are drawn into the active site to form enzyme-substrate complex. Within the enzyme-substrate complex, the enzyme promoted reactions takes place.
- Once the chemical reaction is over, enzyme separates from the substrate and restores its original conditions, becomes available for another reaction.



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.



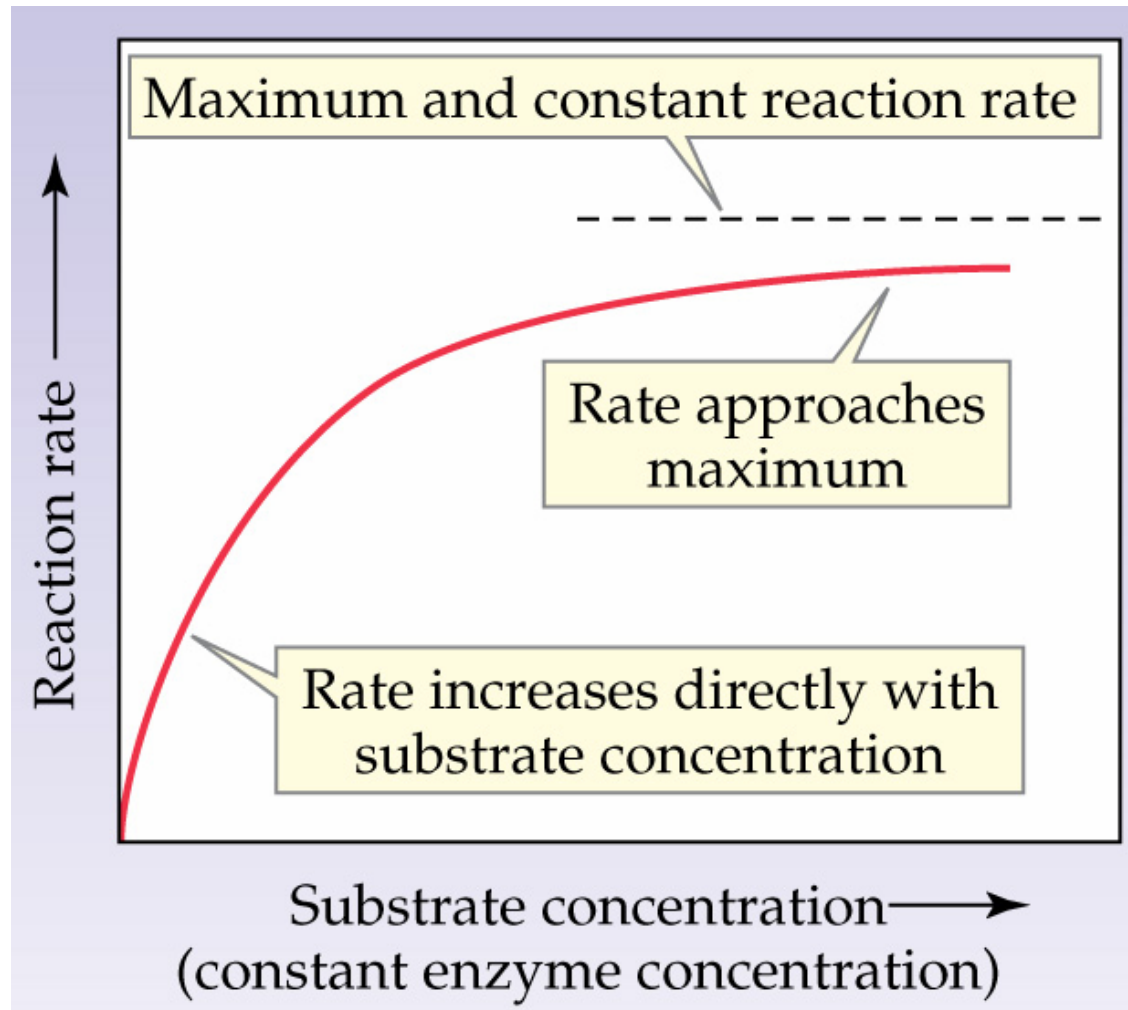
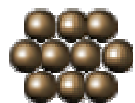
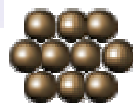
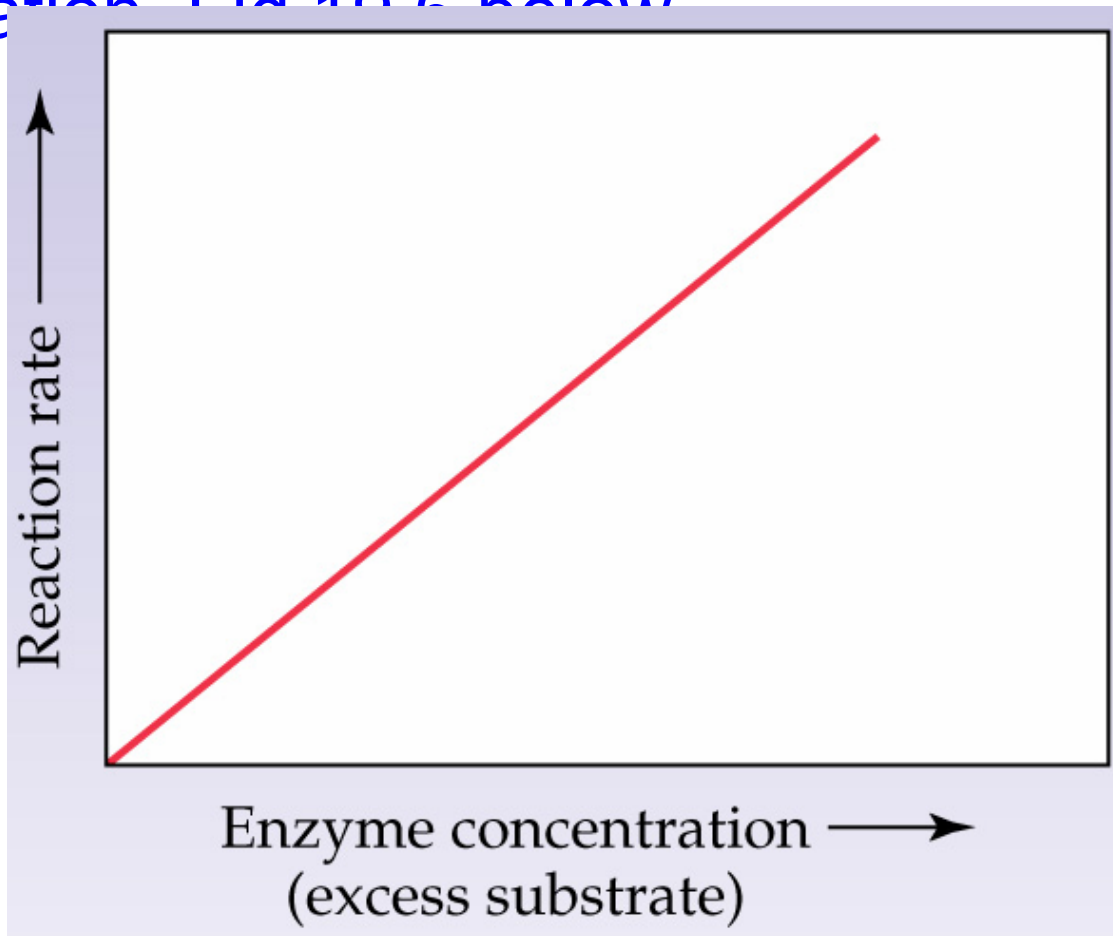


Fig 19.5 Change of reaction rate with substrate concentration when enzyme concentration is constant.



- *Enzyme concentration:* The reaction rate varies directly with the enzyme concentration as long as the substrate concentration does not become a limitation. Fig 10.6 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.



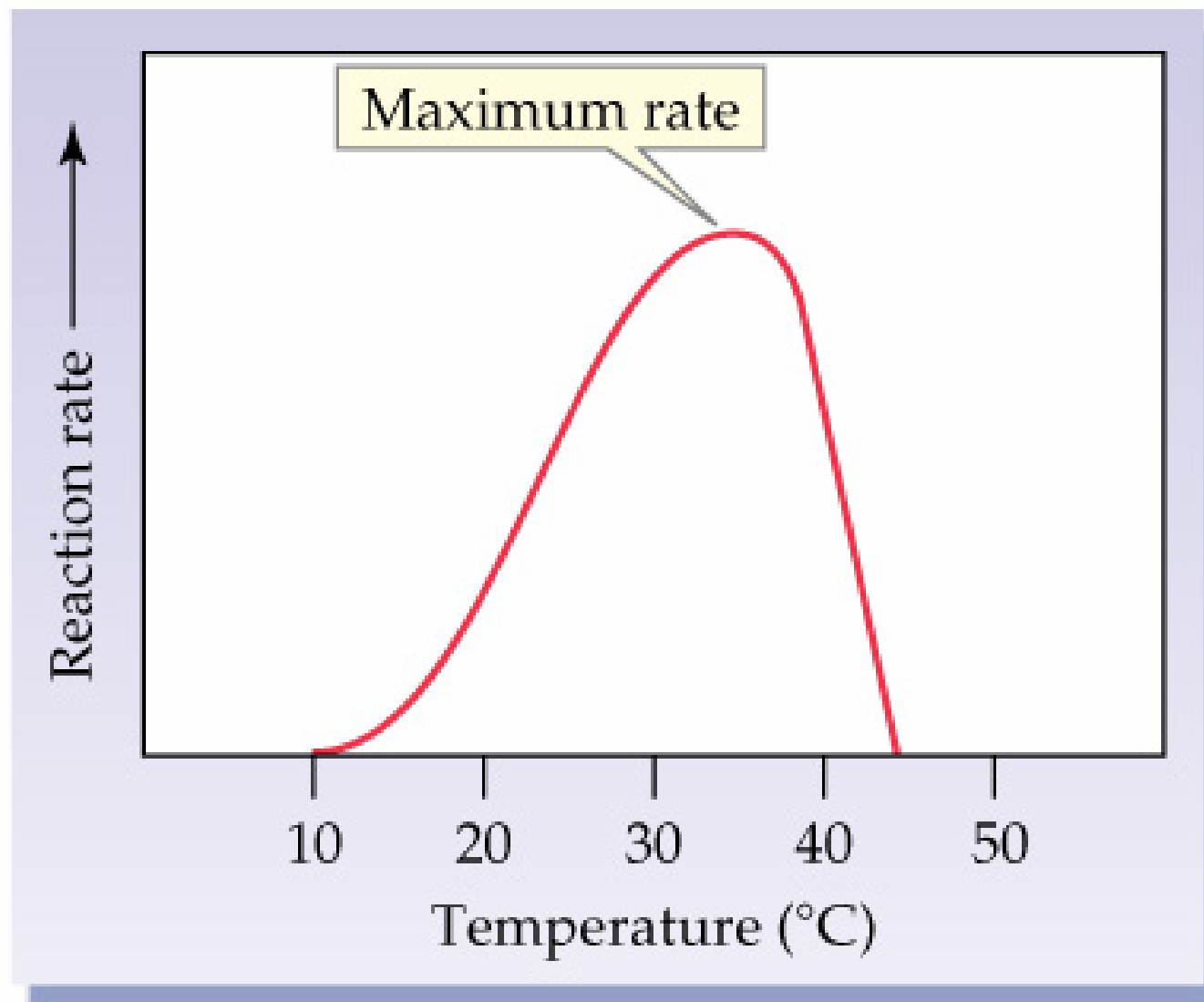
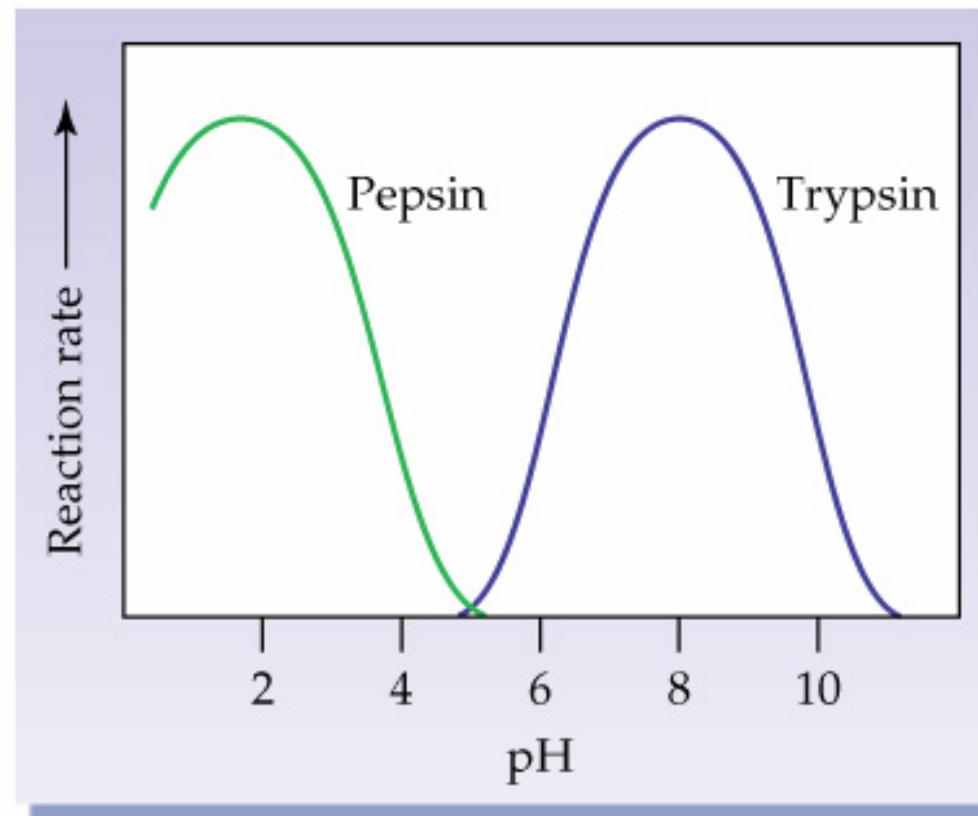


Fig 19.7 (a) Effect of temperature on reaction rate



- 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 mechanisms that control the enzyme's activity are:

- **Feedback control:** Regulation of an enzyme's activity by the product of a reaction later in a pathway.

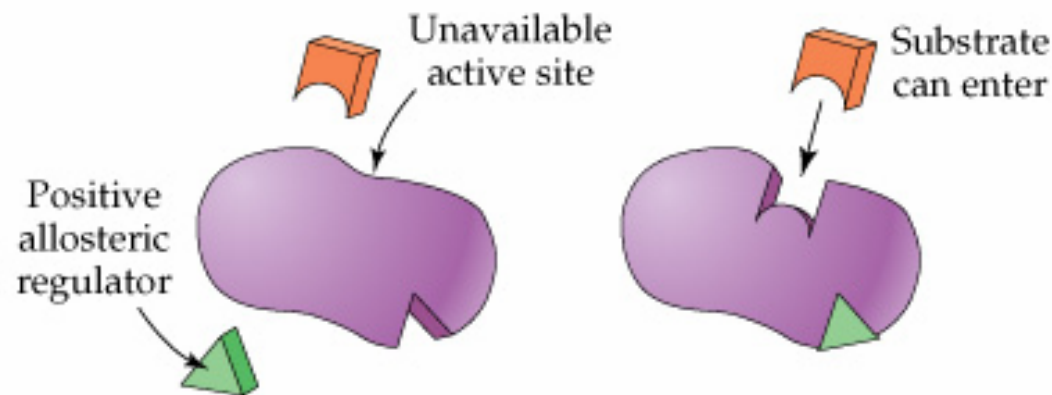
- **Allosteric control:** Activity of an enzyme is controlled by the binding of an activator or inhibitor at a location other than the active site. Allosteric controls are further classified as positive or negative.

- - 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

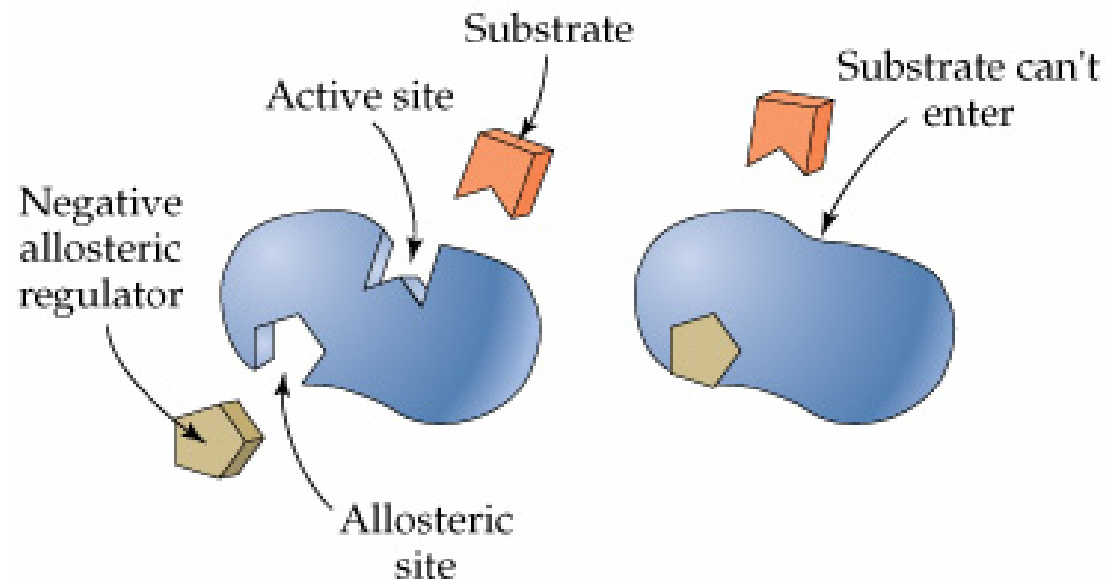


Positive allosteric control



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.



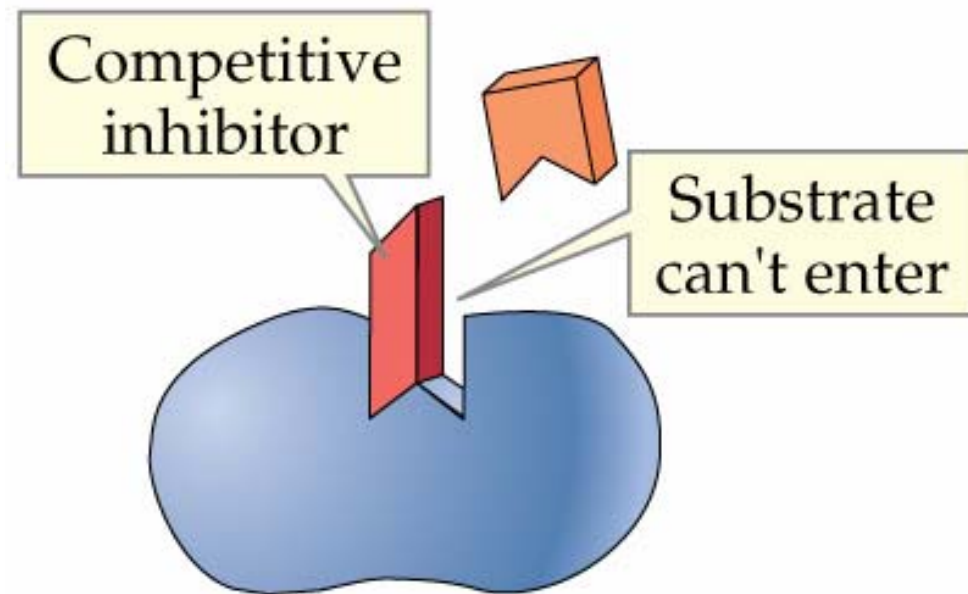
19.8 Enzyme Regulation: Inhibition

- 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.



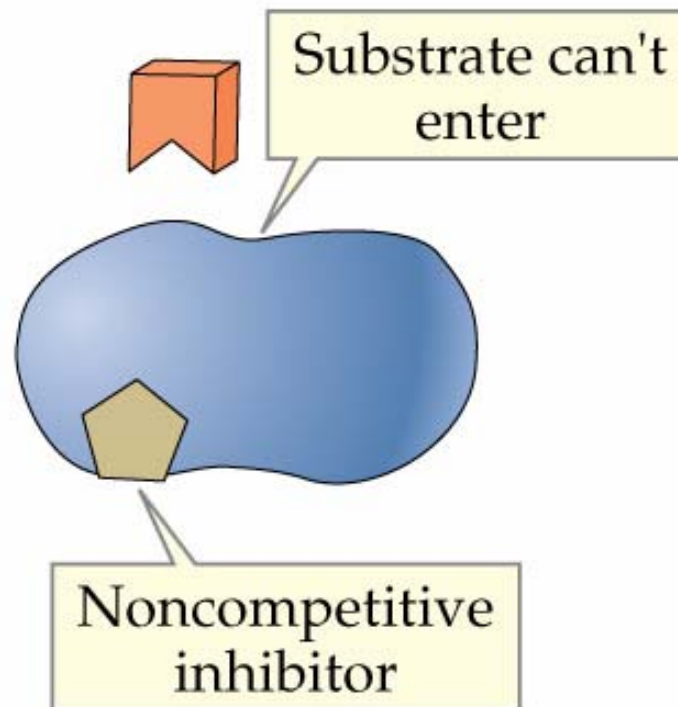
- Inhibitions are further classified as:
- *Competitive inhibition* if the inhibitor binds to the active site.

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.

