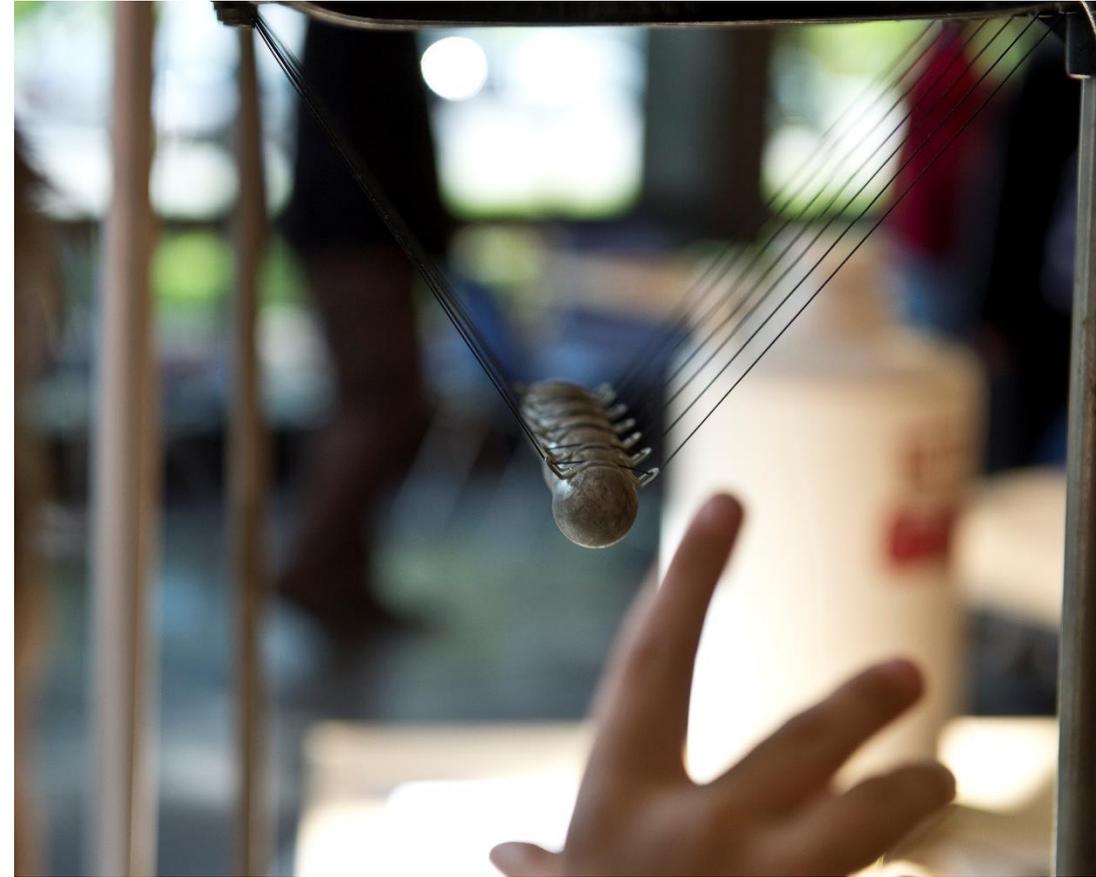


BIOLOGICAL PHYSICS

CHAPTER 3 –AMINO ACIDS

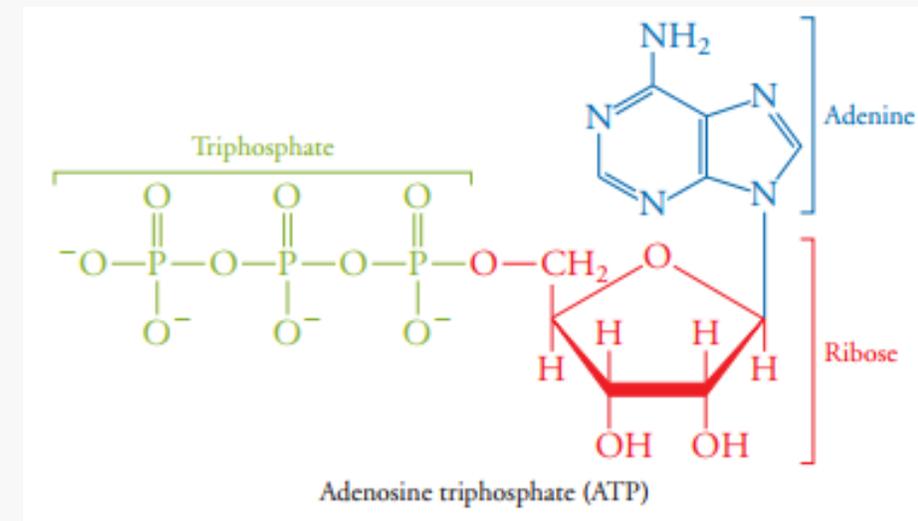
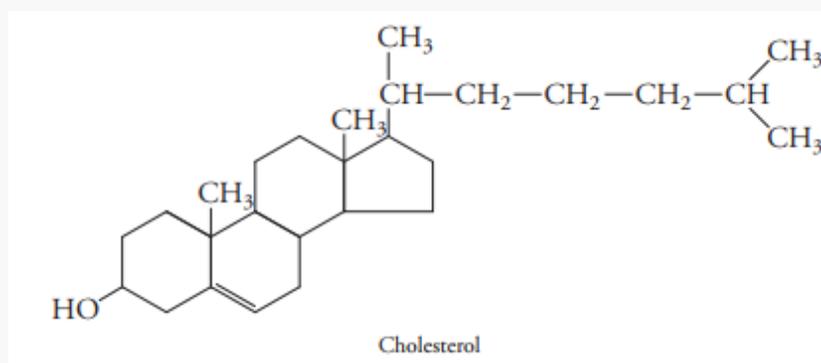
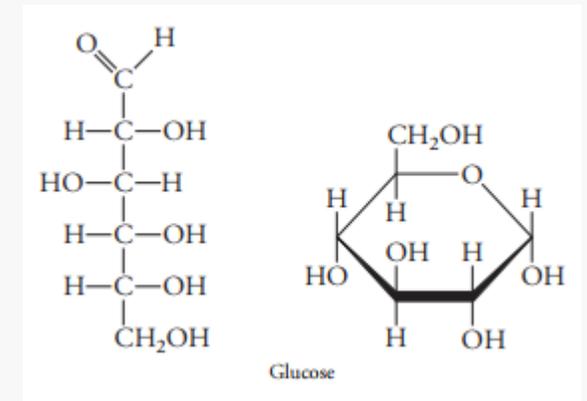
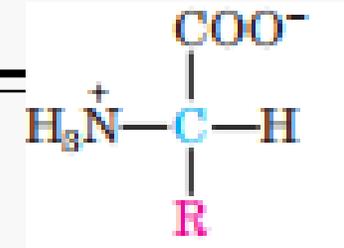
Poopalasingam Sivakumar
Department of Physics, SIUC



Smaller Biomolecules

Most of the smaller biomolecules can be divided into four classes, note each class contains numbers members:

- **Amino acids:** Building blocks of proteins, Contain amino ($-NH_2$) and a carboxylic acid ($-COOH$) groups.
- **Carbohydrate,** Energy sources and structural components. Monosaccharides (e.g., glucose) have the formula.
- **Nucleotides:** Components of nucleic acids (DNA, RNA). Composed of a sugar, nitrogenous base, and phosphate group(s). Example: ATP (energy carrier).
- **Lipids:** poorly soluble in water, e.g., cholesterol.

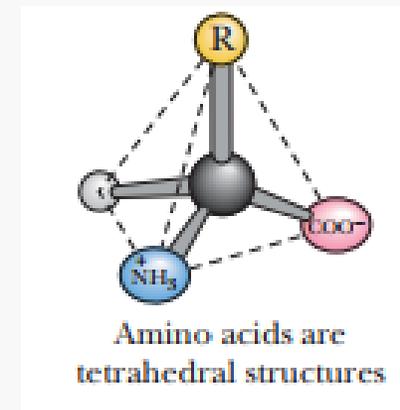
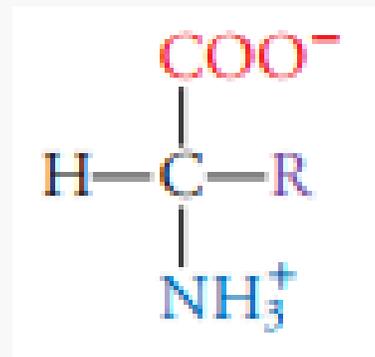
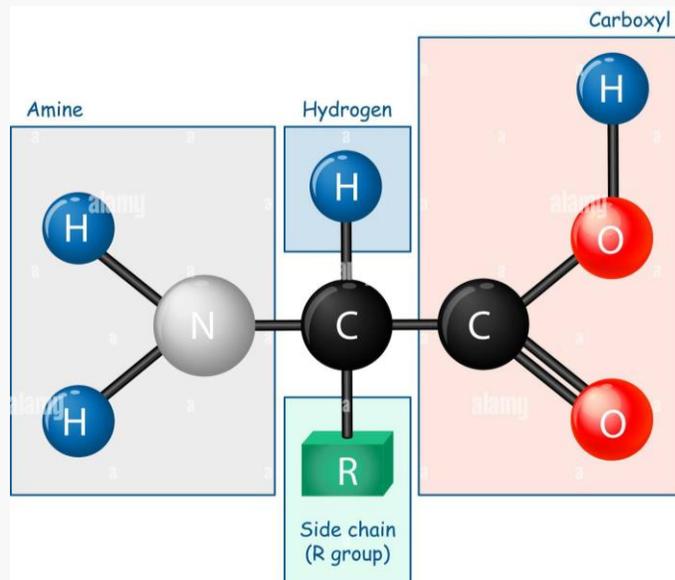


The 20 Building Blocks of Life: Amino Acids

- Proteins are vital for biological function, with Amino Acids serving as the fundamental build blocks.
- Polypeptides: Linear chains of amino acids.
- **20 Standard Amino Acids:** The common set of amino acids found in proteins.
- **Vast Protein Diversity:** The 20 amino acids can be combined in countless ways to create a huge variety of proteins.

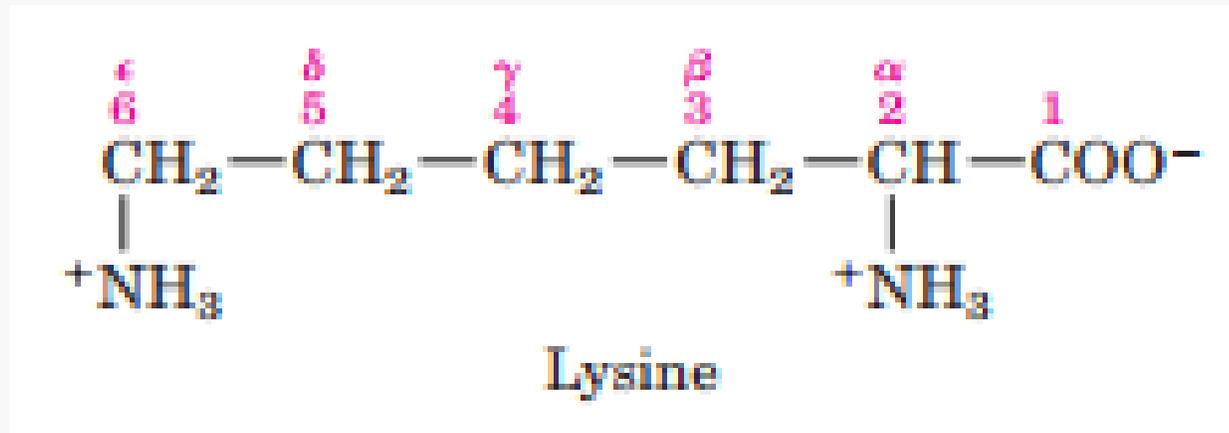
Amino Acids

- Amino acids, the fundamental units of proteins, have a central structure with a tetrahedral alpha carbon (C_α).
- The C_α is covalently linked to both an amino group ($-NH_2$) and a carboxylic acid group ($-COOH$).
- The side-chain, or R group, is a varying substituent bound to C_α and may contain elements like N, O, or S.



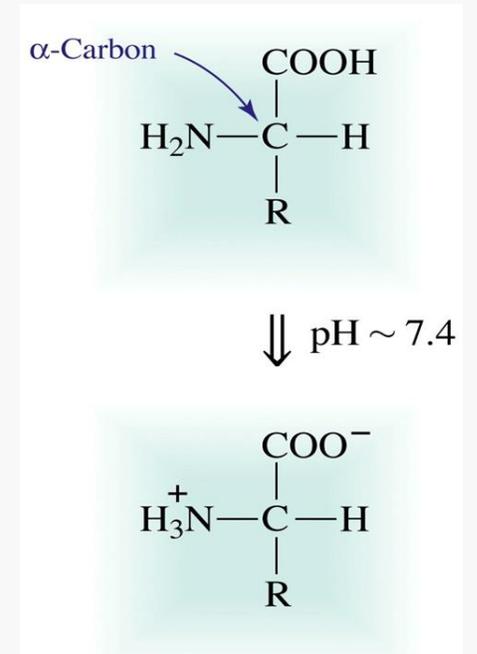
Nomenclature of Carboxylic Acids

- Traditional (Common) Names: Carbons near the carboxyl group (-COOH) are designated using Greek letters: α (alpha), β (beta), γ (gamma), δ (delta), ϵ (epsilon), ζ (zeta), η (eta), and so on.
- IUPAC/IUBMB (Systematic) Names: The carboxyl carbon is numbered 1, and subsequent carbons in the chain are numbered sequentially..



Amino Acids Ionization & Zwitterions

- At physiological pH (approximately 7.4), amino acids don't exist as neutral uncharged molecules. Instead, they form zwitterions:
 - Amino group ($-\text{NH}_2$) is protonated ($-\text{NH}_3^+$) due to its $\text{pK}_a \sim 9$.
 - Carboxyl group ($-\text{COOH}$) is deprotonated ($-\text{COO}^-$) due to its $\text{pK}_a < 3$.
- Zwitterion Formation: At physiological pH (6.8-7.4), amino acids exist predominantly as zwitterions.
 - Dual Charge: Zwitterions possess both a positive ($-\text{NH}_3^+$) and a negative ($-\text{COO}^-$) charge within the same molecule.
 - Net Charge: Despite the presence of these charges, a zwitterion has an overall net charge of zero.
 - Dipolar Ions: Zwitterions are also sometimes referred to as dipolar ions due to this separation of charge. (word "Zwitter" is German for "hybrid" or "between.")



Common Names of Amino Acids

Alanine: probably from aldehyde + “an” (for convenience) + amine (1849)

Arginine: crystallizes as a silver salt, from Latin *argentum* (silver) (1886)

Asparagine: first isolated from asparagus (1813)

Aspartate: similar to asparagine (1836)

Glutamate: first identified in the plant protein gluten (1866)

Glutamine: similar to glutamate (1866)

Glycine: from the Greek *glykys* (sweet), tastes sweet (1848)

Cysteine: from the Greek *kystis* (bladder), discovered in bladder stones (1882)

Histidine: first isolated from sturgeon sperm, named for the Greek *histidin* (tissue) (1896)

Isoleucine: isomer of leucine

Leucine: from the Greek *leukos* (white), forms white crystals (1820)

Lysine: product of protein hydrolysis, from the Greek *lysis* (loosening) (1891)

Methionine: side chain is a sulfur (Greek *theion*) atom with a methyl group (1928)

Phenylalanine: alanine with a phenyl group (1883)

Proline: a corrupted form of “pyrrolidine” because it forms a pyrrolidine ring (1904)

Serine: from the Latin *sericum* (silk), serine is common in silk (1865)

Threonine: similar to the four-carbon sugar threose (1936)

Tryptophan: isolated from a tryptic digest of protein 1 Greek *phanein* (to appear) (1890)

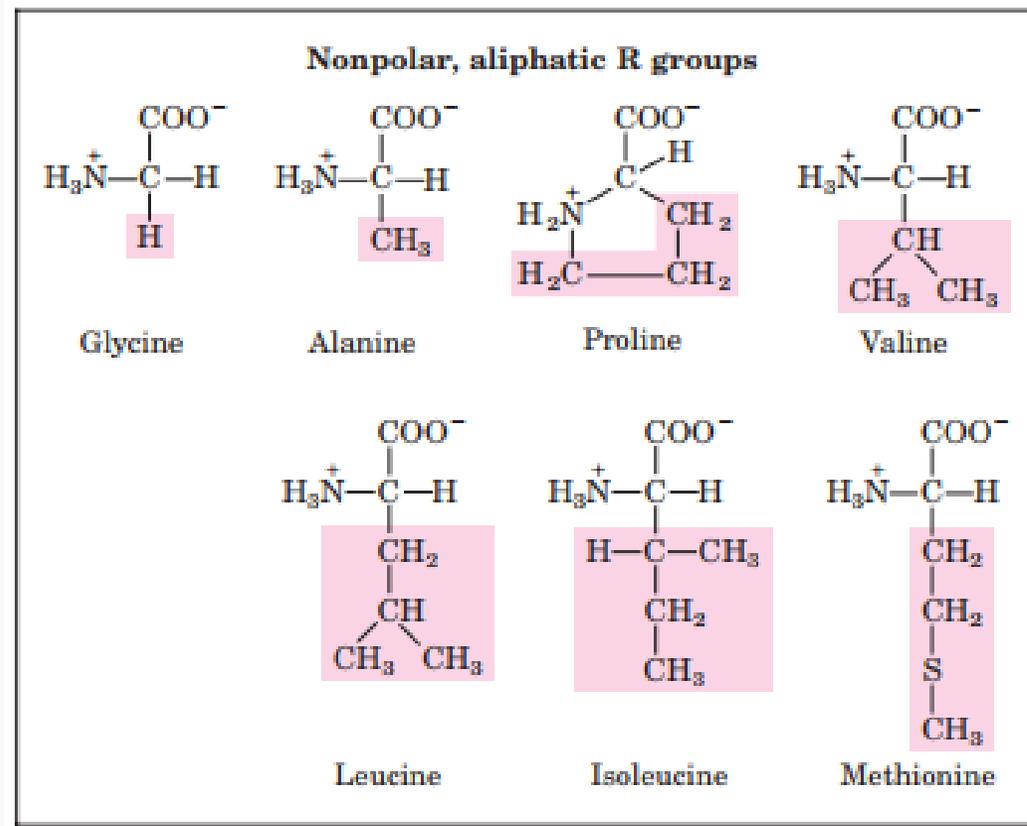
Tyrosine: found in cheese, from the Greek *tyros* (cheese) (1890)

Valine: derivative of valeric acid from the plant genus *Valeriana* (1906)

Sources: *Oxford English Dictionary* 2nd ed., and Leung, S.H. (2000) Amino acids, aromatic compounds, and carboxylic acids: how did they get their common names? *J. Chem. Educ.* 77: 48–49.

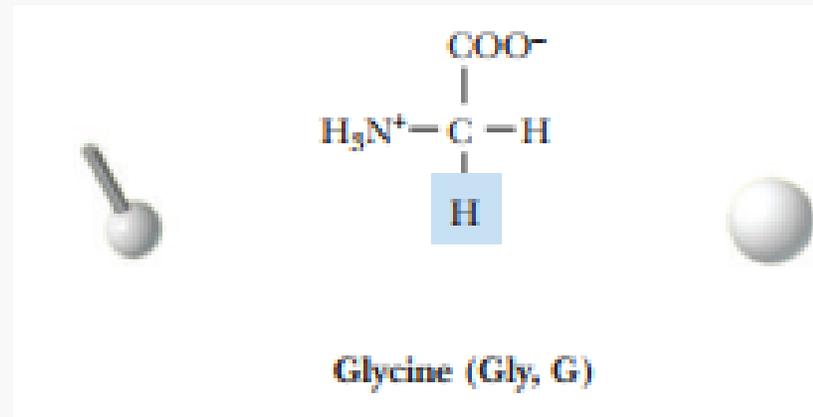
Nonpolar, Aliphatic R groups

- The R groups in this class of amino acids are nonpolar (hydrophobic) *aliphatic* hydrocarbon groups. In organic chemistry, *aliphatic* term refers to the absence of a benzene ring or related structure.



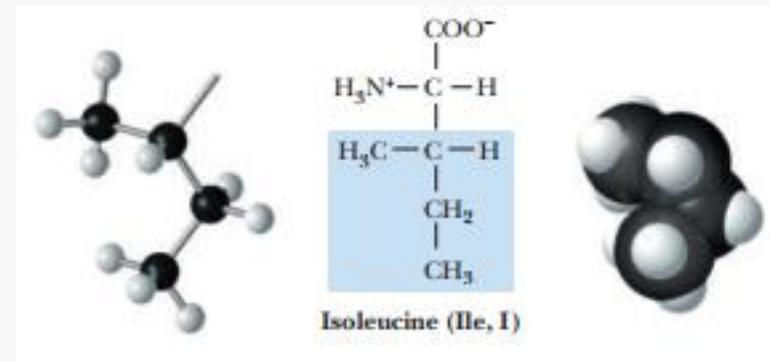
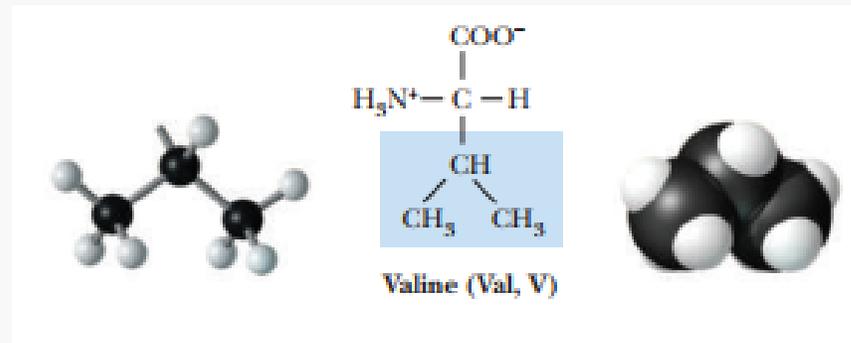
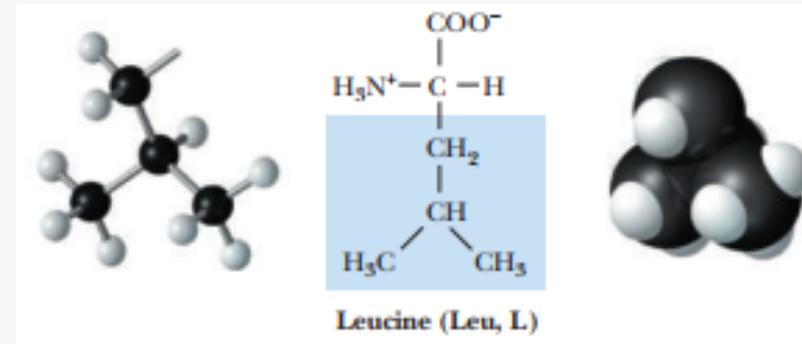
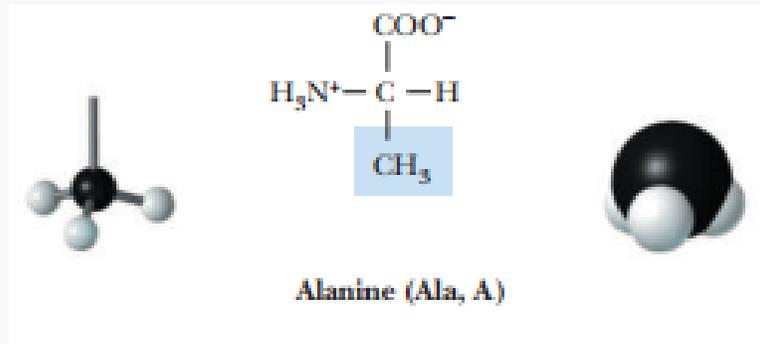
Nonpolar, Aliphatic R groups

- **Glycine (Gly, G)** is the smallest amino acid with simple structure.
- It is the only achiral (*can superpose on its mirror image by any combination of rotations, translation, and some conformational changes*) amino acid, as its R group consists of H atoms.
- Due to its two hydrogen atoms, Glycine makes minimal (or no) contribution to hydrophobic interactions.
- Glycine plays a distinctive role in protein structures because its small side chain can fit into niches that cannot accommodate any other amino acid.



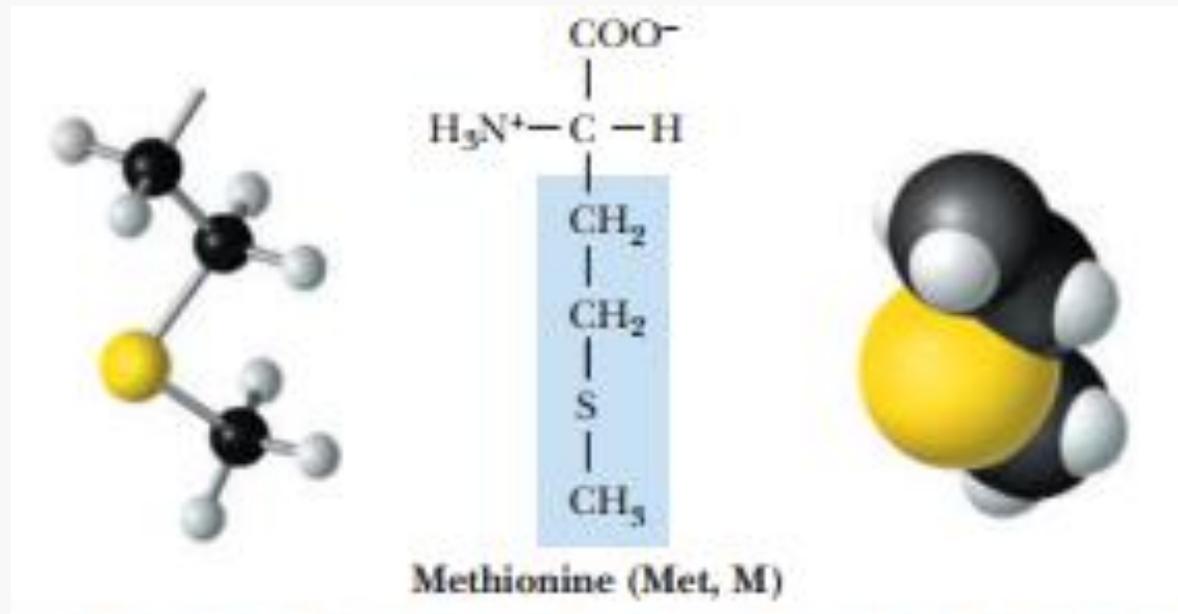
Nonpolar, Aliphatic R groups

- Four amino acids--**Alanine (Ala, A)**, **Valine (Val, V)**, **Leucine (Leu, L)**, and **Isoleucine**--have saturated aliphatic side chain.
- These amino acids plays an important role in establishing and maintaining the 3D structure of proteins because their side chains tend to cluster within proteins, away from water.



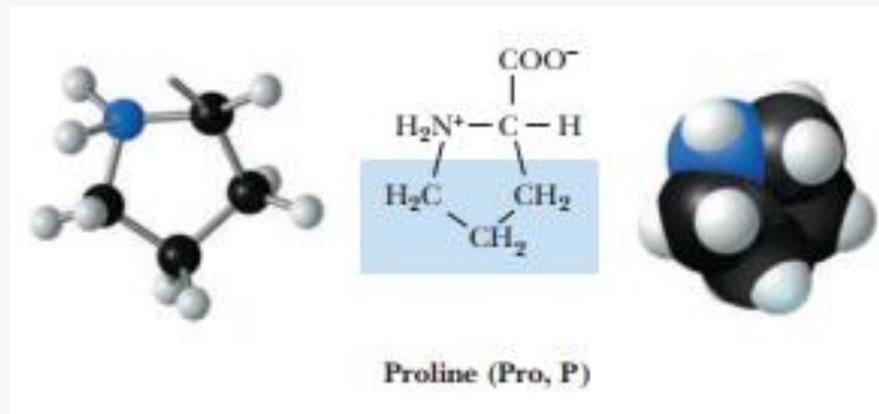
Nonpolar, Aliphatic R groups

- **Methionine (Met, M)**, one of the two sulfur-containing amino acids, has a non-polar thioether group in its side chain. This makes it one of the more hydrophobic amino acids.
- It plays a special role in protein synthesis because it is almost always the 1st amino acid in a growing polypeptide chain.



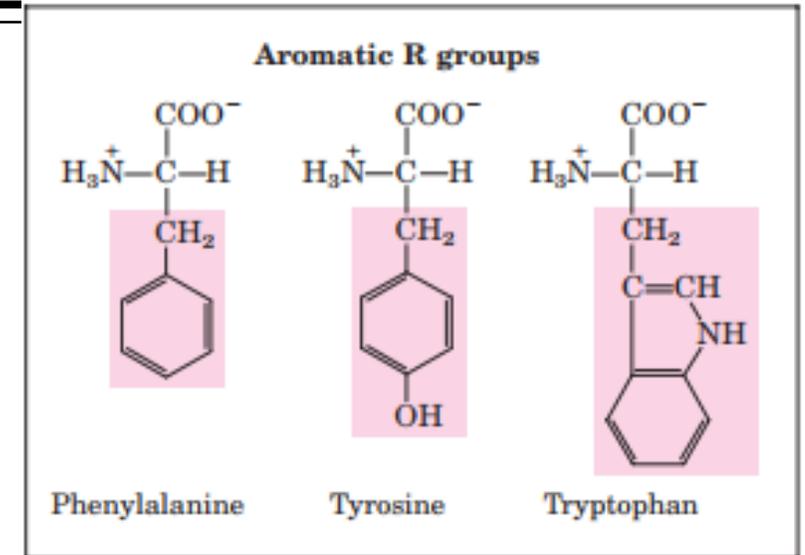
Nonpolar, Aliphatic R groups

- **Proline (Pro, P)** stands out from the other 19 amino acids because its three-carbon side chain is bonded to the nitrogen of its C_α creating a cyclic molecule.
- As a result, proline contains a secondary amino group rather than a primary one. Group of proline residues is held in a rigid conformation that reduces the structural flexibility of polypeptide regions containing proline.
- The heterocyclic pyrrolidine ring of proline restricts the geometry of polypeptides, occasionally leading to abrupt changes in the direction of the peptide chain.
- The cyclic structure of proline makes it much less hydrophobic compared to valine, leucine, and isoleucine.



Amino Acids: Aromatic R Groups

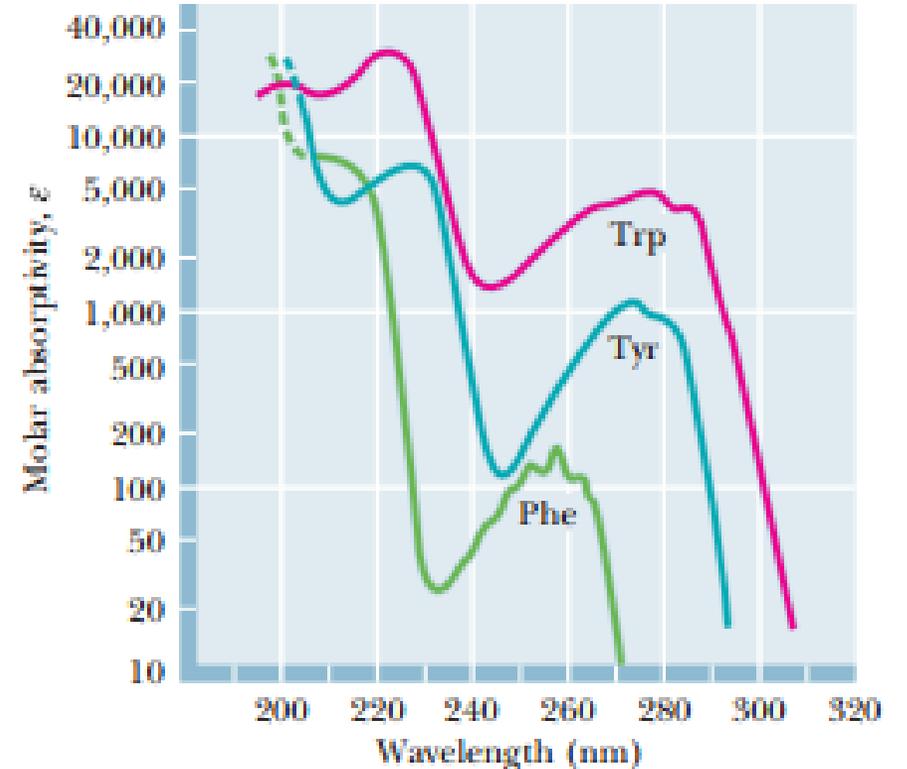
Aromatic R Groups: Phenylalanine (**Phe**, **F**), tyrosine (**Tyr**, **Y**), and tryptophan (**Trp**, **W**), with their aromatic side chains, are *relatively nonpolar (hydrophobic)*. The hydroxyl group of tyrosine can form hydrogen bonds, and it is an important functional group in some enzymes. **Tyr** and **Trp** are significantly more polar than **Phe**. **Tyr** interact with water hydroxyl group and **Trp** via the N-H moiety of the indole ring.



Amino Acids: Aromatic R Groups

Aromatic R Groups: These three amino acids absorb UV light, unlike saturated aliphatic amino acids due to delocalize π -electrons.

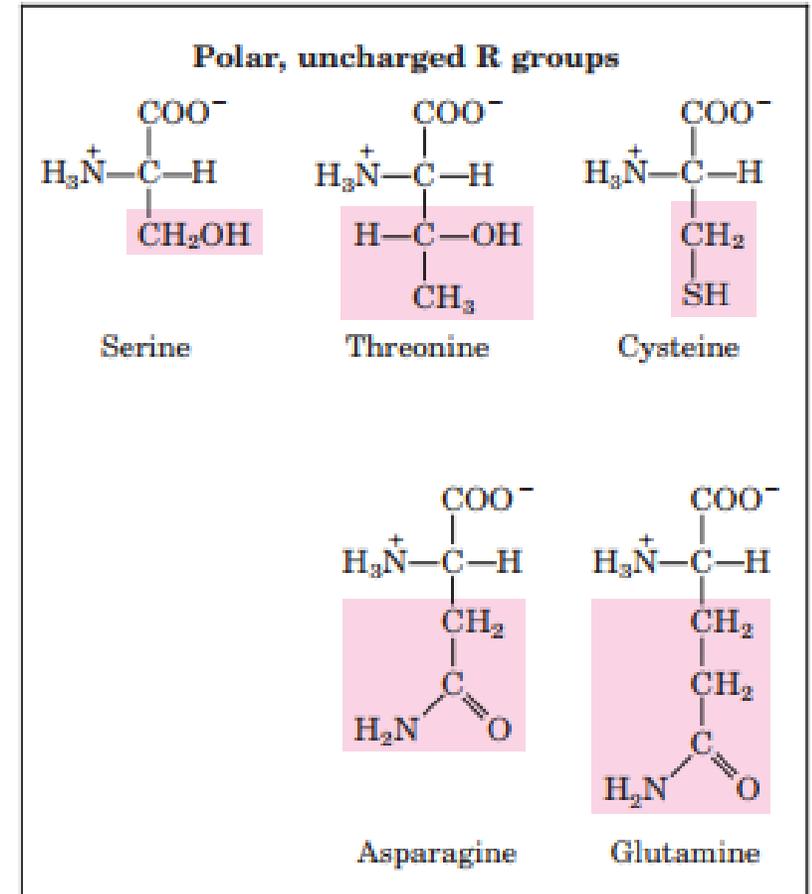
Trp and Tyr at PH 7 absorb UV light at 280 nm, but not **Phe** (almost transparent), **Phe** absorb at 260 nm. Strong absorption of light by most proteins at 280 nm, characteristic of proteins.



Amino Acids: Polar, Uncharged R groups

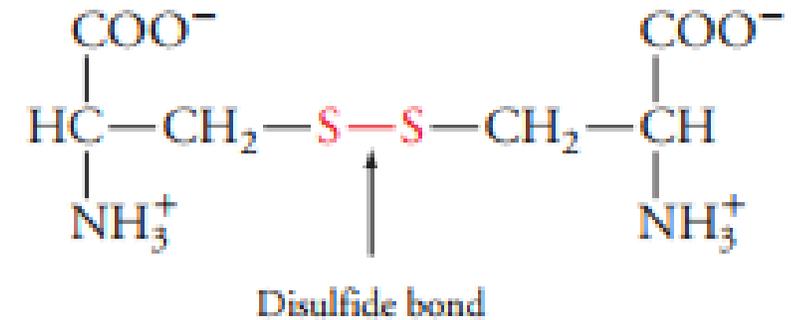
Serine (**Ser, S**), threonine (**Thr, T**), cysteine (**Cys, C**), asparagine (**Asn, N**), and glutamine (**Gln, Q**) acids are more soluble in water than the nonpolar amino acids, because they contain functional group that form hbonds with water.

Asn and Gln are the amides of two other amino acids also found in proteins, aspartate and glutamate, respectively, to which **Asn** and **Gln** are easily hydrolyzed by acid or base.



Amino Acids: Polar, Uncharged R groups

- Cysteine (**Cys**, **C**) is readily oxidized (deprotonated), yielding a thiolate anion.
- Cysteine's thiol group can undergo oxidation with another thiol group, such as another **Cys** side chain, to form a disulfide bond which is dimeric amino acid called **cystine**. Disulfide-linked residues are strongly hydrophobic.
- **Cys** plays special role in the structures of many proteins by forming covalent links between parts of a protein molecule or between two different polypeptide chains.



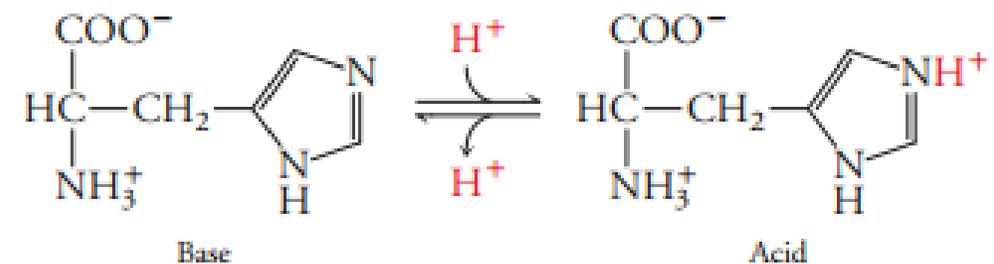
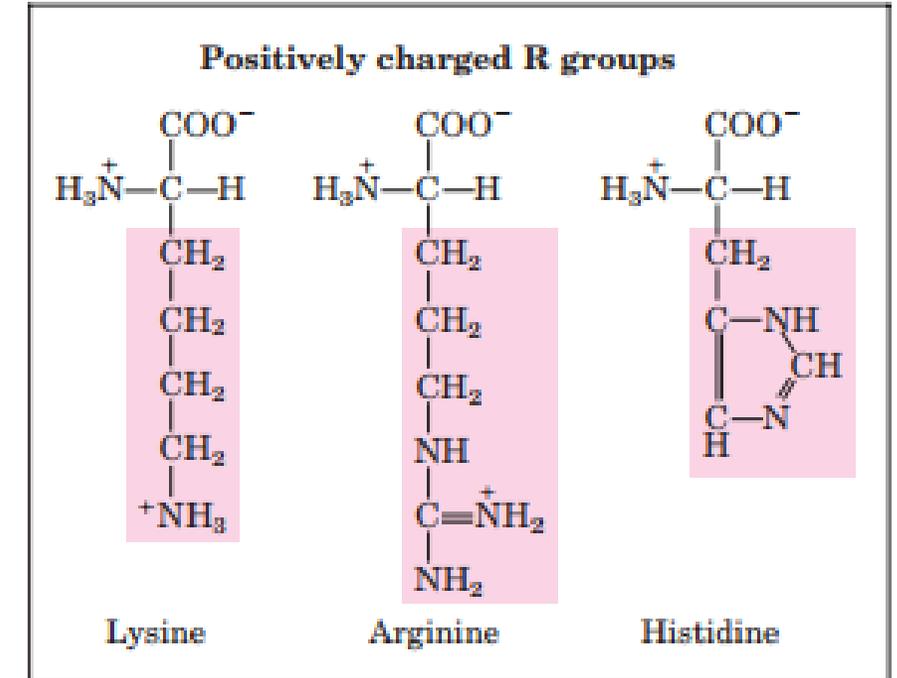
Oxidation of two molecules of **Cys**. Disulfide bonds between **Cys** residues stabilize the structures of many proteins.

Amino Acids: Positively Charged R groups

Lysine (**Lys, K**), Arginine (**Arg, R**), Histidine (**His, H**) have hydrophilic side chains that are nitrogen bases. The side chains can be positively charged (protonate under all condition normally) at physiological pH.

Lys's R group is significant positive charge at pH 7.0 due to secondary amino group at aliphatic chain. **Arg** has a positively charged guanidino group

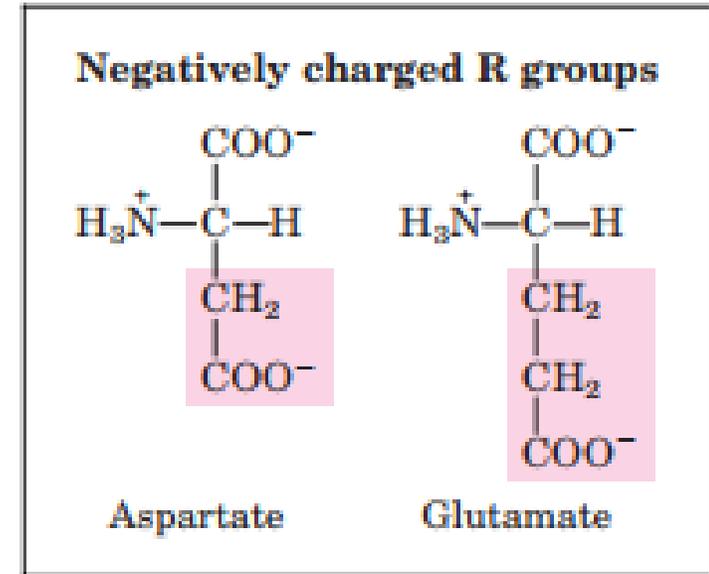
His is having an ionizable side chain. At pH 7 most **His** are neutral (base form). It becomes more common at slightly lower pH. In many enzyme-catalyzed reactions, His residue facilitates the reaction by serving as proton donor/acceptor. For example, **His** can accept a proton to form an imidazolium ion (an acid).



Amino Acids: Negatively Charged R groups

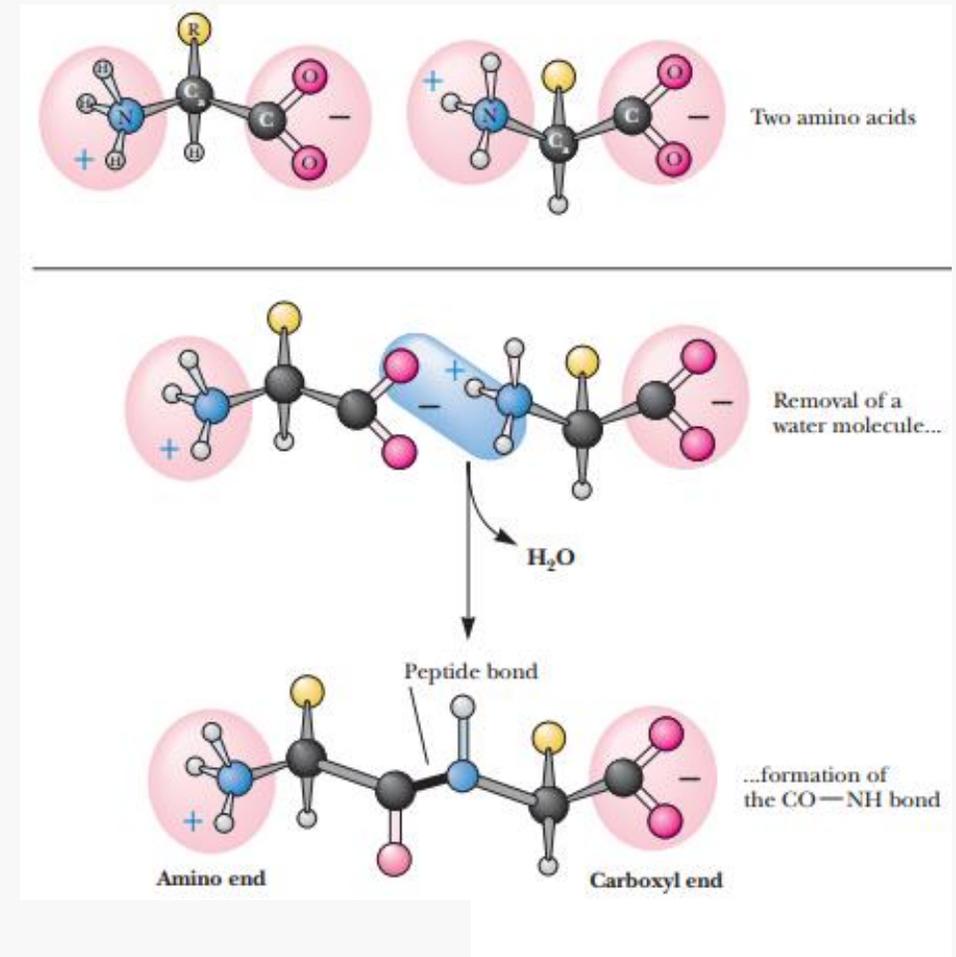
Aspartate (**Asp, D**) and glutamate (**Glu, E**), side chain with carboxyl (acidic, COO^-), acids hydrophilic R groups are negatively charged at pH 7.

These negatively charged amino acids play several important roles in proteins, specifically metal-binding sites containing one or more **Asp** and **Glu**



Peptide Bond Formation

Peptide Bond Formation: Two amino acids can react, eliminating a water molecule (H_2O), to form a covalent peptide bond (an amide bond).



20 Common Amino Acids

- Commonly found amino acids (20) in proteins can be classified based on the polarity of the side chain (R).
- Classification done into group based on their R groups polarity or tendency to interact with water at pH 7.0 (biological pH).
- Standard three-letter and one-letter codes used to represent the amino acids, facilitating the display and comparing of protein sequences.

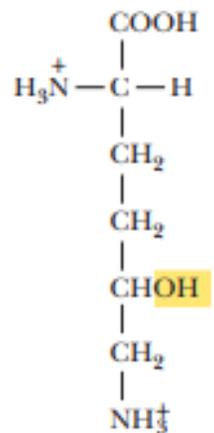
Names and Abbreviations of the Common Amino Acids

Amino Acid	Three-Letter Abbreviation	One-Letter Abbreviation
Alanine	Ala	A
Arginine	Arg	R
Asparagine	Asn	N
Aspartic acid	Asp	D
Cysteine	Cys	C
Glutamic acid	Glu	E
Glutamine	Gln	Q
Glycine	Gly	G
Histidine	His	H
Isoleucine	Ile	I
Leucine	Leu	L
Lysine	Lys	K
Methionine	Met	M
Phenylalanine	Phe	F
Proline	Pro	P
Serine	Ser	S
Threonine	Thr	T
Tryptophan	Trp	W
Tyrosine	Tyr	Y
Valine	Val	V

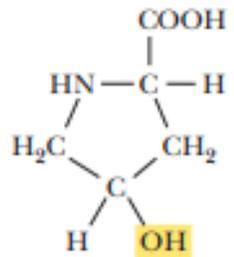
Uncommon Amino Acids: Rarely occurring

Here are uncommon amino acids found in proteins which are typically derivative of common amino acids, Extra functional group added by modification reactions (yellow or red). **Hydroxyproline** and **Hydroxylysine** are found mainly in the collagen and gelatin protein. **Pyroglutamic acid** found in a light-driven proton-pumping protein called bacteriorhodopsin. **γ -carboxyglutamic acid** found in calcium-binding proteins. Lysine derivative, **Pyrrolysine** found in several archaeal species, including *Methanosarcina barkeri*, micros of freshwater lakes. **Pyrrolysine** and **Selenocysteine** both are incorporated naturally into proteins via adapting RNA molecules. **Desmosine** is formed from four Lys residues.

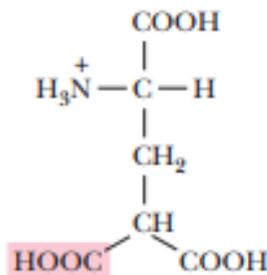
5-Hydroxylysine



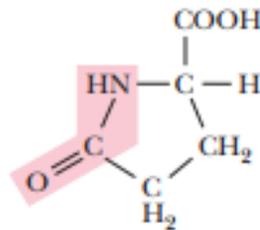
4-Hydroxyproline



γ -Carboxyglutamic acid

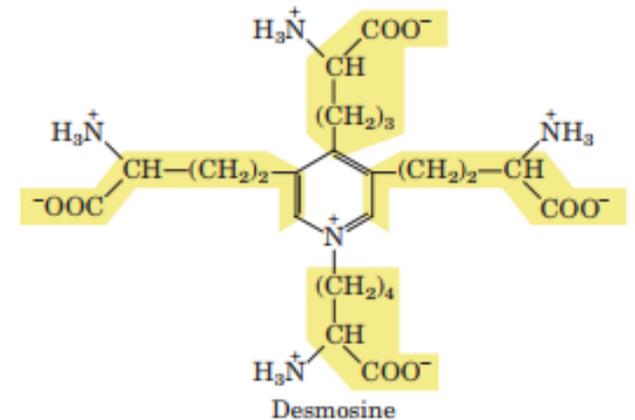
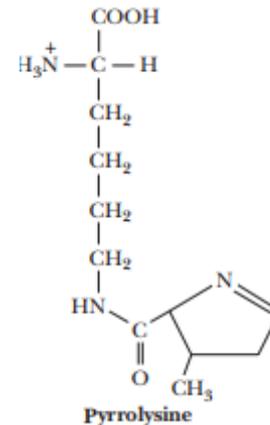


Pyroglutamic acid



$\text{HSe}-\text{CH}_2-\text{CH}-\text{COO}^-$

Selenocysteine

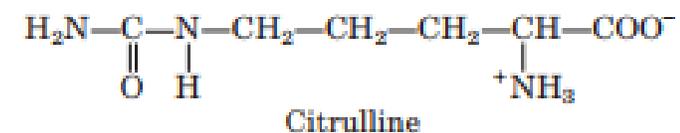
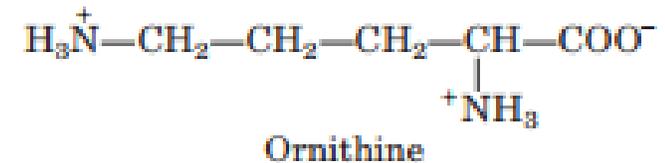
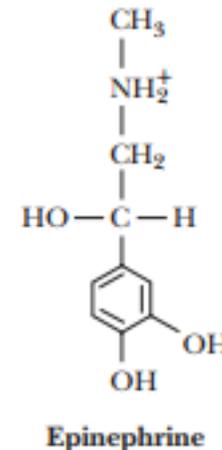
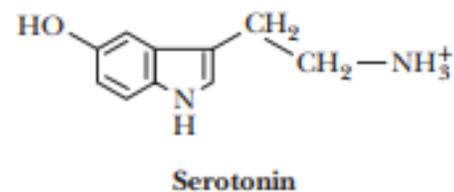
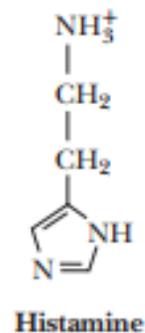
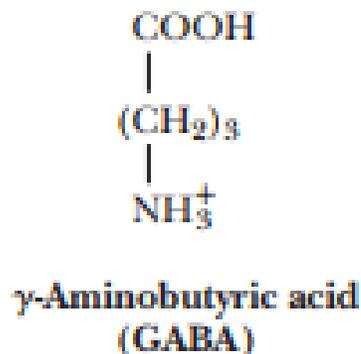


Uncommon Amino Acids: Rarely occurring

Certain amino acids and their derivatives, although not found in proteins, nonetheless are biochemically important. γ -**Aminogutyric acid** is produced by the decarboxylation of **glutamic acid** and is a potential neurotransmitter. **Histamine** (derived from synthesized by decarboxylation of **histidine**) and **Serotonin** (derived from **tryptophan**) are potential neurotransmitter and regulators.

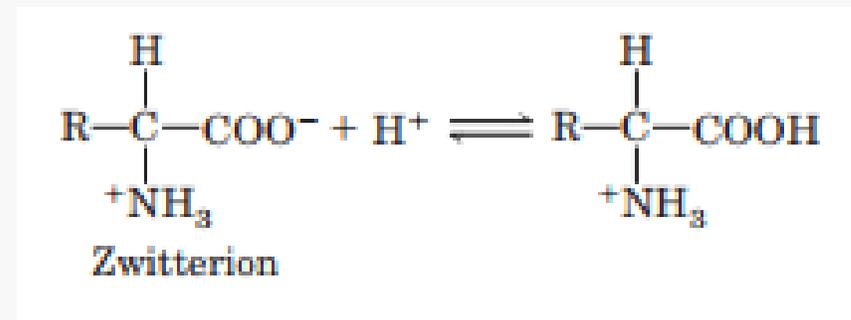
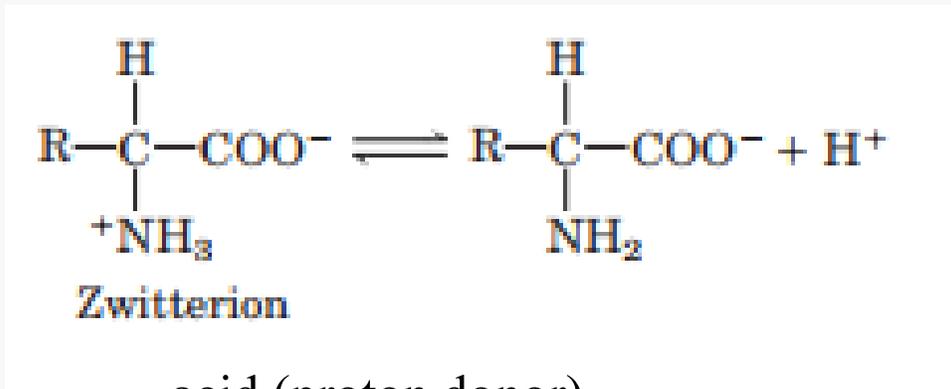
pinephrine (also known as **adrenaline**), derived from **tyrosine**, in an important hormone.

Ornithine and **citrulline** are not found in proteins and these are key intermediate (metabolites) in the biosynthesis of **arginine** and in the urea cycle. We will learn later.



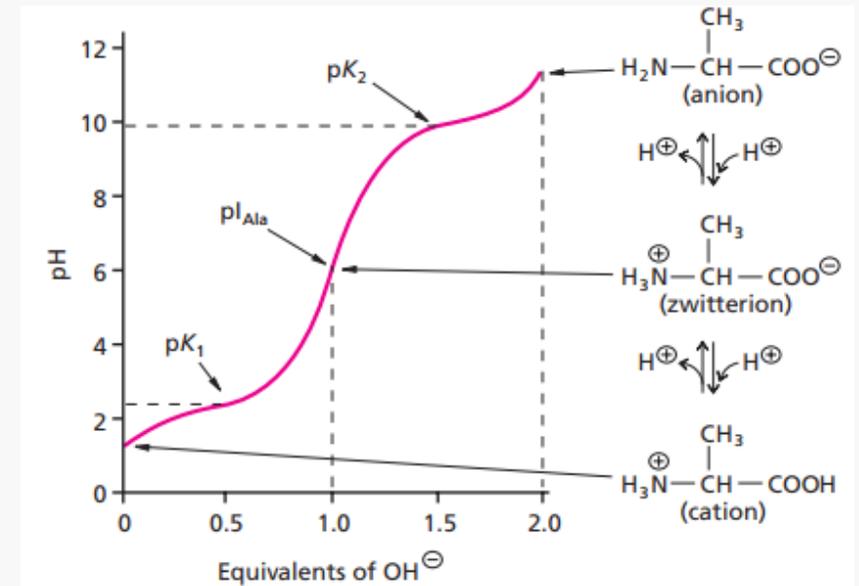
Acids-Bases Nature of Amino Acids

- Amino acids can function as both acids and bases.
- In water, they exist as dipolar ions known as zwitterions (from the German word for "hybrid ion").
- They can donate a proton (acting as an acid) or accept a proton (acting as a base).



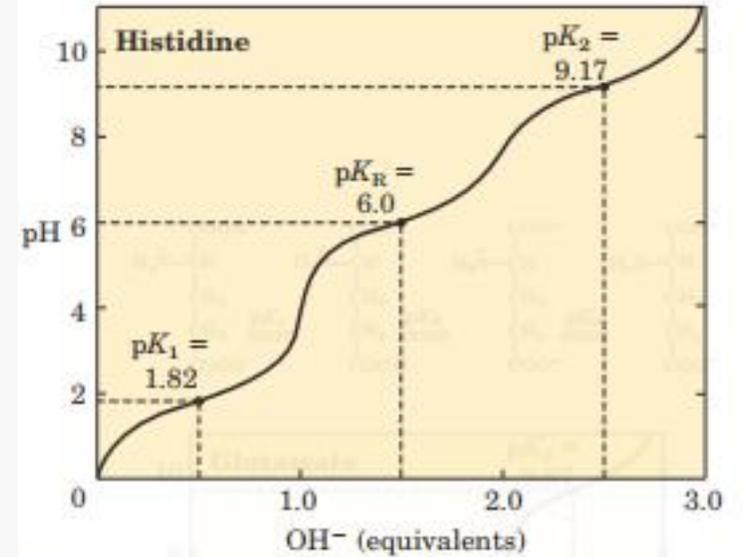
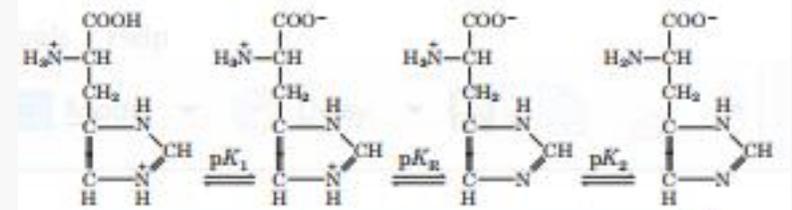
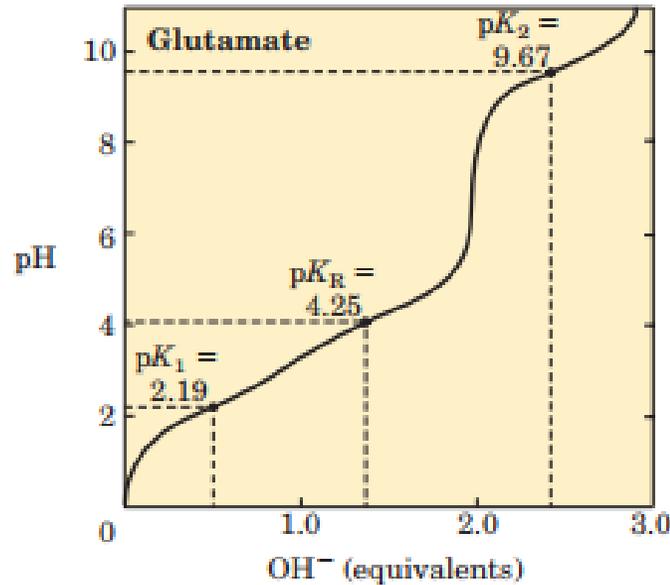
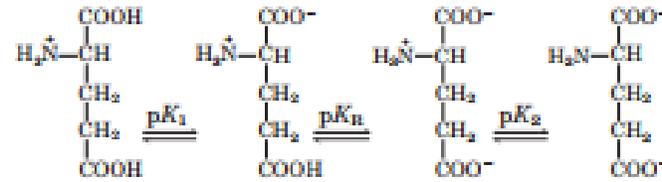
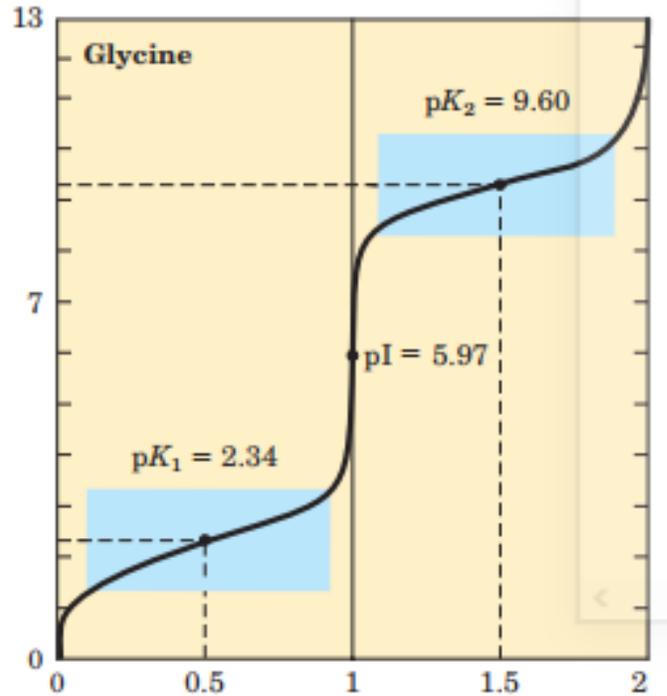
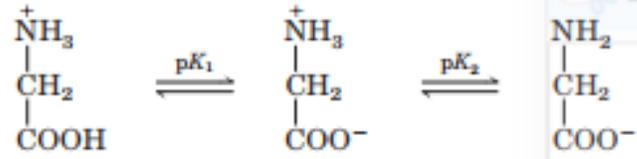
Importance of Ionic States of Amino Acids Side Chains

- **Protein Structure:** The charged state of amino acid side chains influences protein folding and overall three-dimensional structure (discussed later, Part II).
- **Enzyme Mechanisms:** Understanding the ionic properties of amino acids in enzyme active sites aids in comprehending enzyme mechanisms (discussed later, Part II).
- **Determining ionic States:** The pK_a values of amino acids are determined from titration curves (Figure).
- Example- Alanine (Ala) has two ionizable groups
 - α -carboxyl group with a $pK_a \approx 2.4$
 - protonated α -amino group with $pK_a \approx 9.9$



Titration curve of alanine. Two pK_a values one at 2.4 and another at 9.9

Amino Acids: Acids/Bases Nature



Acids/Bases Nature of Amino Acids and Isoelectric Point

- **Titration curves** Titration curves show how the ionization state of an amino acid changes as the pH changes. This allows us to predict the net electric charge of an amino acid at different pH values.
- **Isoelectric Point (pI)** (or isoelectric pH) is the pH at which an amino acid has **no net electric charge**. (i.e., the molecule exists primarily as a zwitterion).

At $\text{pH} = \text{pI}$, the amino acid has:

- no net electrical charge
- minimum solubility (often)
- no migration in an electric field

Amino acid	Abbreviation/ symbol	M_r	pK_a values			pI
			pK_1 ($-\text{COOH}$)	pK_2 ($-\text{NH}_3^+$)	pK_R (R group)	
Nonpolar, aliphatic						
R groups						
Glycine	Gly G	75	2.34	9.60		5.97
Alanine	Ala A	89	2.34	9.69		6.01
Proline	Pro P	115	1.99	10.96		6.48
Valine	Val V	117	2.32	9.62		5.97
Leucine	Leu L	131	2.36	9.60		5.98
Isoleucine	Ile I	131	2.36	9.68		6.02
Methionine	Met M	149	2.28	9.21		5.74
Aromatic R groups						
Phenylalanine	Phe F	165	1.83	9.13		5.48
Tyrosine	Tyr Y	181	2.20	9.11	10.07	5.66
Tryptophan	Trp W	204	2.38	9.39		5.89
Polar, uncharged						
R groups						
Serine	Ser S	105	2.21	9.15		5.68
Threonine	Thr T	119	2.11	9.62		5.87
Cysteine	Cys C	121	1.96	10.28	8.18	5.07
Asparagine	Asn N	132	2.02	8.80		5.41
Glutamine	Gln Q	146	2.17	9.13		5.65
Positively charged						
R groups						
Lysine	Lys K	146	2.18	8.95	10.53	9.74
Histidine	His H	155	1.82	9.17	6.00	7.59
Arginine	Arg R	174	2.17	9.04	12.48	10.76
Negatively charged						
R groups						
Aspartate	Asp D	133	1.88	9.60	3.65	2.77
Glutamate	Glu E	147	2.19	9.67	4.25	3.22

Acids/Bases Nature of Amino Acids and Isoelectric Point

Amino Acids with Two Ionizable Groups

For amino acids that have only:

- one α -carboxyl group ($-\text{COOH}$)
- one α -amino group ($-\text{NH}_3^+$)

the isoelectric point is:

$$pI = \frac{(pK_1 + pK_2)}{2}$$

where

- pK_1 = pKa of the carboxyl group
- pK_2 = pKa of the amino group

Amino acid	Abbreviation/ symbol	M_r	pK_a values			pI
			pK_1 ($-\text{COOH}$)	pK_2 ($-\text{NH}_3^+$)	pK_R (R group)	
Nonpolar, aliphatic						
R groups						
Glycine	Gly G	75	2.34	9.60		5.97
Alanine	Ala A	89	2.34	9.69		6.01
Proline	Pro P	115	1.99	10.96		6.48
Valine	Val V	117	2.32	9.62		5.97
Leucine	Leu L	131	2.36	9.60		5.98
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Acids/Bases Nature of Amino Acids and Isoelectric Point

Example- Glycine (Gly)

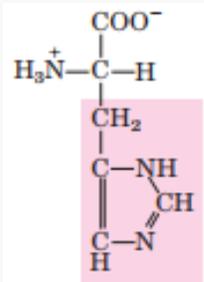
$$pI = \frac{1}{2}(2.34 + 9.60) = 5.97$$

pH Condition	Dominant Form	Net Charge
Low pH (acidic) (pH < pK ₁)	(NH ₃ ⁺ - CH ₂ - COOH)	+1
Near pI (pK ₁ < pH < pK ₂)	(NH ₃ ⁺ - CH ₂ - COO ⁻) (zwitterion)	0
High pH (basic) (pH > pK ₂)	(NH ₂ - CH ₂ - COO ⁻)	-1

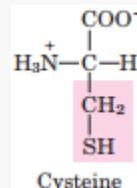
Amino Acids with Three Ionizable Groups

Some amino acids contain a **third ionizable group** in the side chain (R-group).

Examples include **Cysteine (Cys)** and **Histidine (His)**. For these amino acids, the isoelectric point (**pI**) is **not** simply the average of pK_1 and pK_2



Histidine



Cysteine

Amino acid	Abbreviation/ symbol	M_r	pK_a values			pI
			pK_1 (-COOH)	pK_2 (-NH ₃ ⁺)	pK_R (R group)	
Nonpolar, aliphatic						
R groups						
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Amino Acids with Three Ionizable Groups

The **pI** is the average of the two pK_a values that surround the zwitterionic form (the species with net charge = 0).

$$pI = \frac{pK_a(\text{below neutral form}) + pK_a(\text{above neutral form})}{2}$$

For Cysteine has an ionizable thiol group (-SH)

$$pI = \frac{1.96 + 8.18}{2} = 5.07$$

For-Histidine has na ionizable imidazole group in the side chain:

$$pI = \frac{6.0 + 9.17}{2} = 7.59$$

Always choose the **two** pK_a values that correspond to the steps where the amino acid changes from:



Amino acid	Abbreviation/ symbol	M_r	pK_a values			pI
			pK_1 (-COOH)	pK_2 (-NH ₃ ⁺)	pK_R (R group)	
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Amino Acids: Acids/Bases Nature

The α -COOH group of an amino acid acts as a weak acid. This means it can donate a proton (H^+) in solution, becoming negatively charged ($-COO^-$). The degree of ionization depends on the pH of the surrounding environment.

Henderson-Hasselbalch equation to calculate the fraction of the group that is ionized at any given pH.

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

Example-2

What is the pH of a glycine solution in which the $\alpha - \text{NH}_3^+$ group is one-third dissociated?



Chirality and Stereoisomers of Amino Acids

Isomers and Chirality in Amino Acids

Isomers: Isomers are molecules that have the same molecular formula but differ in their structural arrangement. In amino acids, isomerism can strongly affect molecular shape, biological function, and activity.

Chirality in Amino Acids

- Most amino acids are **chiral**, meaning the central carbon atom (α -carbon) is bonded to **four different groups**:
 - $-NH_2$ (amino group)
 - $-COOH$ (carboxyl group)
 - $-H$ (hydrogen)
 - $-R$ (side chain)
-  **Exception: Glycine** is **achiral** because its side chain is also hydrogen, so it does **not** have four different groups.

Chirality and Stereoisomers of Amino Acids

Optical Activity

Chiral molecules are **optically active**, meaning they can rotate **plane-polarized light**. This property results from their **asymmetric 3D structure**.

Stereoisomers of Amino Acids

Enantiomers

The **19 chiral amino acids** exist as **enantiomeric pairs**.

- **Enantiomers are non-superimposable mirror images**
- **Like left and right hands**

They have identical chemical properties in most environments, but can behave differently in biological systems

Chirality and Stereoisomers of Amino Acids

▪ Diastereomers

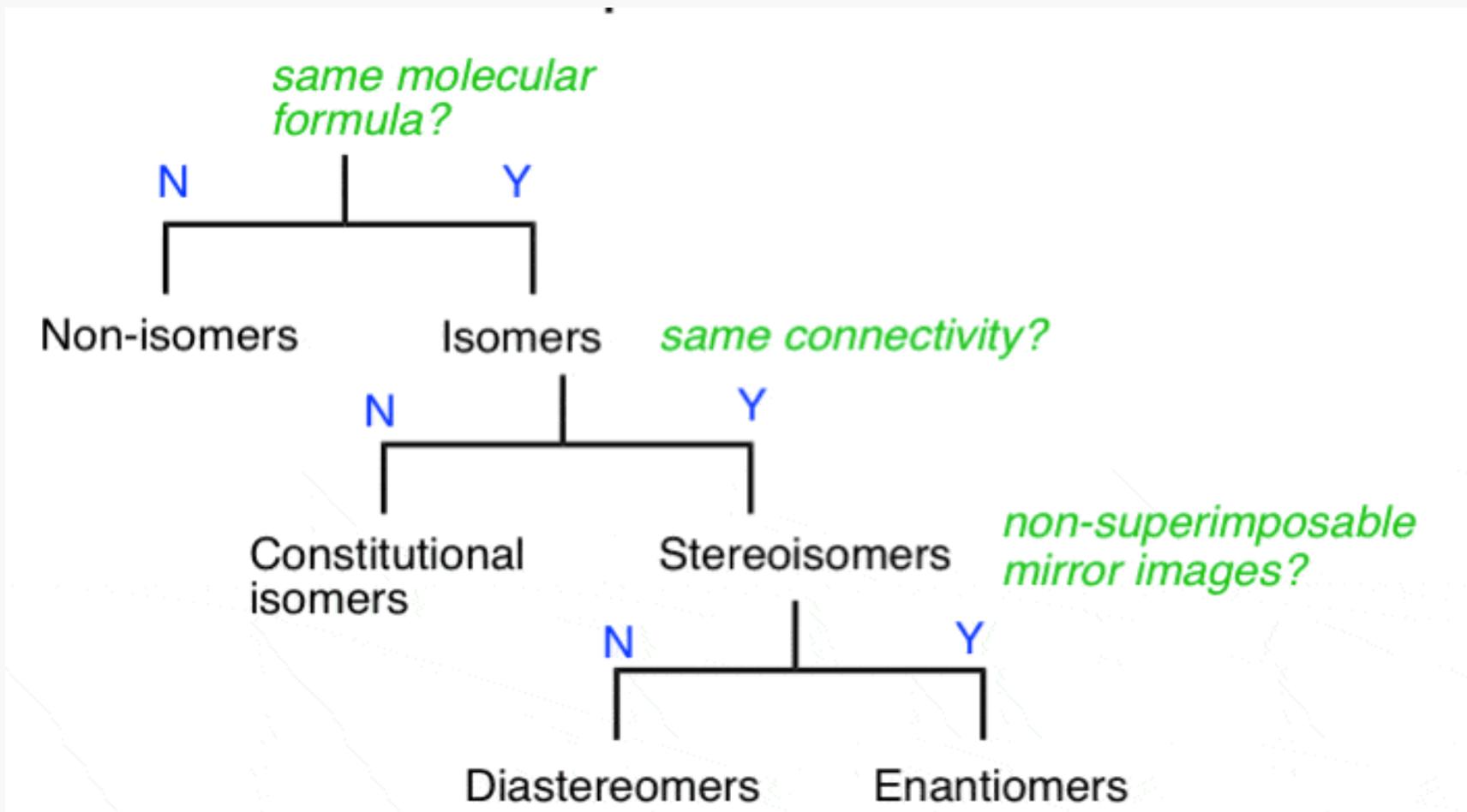
Diastereomers are stereoisomers that are:

- not mirror images
- not identical

have different physical and chemical properties

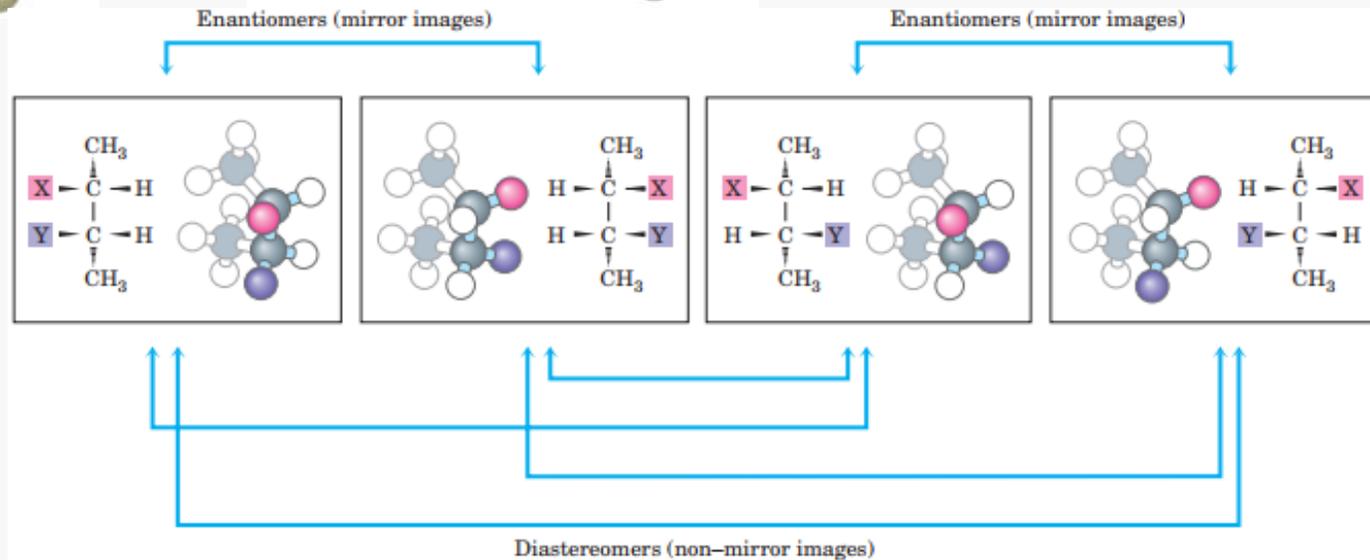
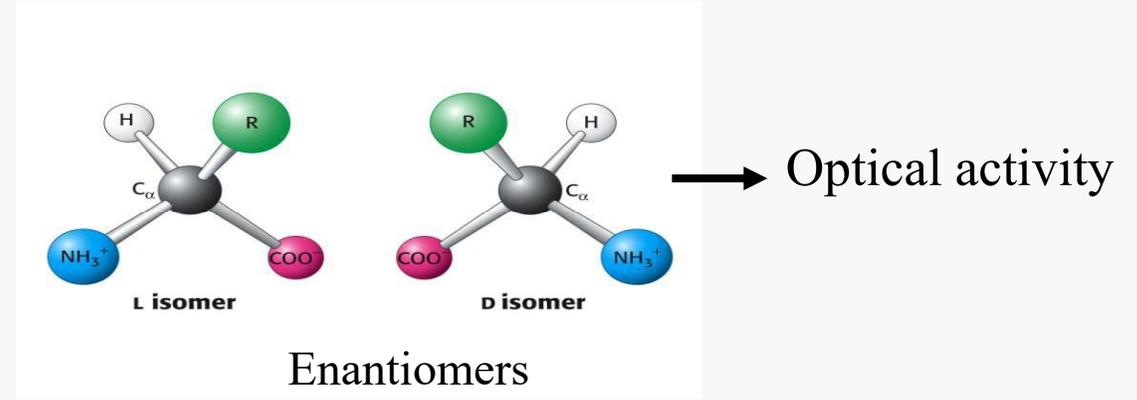
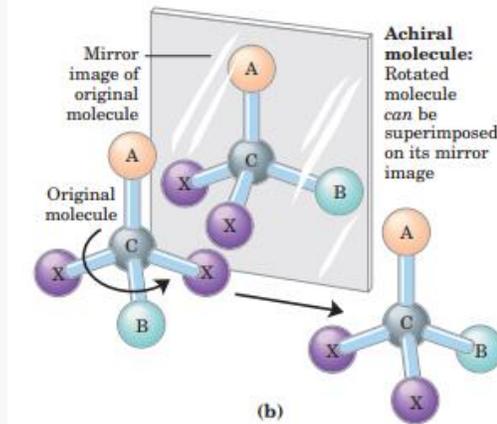
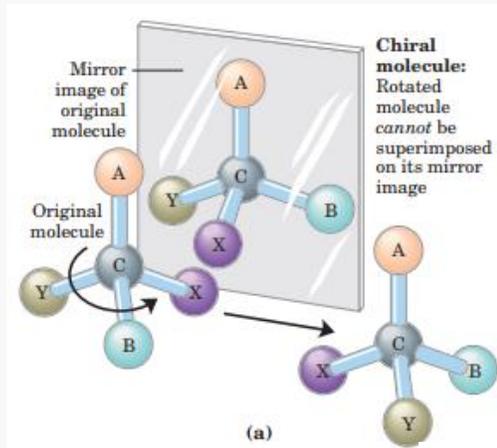
Diastereomers commonly occur in molecules with **more than one chiral center**.

Chirality and Stereoisomers of Amino Acids



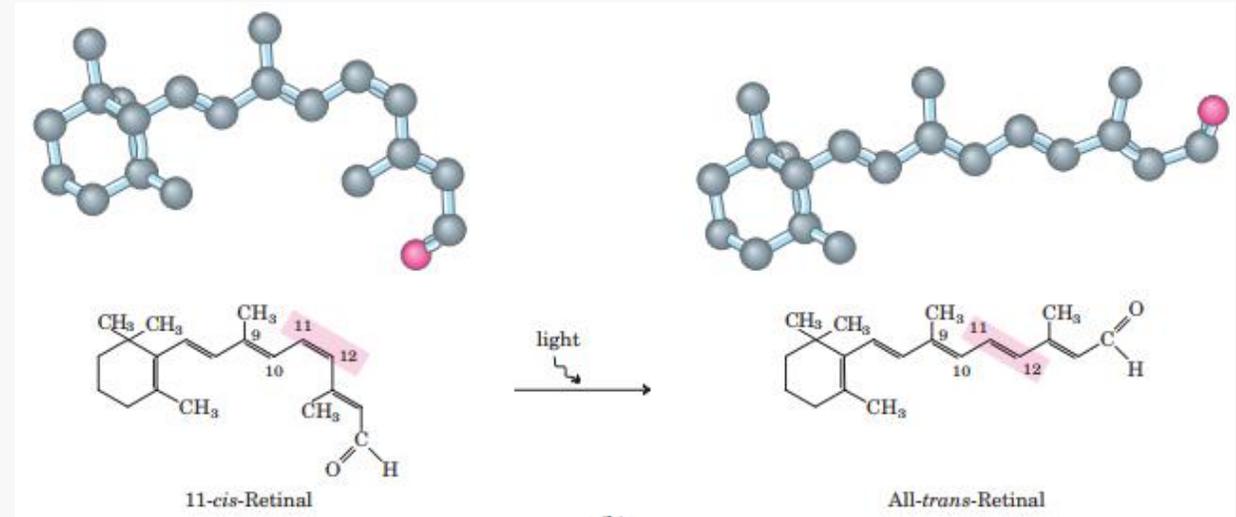
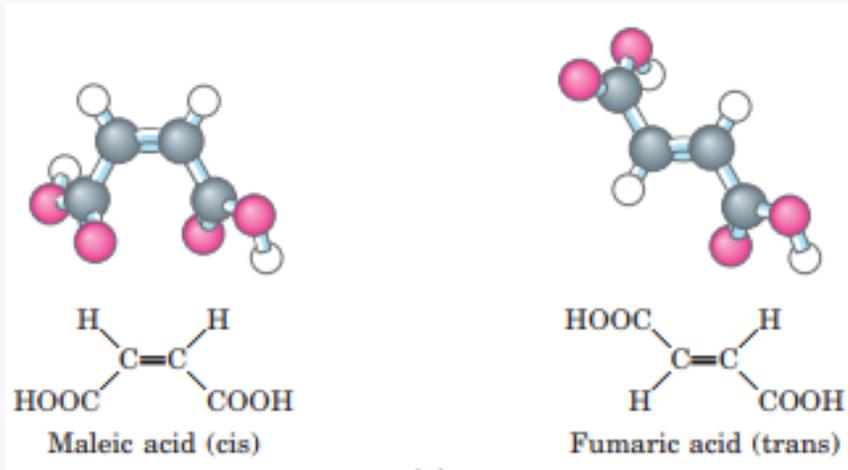
Amino Acids

The 19 chiral amino acids used in the *assembly of proteins are all the L configuration, although a few D-amino acids occur in nature*. Two non-superimposable stereoisomers : D, L system.



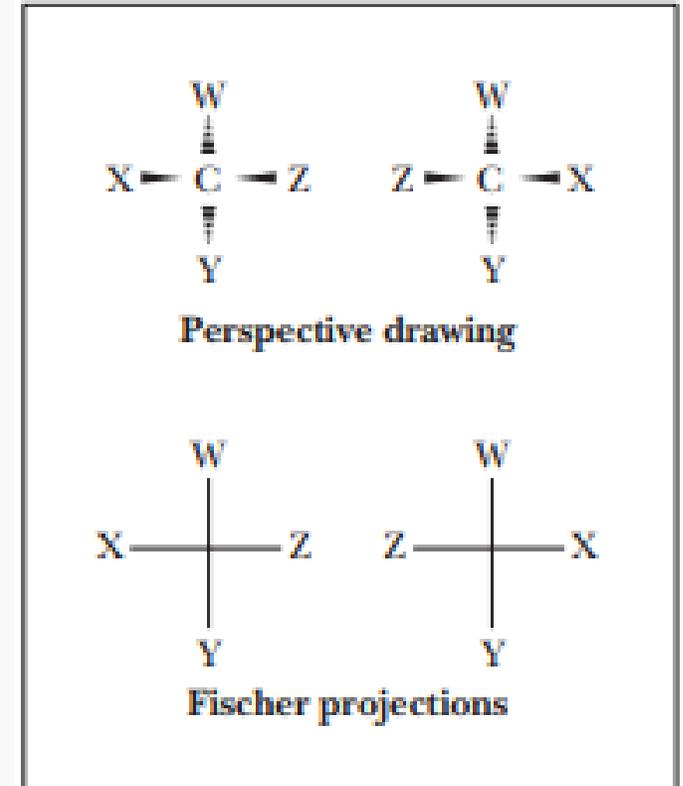
Geometric of Isomers

Configurations of geometric isomers. Isomers such as maleic acid and fumaric acid cannot be interconverted without breaking covalent bonds, which requires the input of much energy.



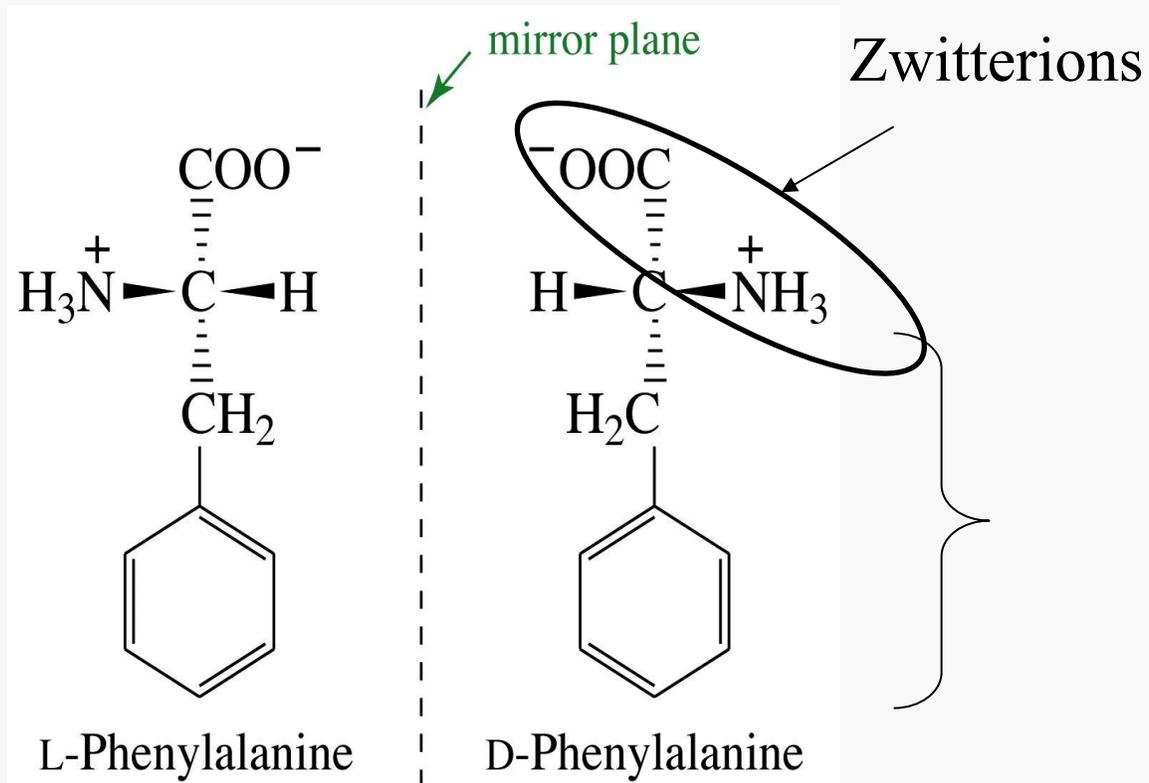
Optical Activity and Amino Acid Configuration

- Clockwise rotation of incident light is referred to as **dextrorotatory (D)** behavior,
- Counterclockwise rotation is called **levorotatory (L)** behavior.
- Proteins are assembled exclusively from L-amino acids in living organisms.
- D-amino acids are rare but occur naturally in:
 - Bacterial cell walls
 - Certain antibiotics
 - Brain neurotransmitters
- Typically, amino acids are assumed to be in L configuration unless specifically designated D.



Amino Acids

e.g. Phenylalanine, Phe (F)



L – Isomer: most commonly found form in nature.

D - Isomer

Thank you very much for your attention