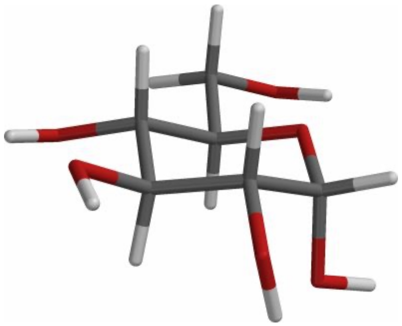
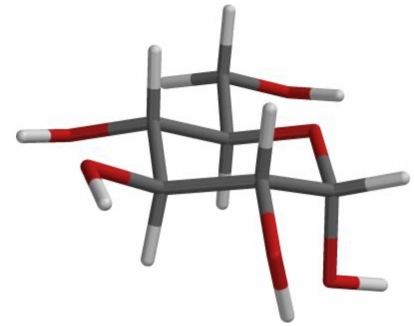




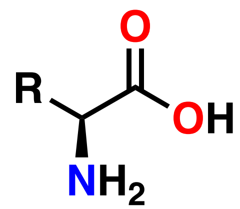
Chem 109 C
Bioorganic Compounds

Armen Zakarian

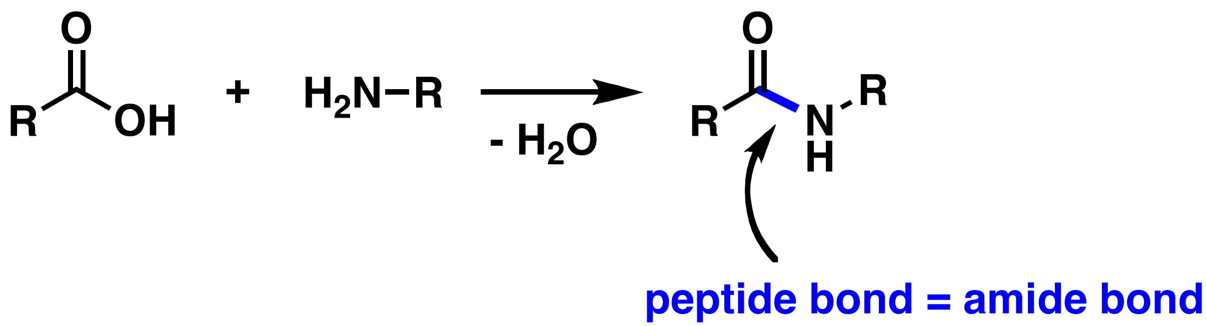
Office: Chemistry Bldn 2217

http://labs.chem.ucsb.edu/~zakariangroup/courses.html

Chapter 21



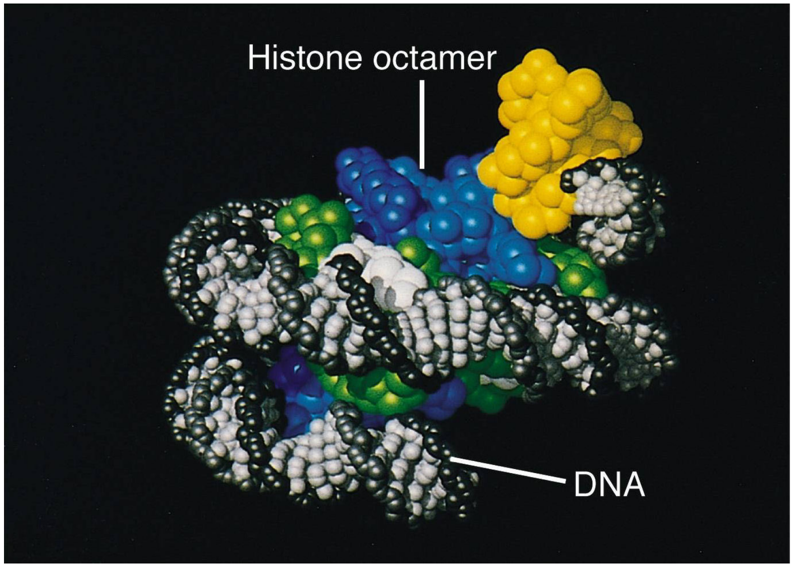
α-amino acid

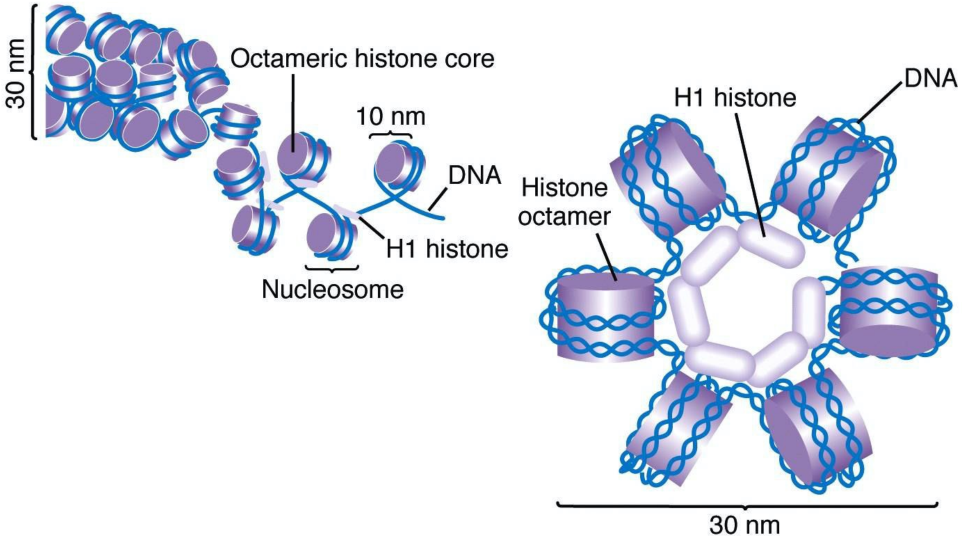


Proteins: Function

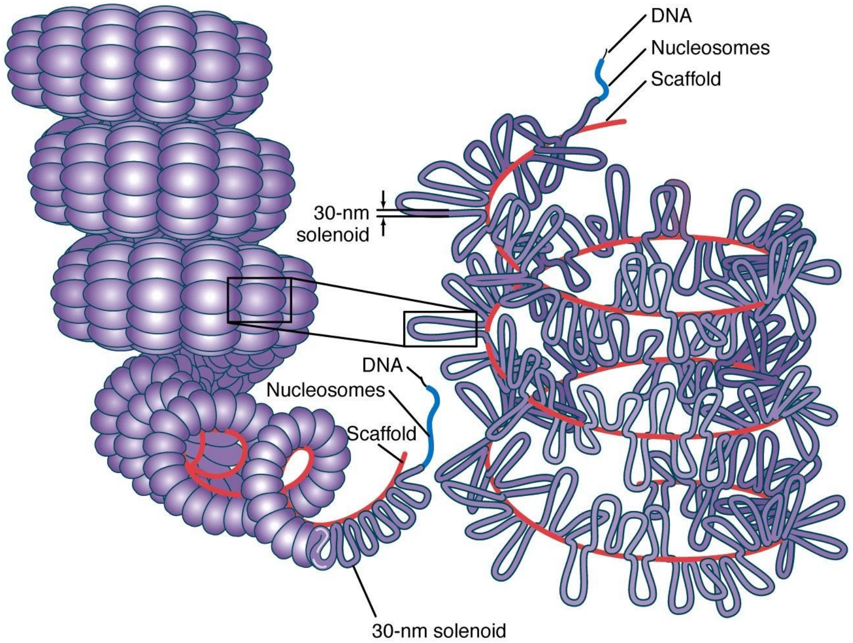
Table 21.1 Examples of the Many Functions of Proteins in Biological Systems

Structural proteins	These proteins impart strength to biological structures or protect organisms from their environment. For example, collagen is the major component of bones, muscles, and tendons; keratin is the major component of hair, hooves, feathers, fur, and the outer layer of skin.
Protective proteins	Snake venoms and plant toxins protect their owners from predators. Blood-clotting proteins protect the vascular system when it is injured. Antibodies and peptide antibiotics protect us from disease.
Enzymes	Enzymes are proteins that catalyze the reactions that occur in living systems.
Hormones	Some of the hormones, such as insulin, that regulate the reactions that occur in living systems are proteins.
Proteins with physiological functions	These proteins are responsible for physiological functions such as the transport and storage of oxygen in the body, the storage of oxygen in the muscles, and the contraction of muscles.





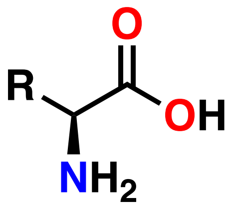
Histone Protein Structure: DNA packaging



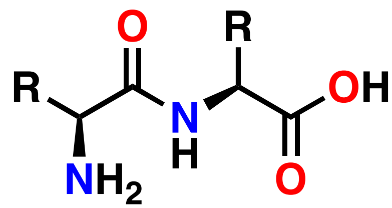
Proteins: Protective

botulinum toxin (botox) structure
most toxic substance known
LD_{50} = 10 ng/kg

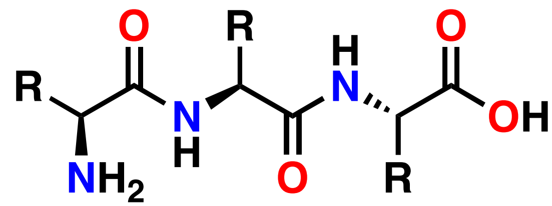
Amino acids, Peptides, Proteins: Introduction



α-amino acid



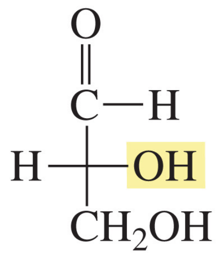
dipeptide



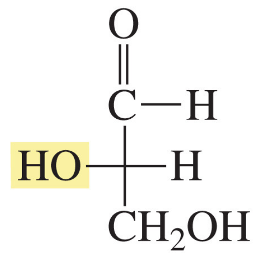
tripeptide

- ✓ oligopeptide: 3 - 10 amino acids
- ✓ polypeptide, or protein: many amino acids

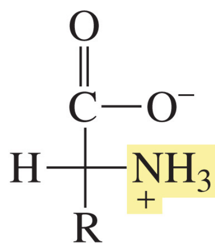
Proteins: Amino Acids, Configuration



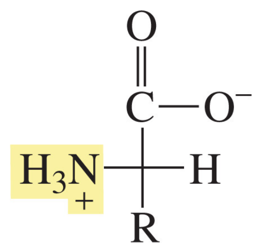
D-glyceraldehyde



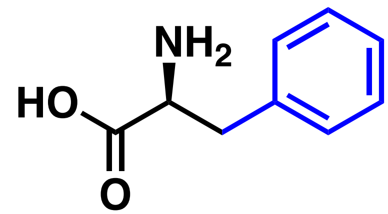
L-glyceraldehyde



D-amino acid

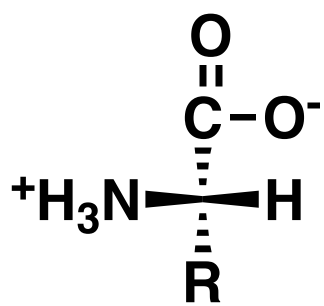


L-amino acid

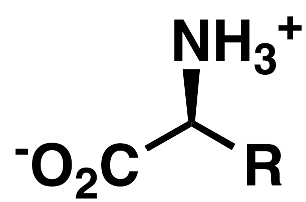


phenylalanine

natural amino acids
have the L configuration (*S*)



same as

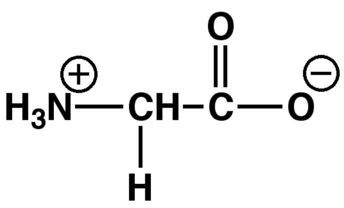


Amino acids: Classification

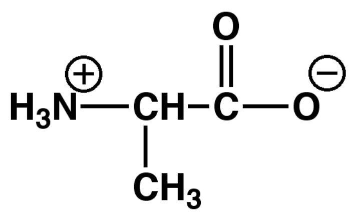
- Hydrophobic: "water-fearing", nonpolar side chains
  - Alkyl side chain

- Hydrophilic: "water-loving" side chains
  - Polar, neutral side chains
  - Anionic
  - Cationic

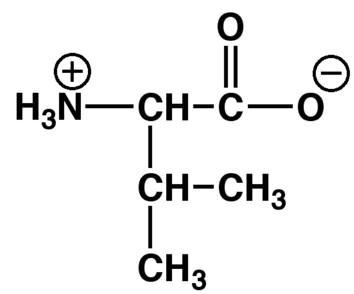
- Table 21.1 lists 20 most common natural occurring amino acids
- The structures of amino acids will be provided on the tests



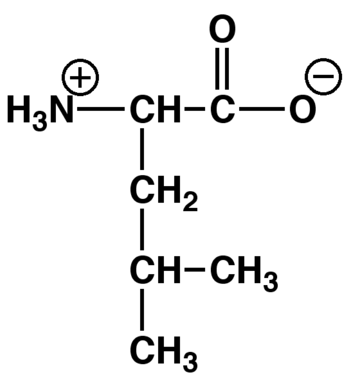
Glycine



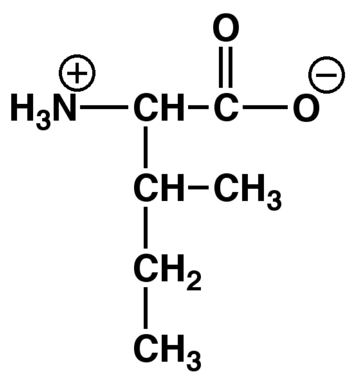
Alanine



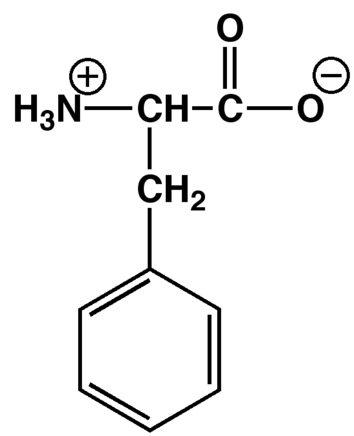
Valine



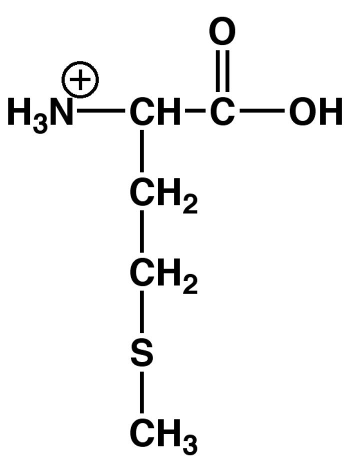
Leucine



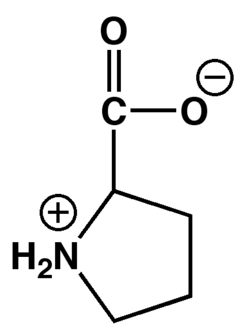
Isoleucine



Phenylalanine



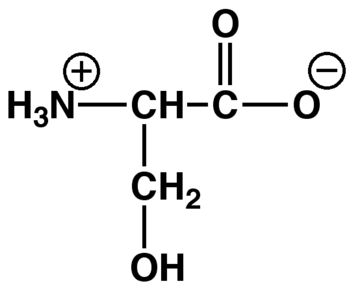
Methionine



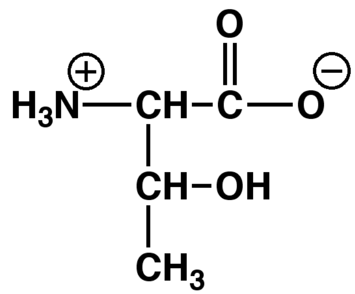
Proline

nonpolar side chains

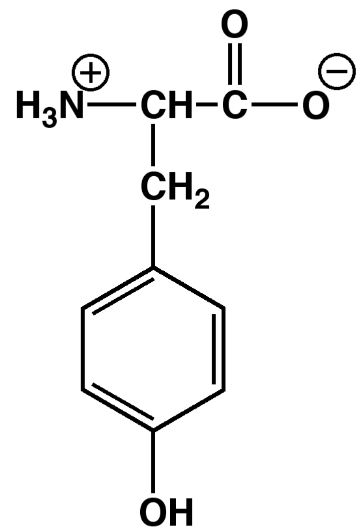
polar neutral (uncharged) side chains



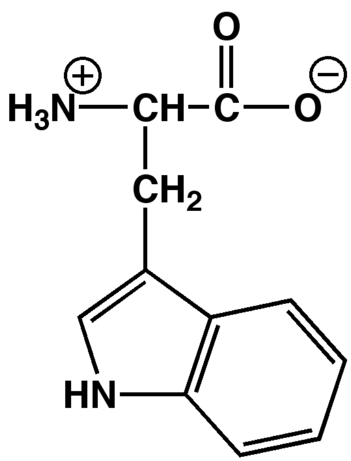
Serine



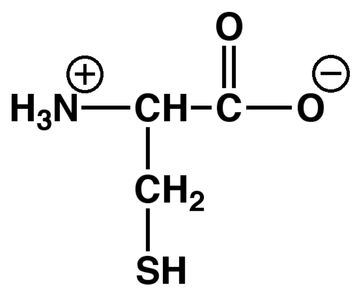
Threonine



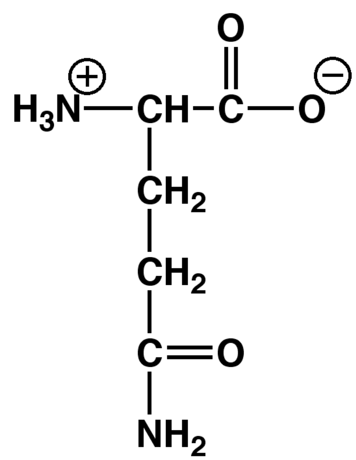
Tyrosine



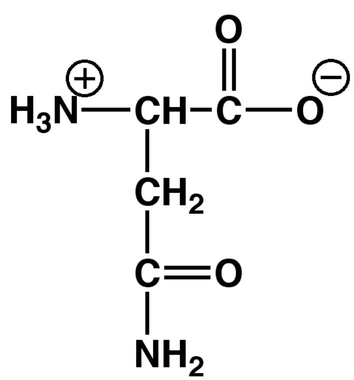
Tryptophan



Cysteine

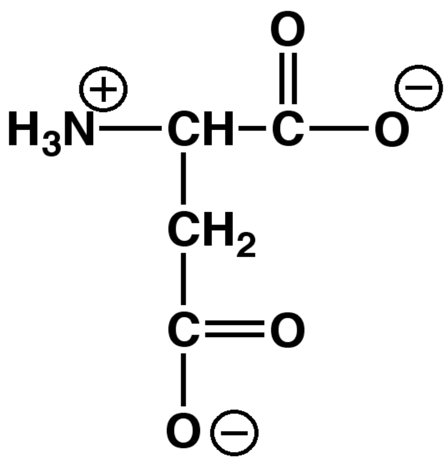


Glutamine

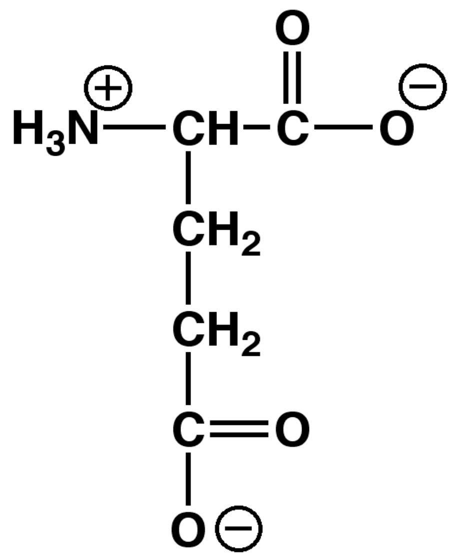


Asparagine

Amino acids: Classification



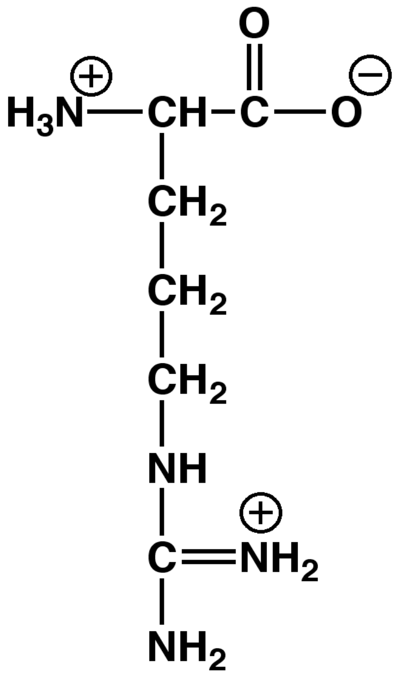
Asparatic Acid



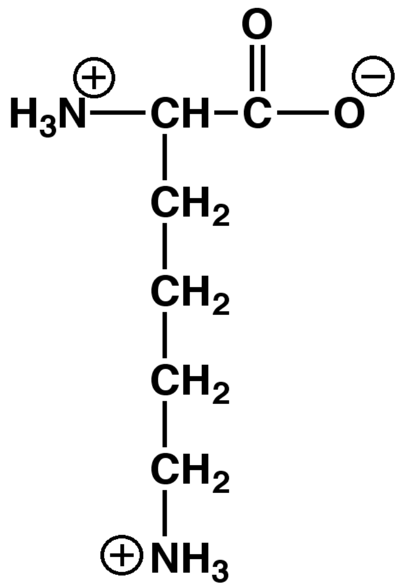
Glutamic Acid

polar acidic (anionic) side chains

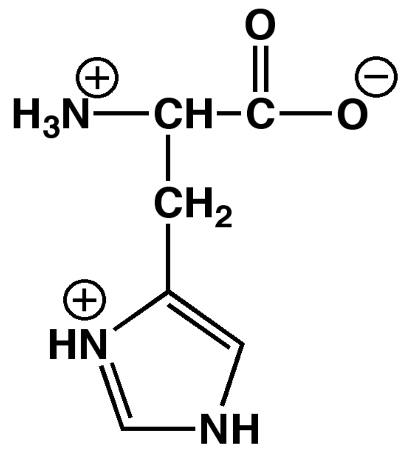
Amino acids: Classification



Arginine



Lysine



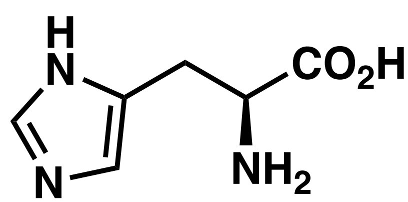
Histidine

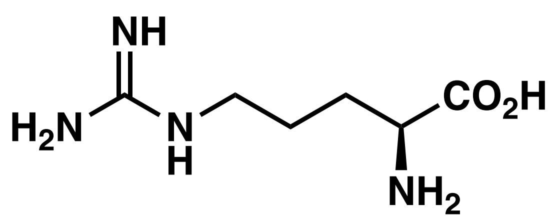
polar basic (cationic) side chains

PROBLEM 1

Explain why when the imidazole ring of histidine is protonated, the double-bonded nitrogen is the nitrogen atom that accepts the proton.

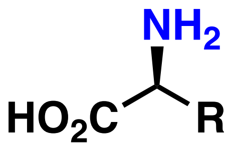
same for guanidine group in arginine.



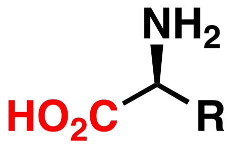


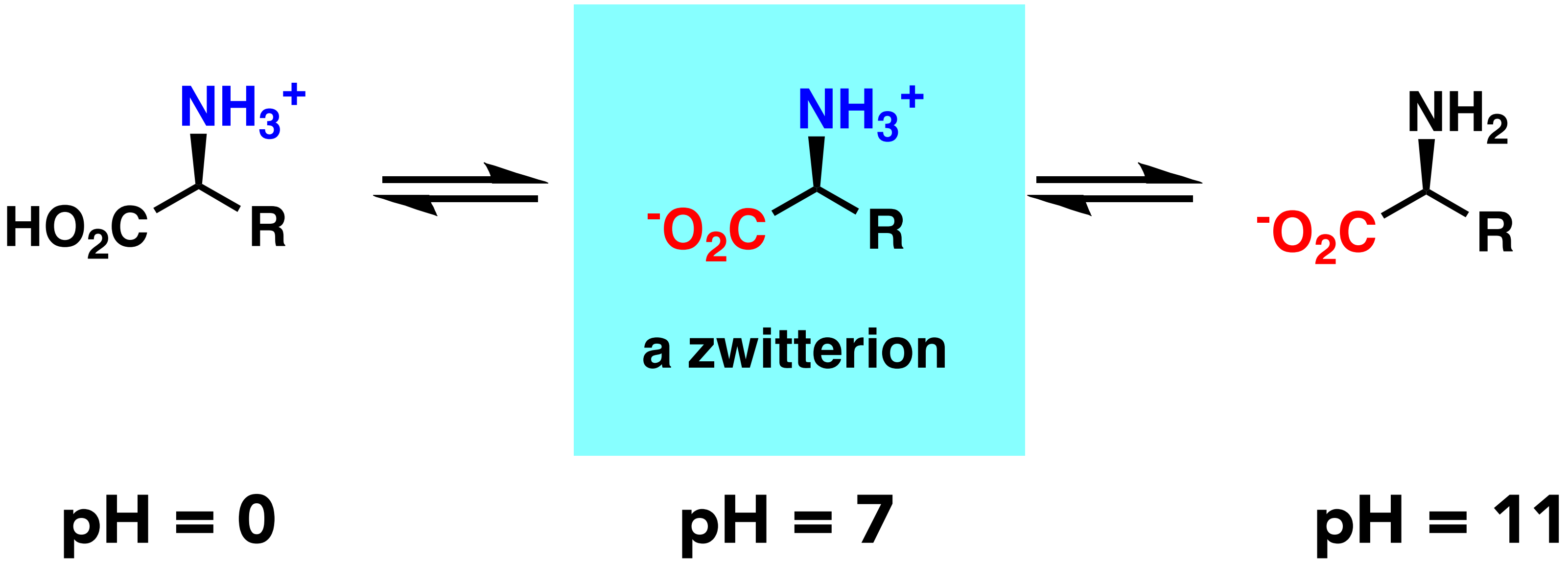
Amino acids: Zwitterions

✓ contain the amino group



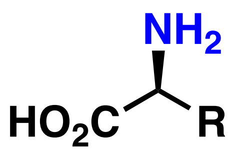
✓ contain the carboxylic acid group:





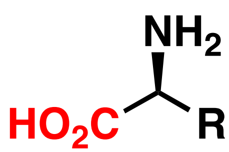
Amino acids: Zwitterions

pK_a of amino acids:



α-amino: 8.84 - 10.60

pK_a of the α-amino group is 9

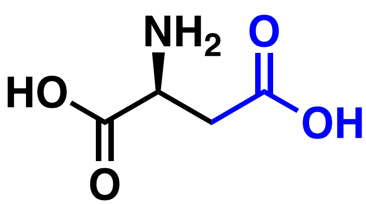


carboxylic acid: 1.82 - 2.63

pK_a of the CO_2H group is 2

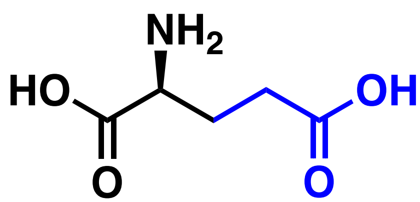
Amino acids: Zwitterions

pKa of side-chains:



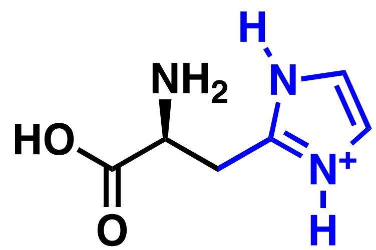
aspartic acid

pKa 3.86



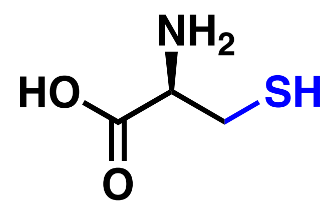
glutamic acid

pKa 4.25



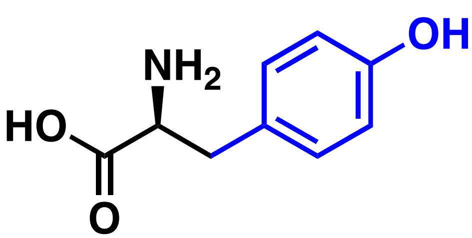
histidine

pKa 6.04



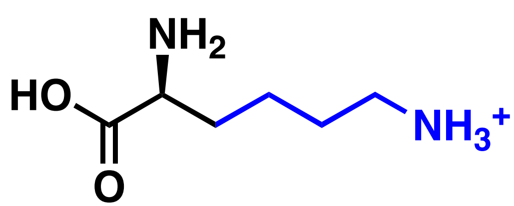
cysteine

pKa 8.35



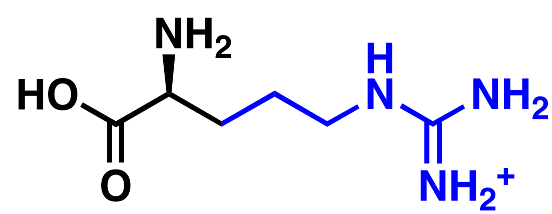
tyrosine

pKa 10.07



lysine

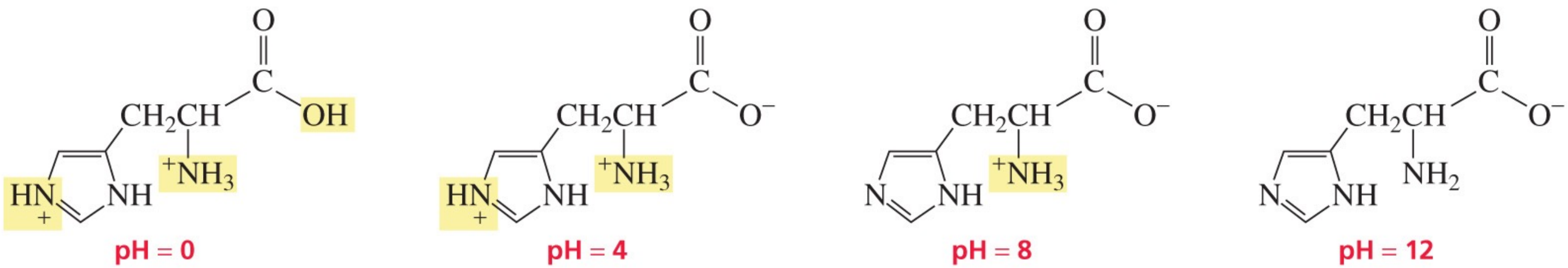
pKa 10.79



arginine

pKa 12.48

Amino acids: Zwitterions



histidine

PROBLEM 8

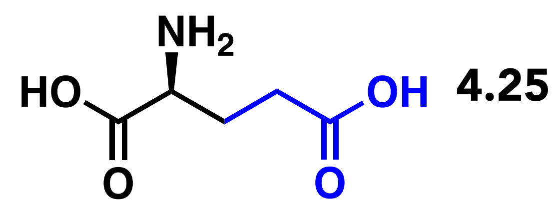
Draw the predominant form of glutamic acid in a solution with the following pH:

a. 0

b. 3

c. 6

d. 11

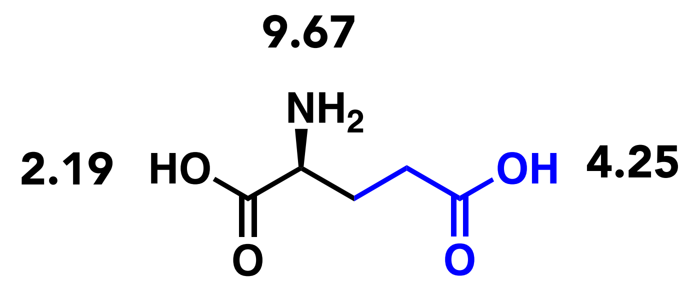


glutamic acid

PROBLEM 8

Draw the predominant form of glutamic acid in a solution with the following pH:

a. 0



glutamic acid

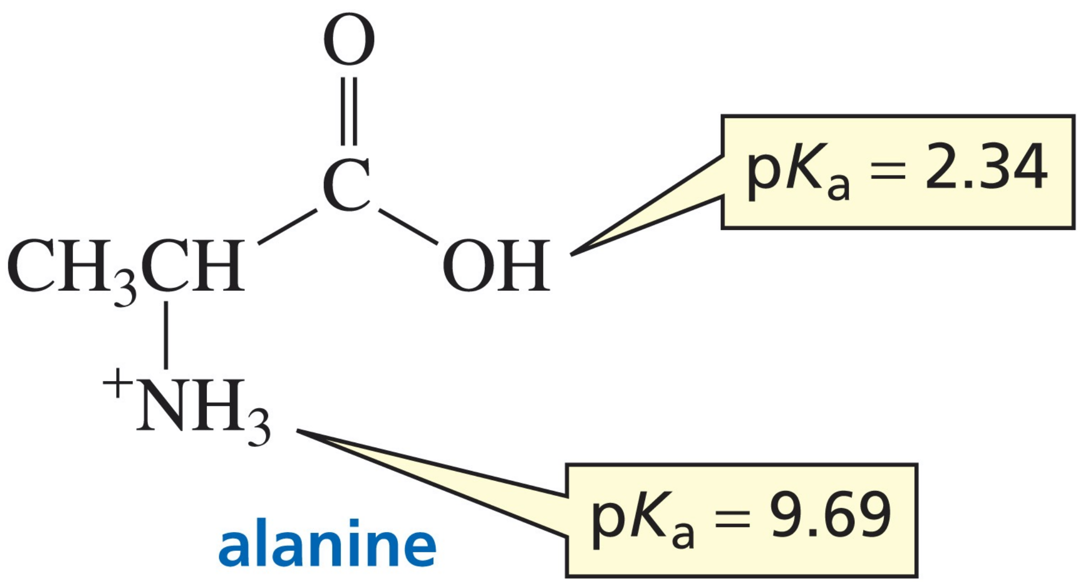
b. 3

c. 6

d. 11

Amino acids: Isoelectric Point (pI)

pI of amino acid is pH at which it has no net charge

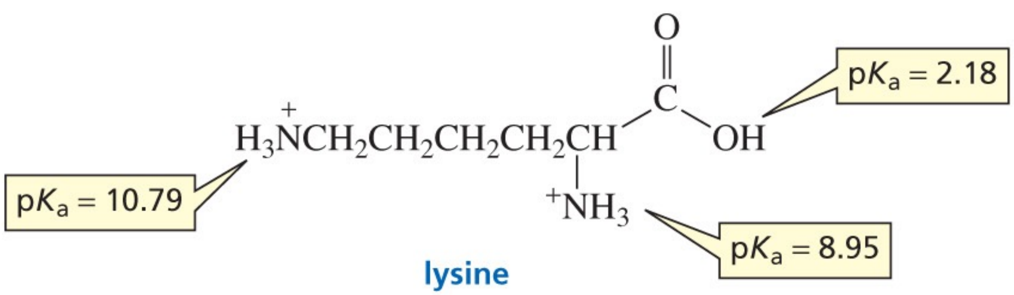


$$pI = \frac{2.34 + 9.69}{2} = \frac{12.03}{2} = 6.02$$

case 1: non-ionizing side chain

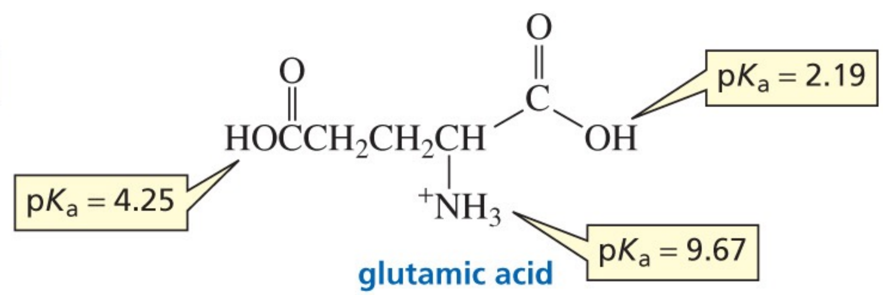
Amino acids: Isoelectric Point (pI)

pI of amino acid is pH at which it has no net charge



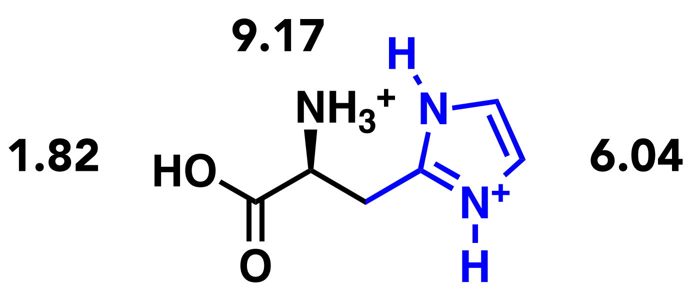
lysine

$$pI = \frac{8.95 + 10.79}{2} = \frac{19.74}{2} = 9.87$$



glutamic acid

$$pI = \frac{2.19 + 4.25}{2} = \frac{6.44}{2} = 3.22$$



case 2: ionizable side chain (acidic or basic)

average of pKa's of similarly ionizing groups

PROBLEM 6

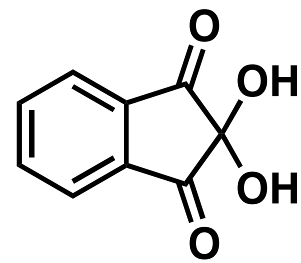
Why are the carboxylic groups of the amino acids more acidic (pK_a ~ 2) than in acetic acid (pK_a 4.76)?

Amino acids: Separation/Purification

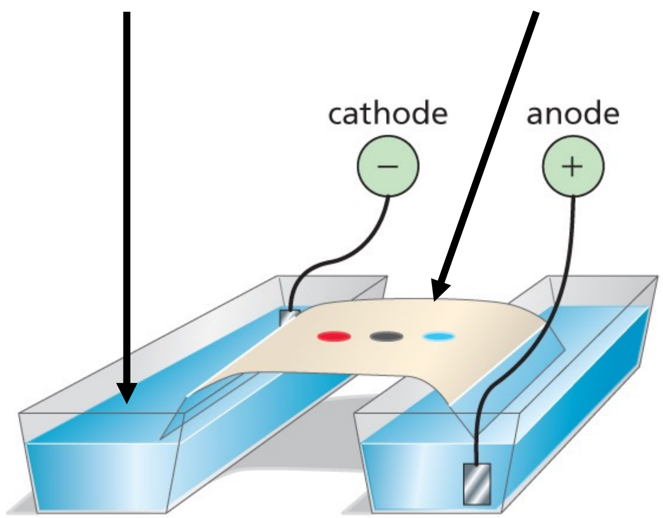
☑ **electrophoresis**

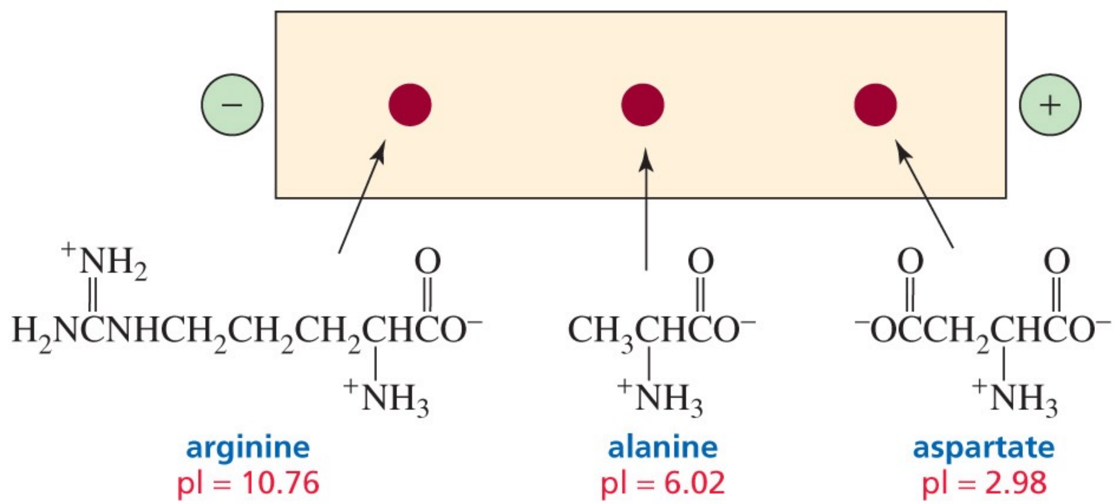
based on pI values of amino acids

visualized with ninhydrin:



buffer **paper or gel**





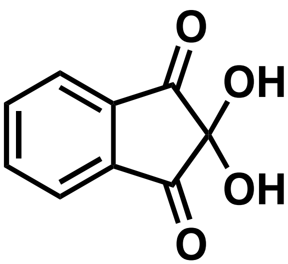
arginine, alanine, and aspartate separated at pH = 5

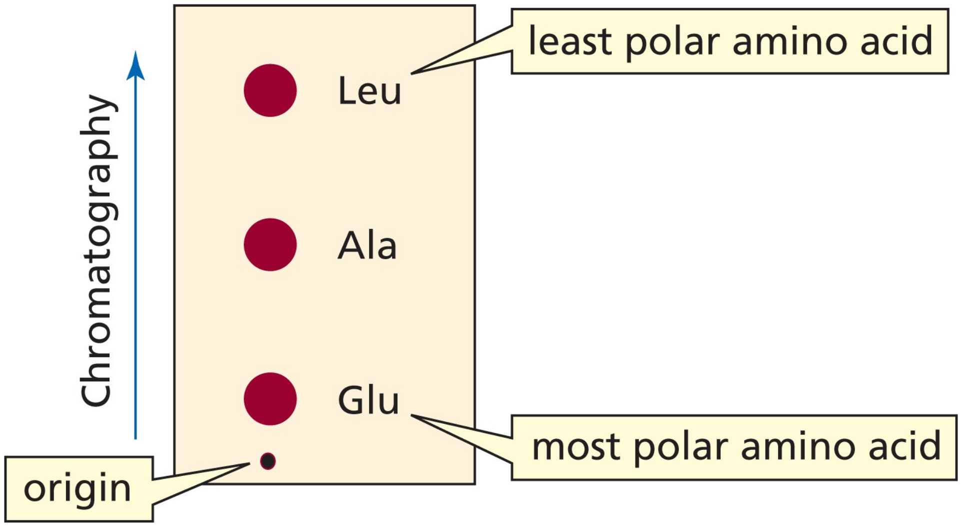
Amino acids: Separation/Purification

☑ paper/thin layer chromatography

based on polarity

visualized with ninhydrin:





glutamate, alanine, and leucine

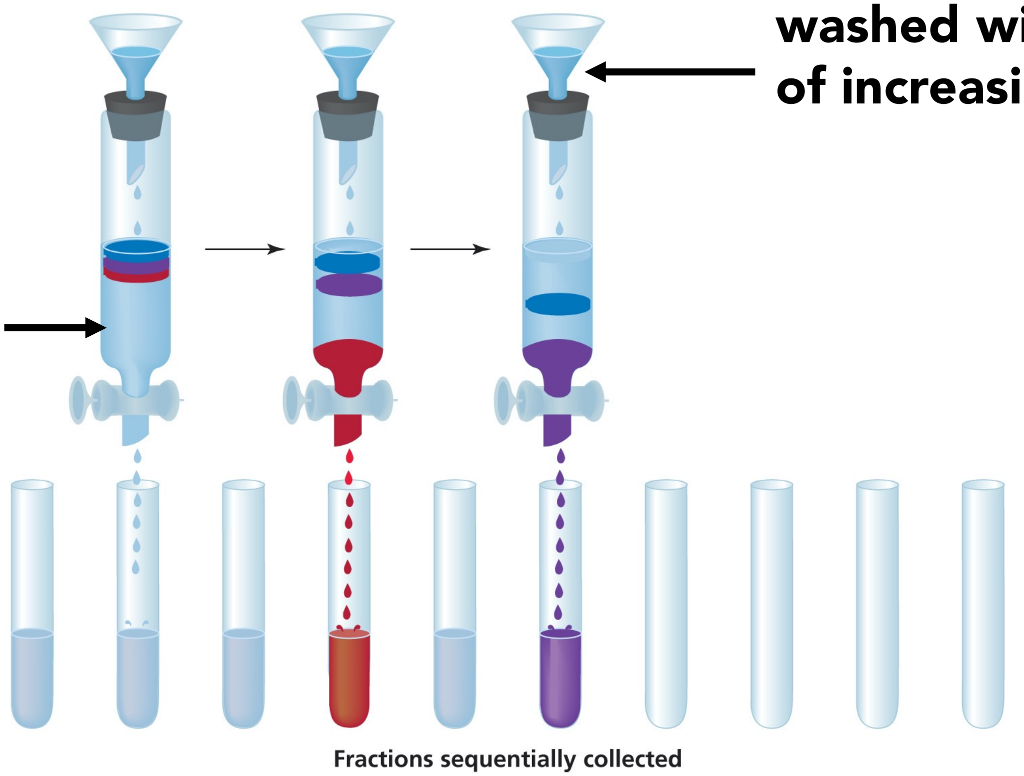
Amino acids: Separation/Purification

☑ **ion-exchange chromatography**

based on ions/charge – (or diff between pI and pH)
used on preparative scale, automated

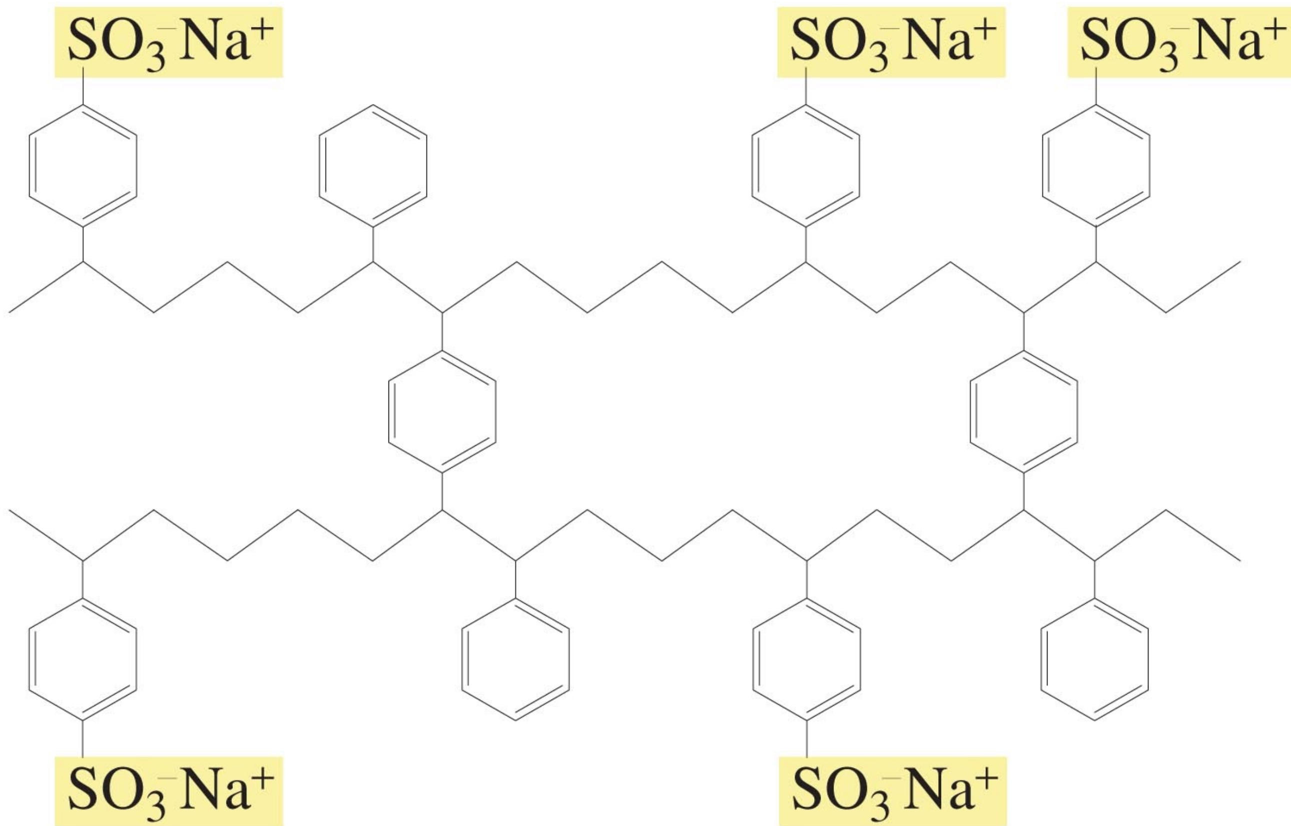
washed with buffers of increasing pH

packed with insoluble resin beads



Amino acids: Separation/Purification

Ion-exchange chromatography can be used to perform preparative separation of amino acids:

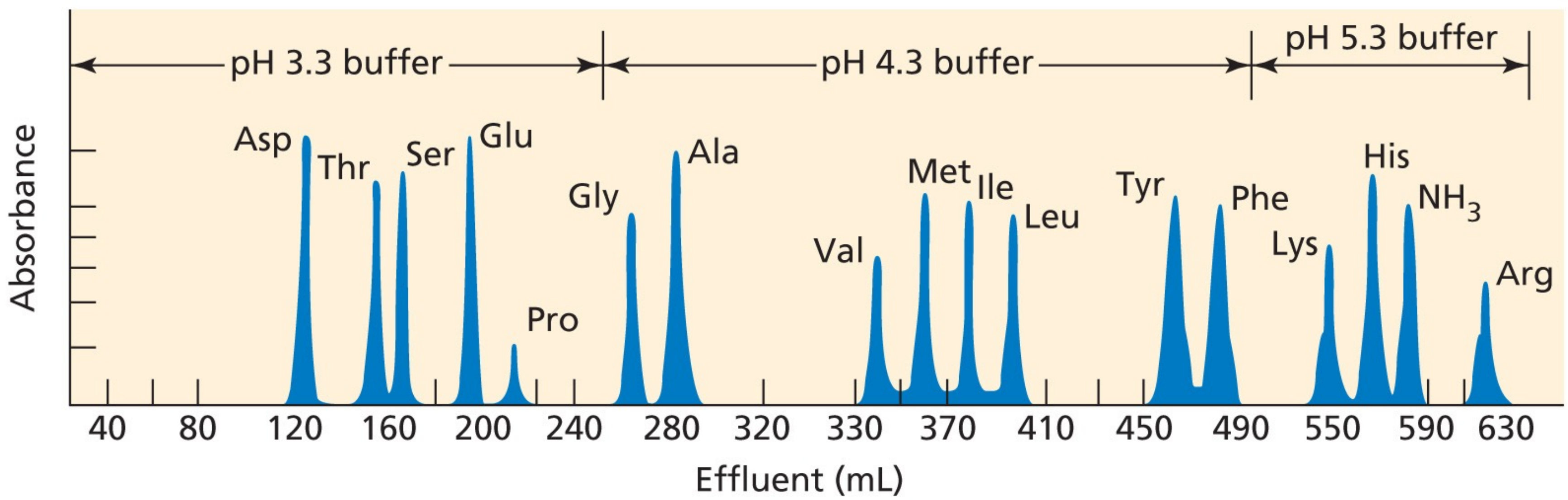


Negatively charged resin binds selectively to positively charged amino acids

Amino acids: Separation/Purification

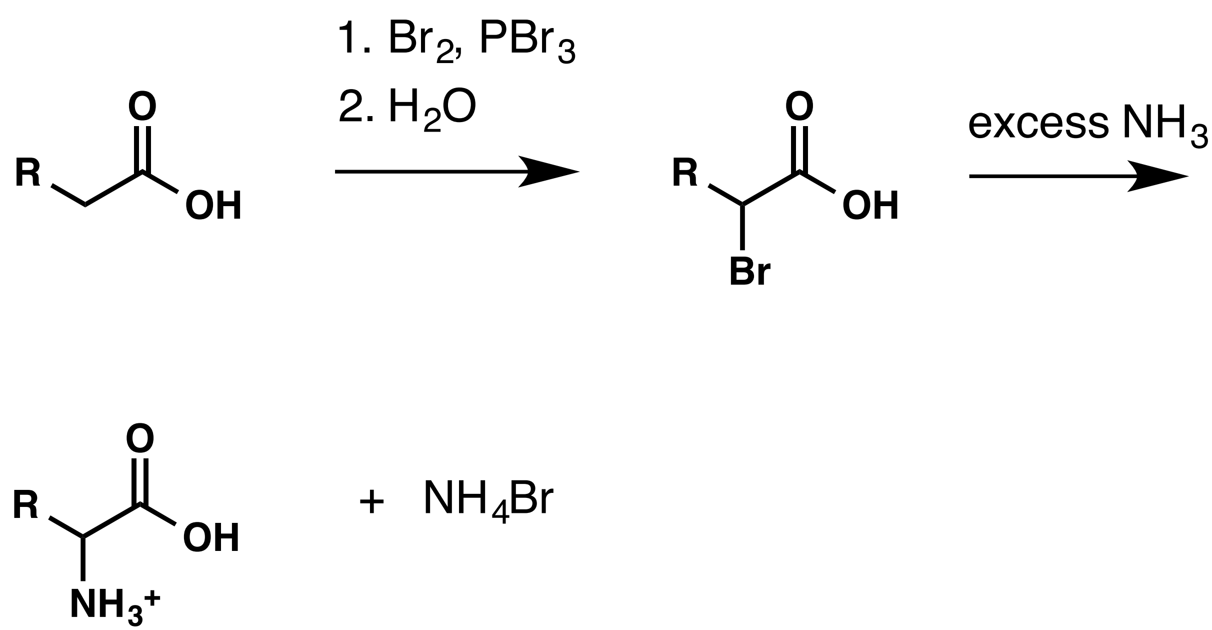
ion-exchange chromatography

A typical chromatogram obtained from separation of amino acids using an automated analyzer



Amino acid synthesis: HVZ reaction

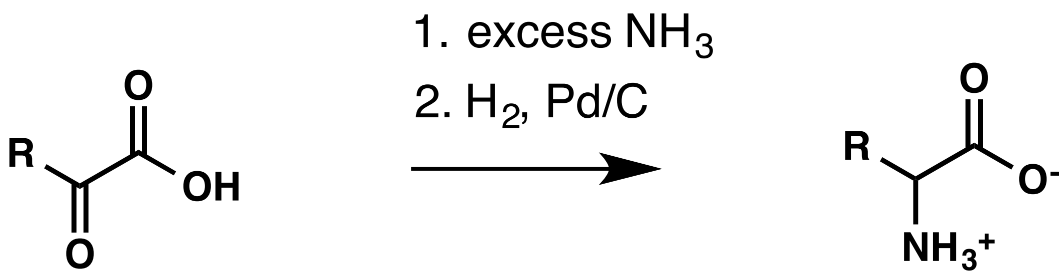
Hell-Volhardt-Zelinski reaction, see Sections 17.5 and 9.2

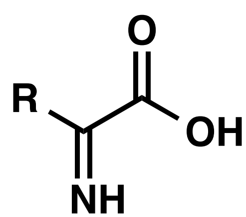


note the source of side-chains....

Amino acid synthesis: reductive amination

review Section 16.4

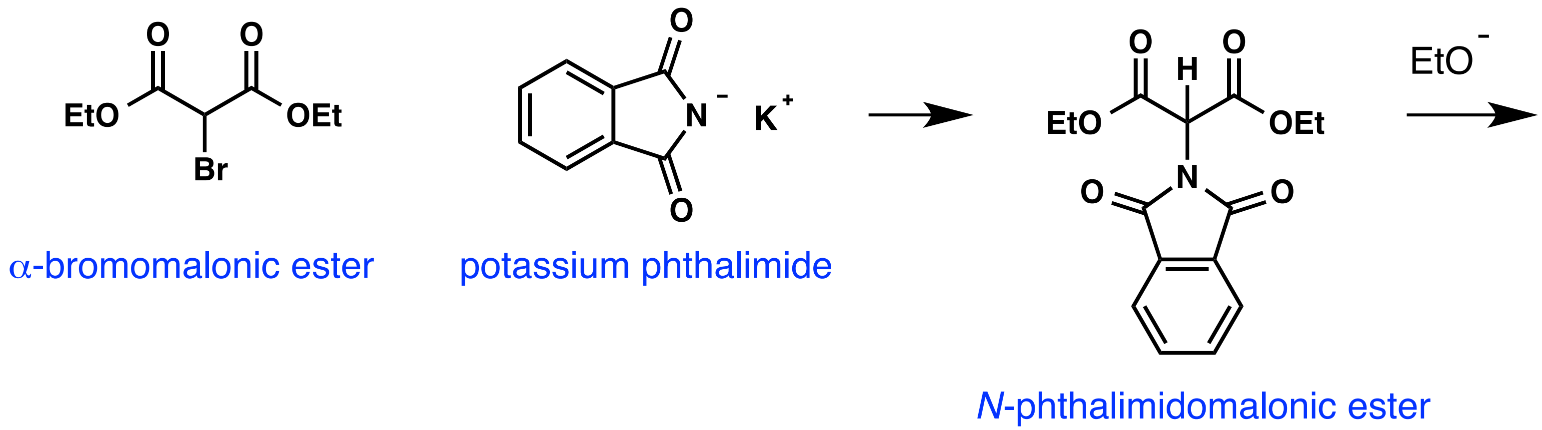


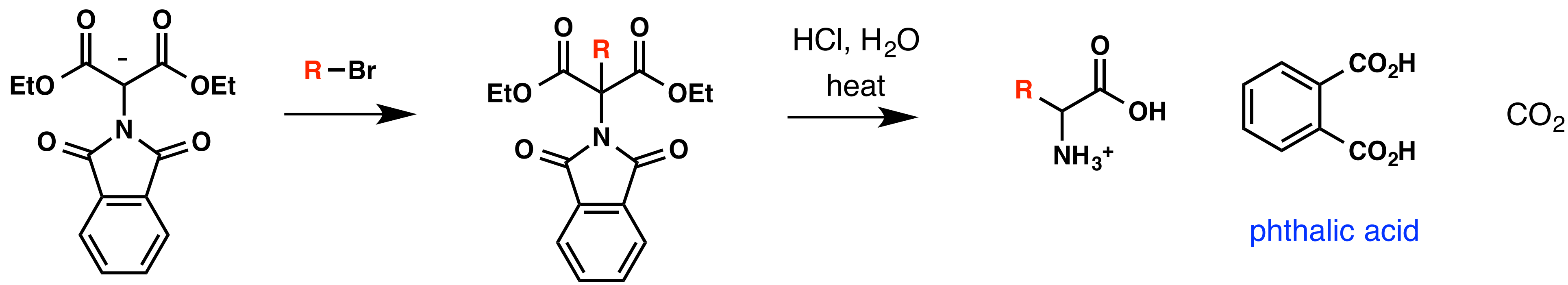


intermediate

note the source of side-chains....

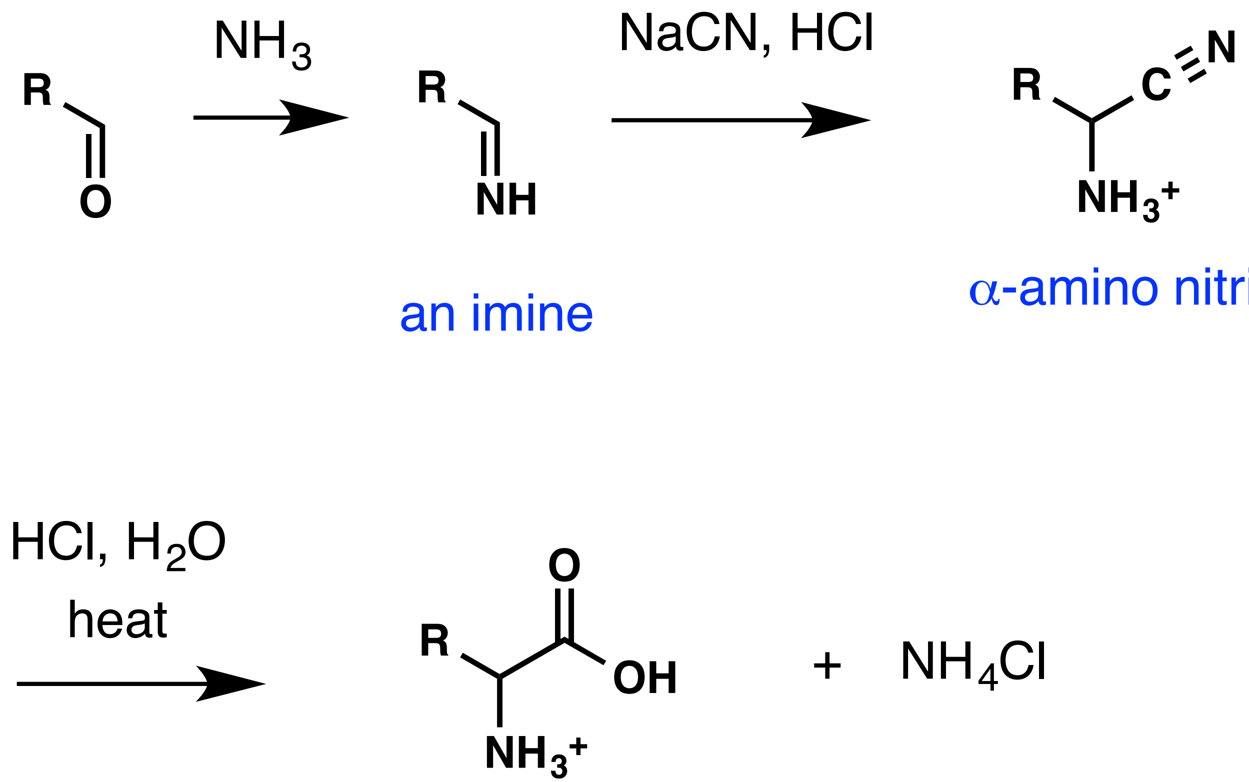
Amino acid synthesis: *N*-phthalimidomalonic





review Sections 15.4, 17.1, and 17.17

Amino acid synthesis: Strecker synthesis



review Section 15.15 for nitrile hydrolysis