Organic Chemistry, *Fourth Edition*

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Chapter 3

Intro. to Organic Molecules and Functional Groups

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Functional Groups

3.1 Functional Groups
3.2 An Overview of Functional Groups
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3.4 Physical Properties
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3.6 Application of Solubility: Soap
3.7 Application: The Cell Membrane
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Biomolecules

Functional Groups

- A functional group is an atom or a group of atoms with characteristic chemical and physical properties.

- Most organic molecules contain a carbon backbone consisting of C-C and C-H bonds to which functional groups are attached.

- Structural features of a functional group include:
  - Heteroatoms—atoms other than carbon or hydrogen.
  - π Bonds most commonly occur in C-C and C-O double bonds.

Functional Groups

- Functional groups distinguish one organic molecule from another.

- They determine a molecule's:
  - geometry
  - physical properties
  - reactivity

Reactivity of Functional Groups

- Heteroatoms and π bonds confer reactivity on a particular molecule.
    - Heteroatoms have lone pairs and create electron-deficient sites on carbon.
    - A π bond makes a molecule a base and a nucleophile, and is easily broken in chemical reactions.

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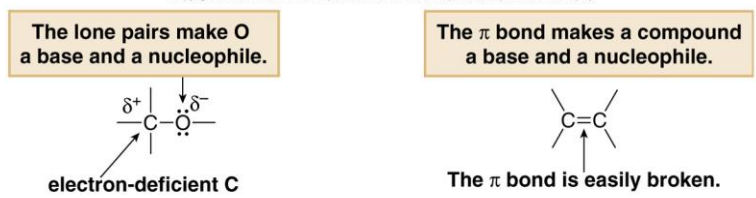

Parts of a Functional Group

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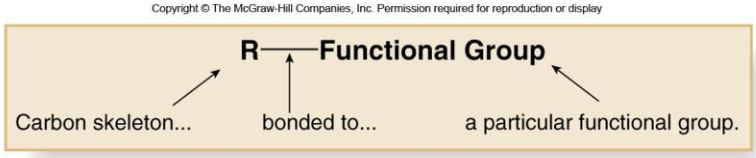

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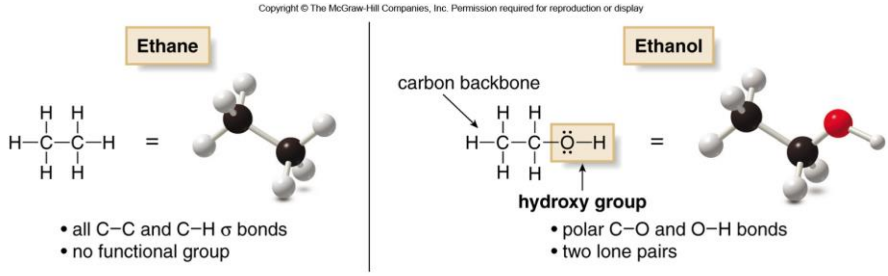

Ethane, a Molecule with No Functional Group

- This molecule has only C—C and C—H σ bonds.
- It contains no polar bonds, lone pairs, or π bonds.
- Therefore, ethane has no reactive sites (functional groups).
- Consequently, ethane and molecules like it (alkanes) are very unreactive.

Ethanol

- This molecule has an OH (called a hydroxy group) attached to its backbone.
- Compounds containing an OH group are called alcohols.
- The hydroxy group makes the properties of ethanol very different from the properties of ethane.
- Ethanol has lone pairs and polar bonds that make it reactive.
- Other molecules with hydroxy groups will have similar properties to ethanol.

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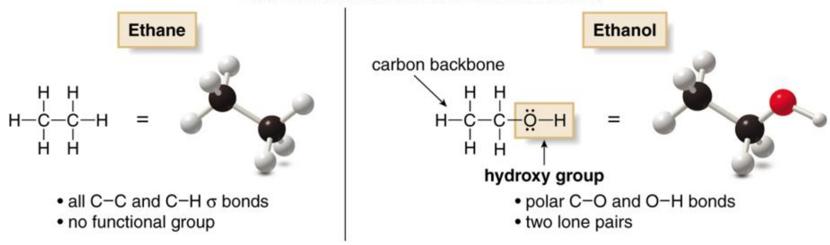

Hydrocarbons

- **Hydrocarbons are compounds made up of only the elements carbon and hydrogen.**
- **They may be aliphatic (ex. alkanes, alkenes, alkynes) or aromatic.**

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Table 3.1 Hydrocarbons

Type of compound	General structure	Example	Functional group
Alkane	R—H	CH_3CH_3	—
Alkene	>C=C<	$H_2C{=}CH_2$	double bond
Alkyne	—C≡C—	H—C≡C—H	triple bond
Aromatic compound			phenyl group

Aliphatic Hydrocarbons

- **Aliphatic hydrocarbons have three subgroups.**
  - **Alkanes have only C—C σ bonds and no functional group.**
  - **Alkenes have a C—C double bond.**
  - **Alkynes have a C—C triple bond.**

Aromatic Hydrocarbons

- **Aromatic hydrocarbons** are so named because many of the earliest known aromatic compounds had strong, characteristic odors.
- **The simplest aromatic hydrocarbon is benzene.**
- **The six-membered ring and three π bonds of benzene comprise a single functional group, found in most aromatic compounds.**

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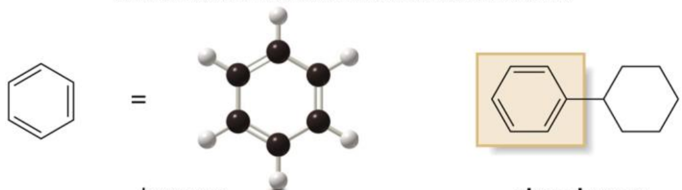

benzene
molecular formula C_6H_6

phenyl group
C_6H_5-
phenylcyclohexane

Functional Groups with Carbon-Heteroatom (C-Z) σ bonds

- **Several types of functional groups contain C-Z σ bonds.**
- **The electronegative heteroatom Z creates a polar bond, making carbon electron deficient.**

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Functional Groups with C-Z σ bonds

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Table 3.2 Compounds Containing C–Z σ Bonds

Type of compound	General structure	Example	3-D structure	Functional group
Alkyl halide	R–X: (X = F, Cl, Br, I)	CH_3–Br:		**–X** halo group
Alcohol	R–ÖH	CH_3–ÖH		**–OH** hydroxy group
Ether	R–Ö–R	CH_3–Ö–CH_3		**–OR** alkoxy group
Amine	R–N̈H_2 or R_2N̈H or R_3N̈	CH_3–N̈H_2		**–NH_2** amino group
Thiol	R–S̈H	CH_3–S̈H		**–SH** mercapto group
Sulfide	R–S̈–R	CH_3–S̈–CH_3		**–SR** alkylthio group

Functional Groups with C=O Group

- **This group is called a "carbonyl group".**
- **The polar C-O bond makes the carbonyl carbon an electrophile, while the lone pairs on O allow it to react as a nucleophile and base.**
- **The carbonyl group also contains a π bond that is more easily broken than a C-O σ bond.**

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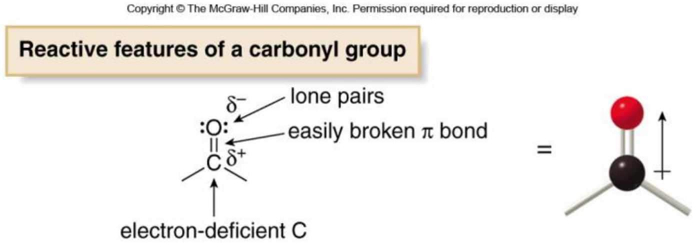

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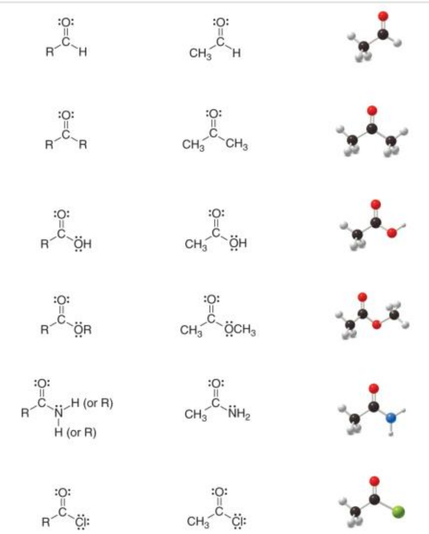


Table 3.3 Compounds Containing a C=O Group

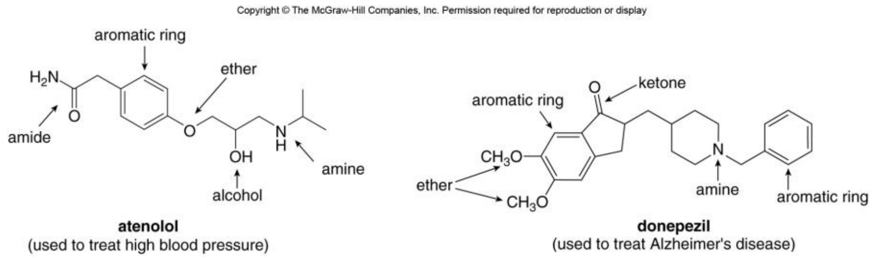
Type of compound	General structure	Example	3-D structure	Functional group
Aldehyde				C=O carbonyl group
Ketone				C=O carbonyl group
Carboxylic acid				–COOH carboxy group
Ester				–COOR
Amide				$-CONH_2$, –CONHR, or $-CONR_2$
Acid chloride				–COCl

Importance of Functional Groups

A functional group determines <u>all</u> of the following properties of a molecule:

- **bonding and shape**
- **type and strength of intermolecular forces**
- **physical properties**
- **nomenclature**
- **chemical reactivity**

Molecules can Contain Several Functional Groups



- **Each of these molecules have several different functional groups**
- **These molecules would also have several different types of reactivity**

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Intermolecular Forces

- **Intermolecular forces are interactions that exist between molecules.**
- **Functional groups determine the type and strength of these interactions.**
- **Ionic and covalent compounds have very different intermolecular interactions.**

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Ion-Ion Interactions

- Ionic compounds contain oppositely charged particles held together by extremely strong electrostatic interactions.
- These ionic interactions are much stronger than the intermolecular forces present between covalent molecules.

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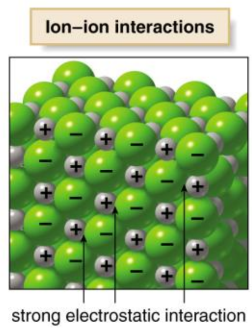

Intermolecular Forces in Covalent Molecules

- Covalent compounds are composed of discrete molecules.
- The nature of the forces between molecules depends on the functional group(s) present.
- There are three different types of interactions, shown below in order of increasing strength:
  - van der Waals forces
  - dipole-dipole interactions
  - hydrogen bonding

van der Waals Forces

- van der Waals forces are also known as London forces.
- They are very weak interactions caused by momentary changes in electron density in a molecule.
- They are the only attractive forces present in nonpolar compounds.

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van der Waals Forces in Methane

- CH_4 has no net dipole.
- At any one instant its electron density may not be completely symmetrical, resulting in a temporary dipole.
- This can induce a temporary dipole in another molecule.

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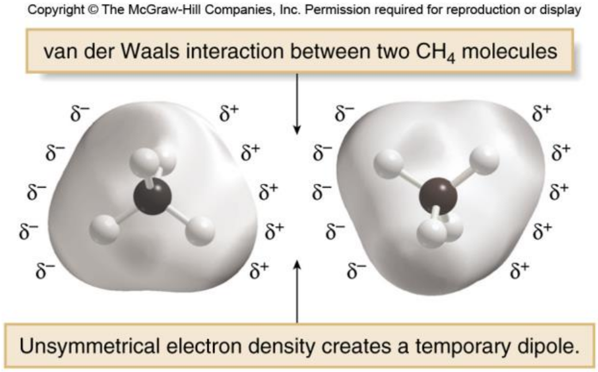

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van der Waals Forces and Surface Area

- All compounds exhibit van der Waals forces.
- The larger the surface area of a molecule, the larger the attractive force between two molecules, and the stronger the intermolecular forces.

Figure 3.1

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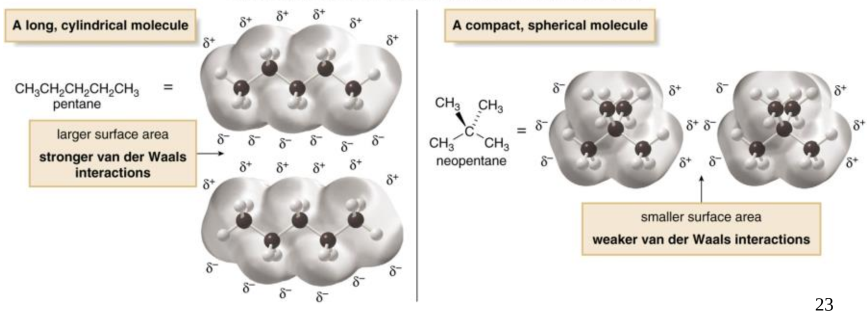

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van der Waals Forces and Polarizability

- **Polarizability** is a measure of how the electron cloud around an atom responds to changes in its electronic environment.

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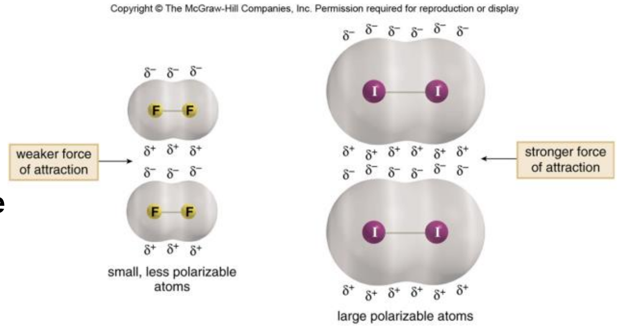
Larger atoms, like iodine, which have more loosely held valence electrons, are more polarizable than smaller atoms like fluorine, which have more tightly held electrons.



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Dipole-Dipole Interactions

- **Dipole-dipole interactions** are the attractive forces between the permanent dipoles of two polar molecules.
- **The dipoles in adjacent molecules (e.g., acetone below) align so that the partial positive and partial negative charges are in close proximity.**
- **These attractive forces caused by permanent dipoles are much stronger than weak van der Waals forces.**

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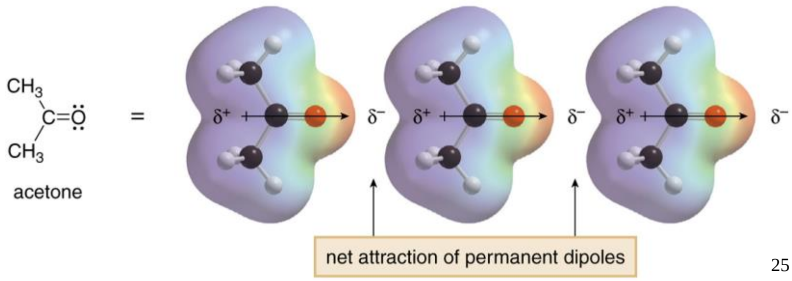

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Hydrogen Bonding

- **Hydrogen bonding** typically occurs when a hydrogen atom bonded to O, N, or F, is electrostatically attracted to a lone pair of electrons on an O, N, or F atom in another molecule.
- **Hydrogen bonding is the strongest of the three types of intermolecular forces.**

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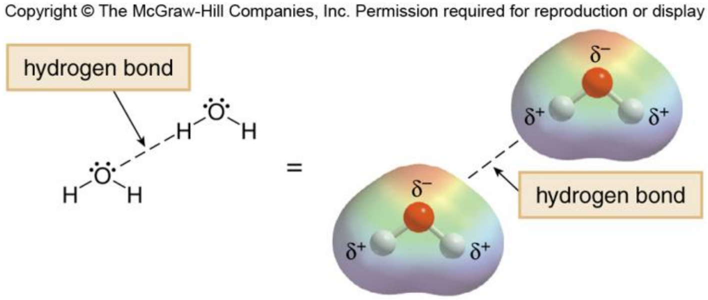

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Intermolecular Forces—Summary

As the polarity of an organic molecule increases, so does the strength of its intermolecular forces.

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Table 3.4 Summary of Types of Intermolecular Forces

Type of force	Relative strength	Exhibited by	Example
van der Waals	weak	all molecules	$CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2OH$
dipole–dipole	moderate	molecules with a net dipole	$CH_3CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2OH$
hydrogen bonding	strong	molecules with an O–H, N–H, or H–F bond	$CH_3CH_2CH_2CH_2OH$
ion–ion	very strong	ionic compounds	NaCl, LiF

Physical Properties—Boiling Point

- **The boiling point of a compound is the temperature at which liquid molecules are converted into gas.**
- **In boiling, energy is needed to overcome the attractive forces in the more ordered liquid state.**
- **The stronger the intermolecular forces, the higher the boiling point.**
- **For compounds with approximately the same molecular weight:**

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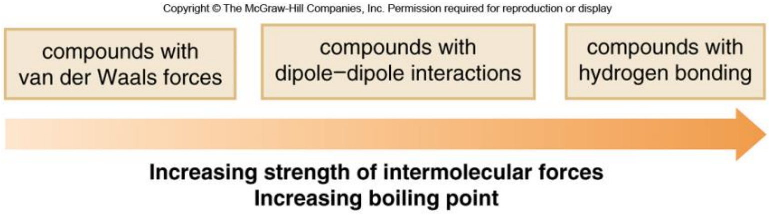

Boiling Point and Intermolecular Forces

- The relative strength of the intermolecular forces increases from pentane to butanal to 1-butanol.
- The boiling points of these compounds increase in the same order.

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$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2CH_2OH$
pentane	butanal	1-butanol
bp = 36 °C	bp = 76 °C	bp = 118 °C

Increasing strength of intermolecular forces
Increasing boiling point

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Other Factors Affecting Boiling Points

- For compounds with similar functional groups:
  - The larger the surface area, the higher the boiling point.
  - The more polarizable the atoms, the higher the boiling point.

Figure 3.2

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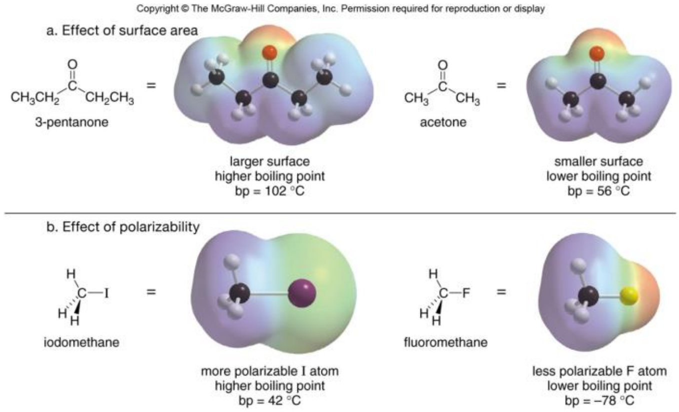

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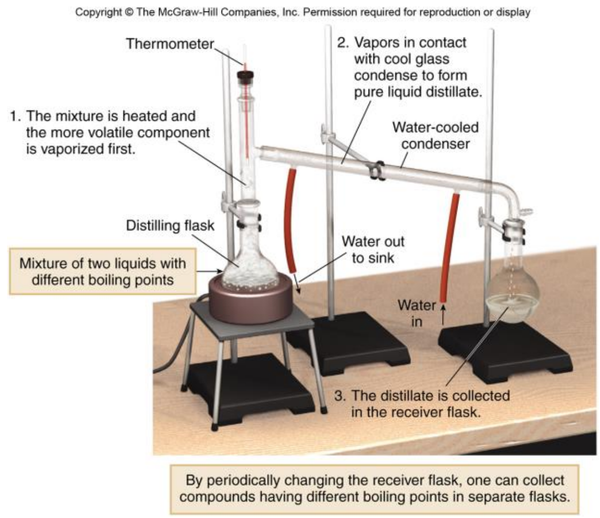
Separation of Liquids Having Different Boiling Points

Figure 3.3
Distillation Apparatus



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Melting Point

- **The melting point is the temperature at which a solid is converted to its liquid phase.**
- **In melting, energy is needed to overcome the attractive forces in the more ordered crystalline solid.**
- **The stronger the intermolecular forces, the higher the melting point.**
- **Given the same functional group, the more symmetrical the compound, the higher the melting point.**

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Melting Point Trends

- **For covalent molecules of approximately the same molecular weight, the melting point depends upon the identity of the functional group.**
- **The stronger the intermolecular attraction, the higher the melting points (the same is true for boiling points).**

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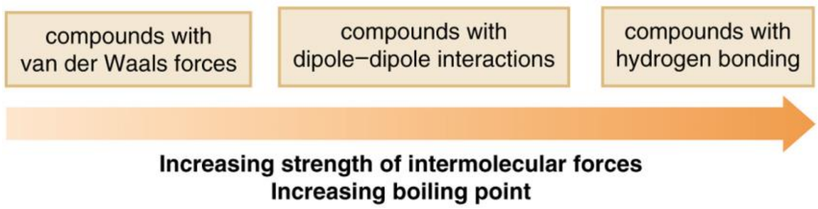

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Effect of Symmetry on Melting Points

- **For compounds having the same functional group and similar molecular weights, the more compact and symmetrical the shape, the higher the melting point.**
- **A compact symmetrical molecule like neopentane packs well into a crystalline lattice whereas isopentane does not.**
- **Neopentane has a much higher melting point than isopentane.**

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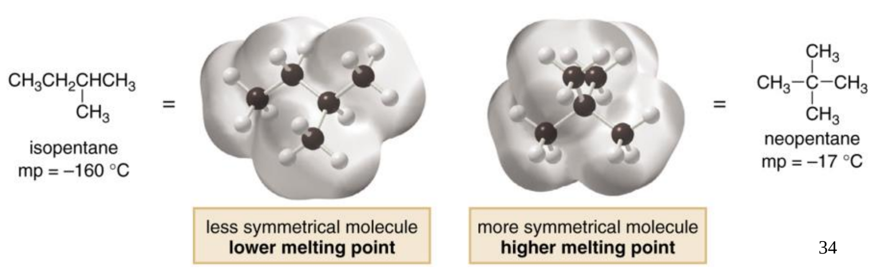

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Solubility

- **Solubility** is the extent to which a compound, called a solute, dissolves in a liquid, called a solvent.
- **The energy needed to break up the interactions between the molecules or ions of the solute comes from new interactions between the solute and the solvent.**

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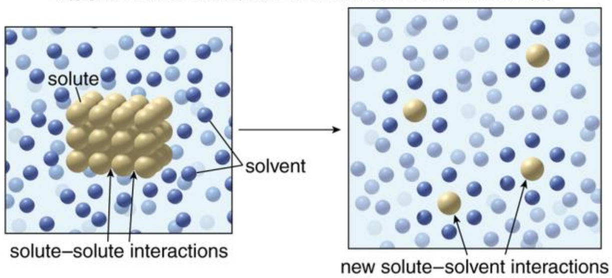

Energy comes from the new interactions of the solute with the solvent.

Solubility Trends

- **Compounds dissolve in solvents having similar kinds of intermolecular forces -- “Like dissolves like.”**
  - **Polar compounds dissolve in polar solvents like water or alcohols capable of hydrogen bonding with the solute.**
  - **Nonpolar or weakly polar compounds dissolve in:**
    - **nonpolar solvents (e.g., carbon tetrachloride and hexane).**
    - **weakly polar solvents (e.g., diethyl ether).**

Solubility of Ionic Compounds

- Most ionic compounds are soluble in water, but insoluble in organic solvents.
- To dissolve an ionic compound, the strong ion-ion interactions must be replaced by many weaker ion-dipole interactions.

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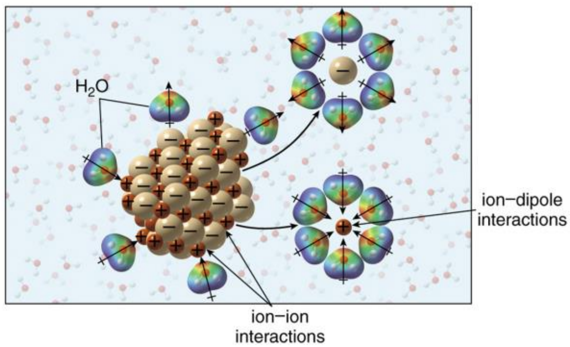
Figure 3.4



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Solubility of Organic Molecules

- An organic compound is water soluble only if it contains one polar functional group capable of hydrogen bonding with the solvent for every five C atoms it contains.
- For example, compare the solubility of butane and acetone in H_2O and CCl_4.

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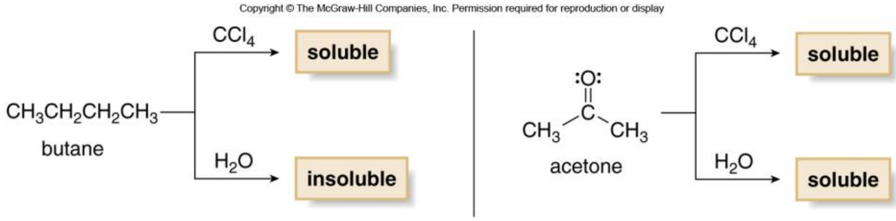

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Butane and Acetone Solubility

- Since butane and acetone are both organic compounds, they are soluble in the organic solvent CCl_4.
- Butane, which is nonpolar, is insoluble in H_2O.
- Acetone is soluble in H_2O because it contains only three C atoms and its O atom can hydrogen bond with an H atom of H_2O.

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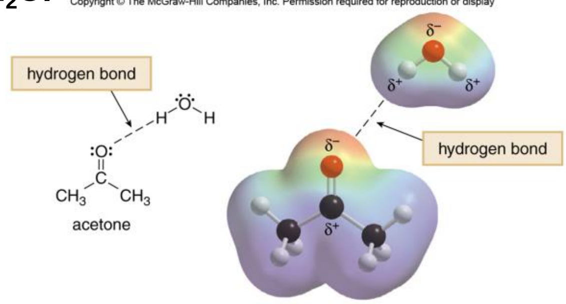

Hydrogen bonding makes the small polar molecule acetone H_2O soluble.

Water Solubility of Organic Molecules

- The size of an organic molecule with a polar functional group determines its water solubility.
- A low molecular weight alcohol like ethanol is water soluble.
- Cholesterol, with 27 carbon atoms and only one OH group, has a carbon skeleton that is too large for the OH group to solubilize by hydrogen bonding.
- Therefore, cholesterol is insoluble in water.

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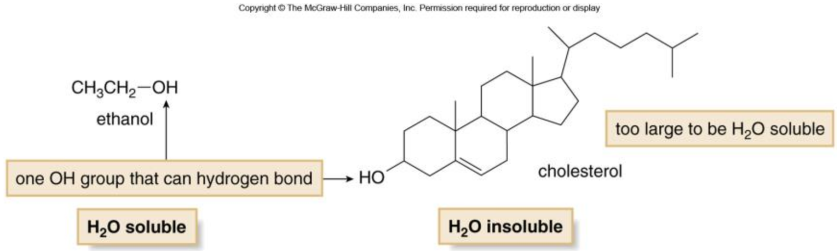

Hydrophobic and Hydrophilic

- The nonpolar part of a molecule that is not attracted to H_2O is said to be **hydrophobic**.
- The polar part of a molecule that can hydrogen bond to H_2O is said to be **hydrophilic**.
- In cholesterol, for example, the hydroxy group is hydrophilic, whereas the carbon skeleton is hydrophobic.

Solubility Properties of Representative Compounds

Figure 3.5

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Type of compound	Solubility in H_2O	Solubility in organic solvents (such as CCl_4)
• Ionic		
NaCl	**soluble**	**insoluble**
• Covalent		
$CH_3CH_2CH_2CH_3$	**insoluble** (no N or O atom to hydrogen bond to H_2O)	**soluble**
$CH_3CH_2CH_2OH$	**soluble** (≤ 5 C's and an O atom for hydrogen bonding to H_2O)	**soluble**
$CH_3(CH_2)_{10}OH$	**insoluble** (> 5 C's; too large to be soluble even though it has an O atom for hydrogen bonding to H_2O)	**soluble**

Application—Vitamins

- **Vitamins** are organic compounds needed in small amounts for normal cell function.
- **Most cannot be synthesized in our bodies, and must be obtained from the diet.**
- **Most are identified by a letter, such as A, C, D, E, and K.**
- **There are several different B vitamins, so a subscript is added to distinguish them. Examples are B_1, B_2, and B_{12}.**
- **Vitamins can be fat soluble or water soluble depending on their structure.**

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Vitamin A

- **Vitamin A is an essential component of the vision receptors in our eyes.**
- **Vitamin A, or retinol, may be obtained directly from the diet.**
- **It also can be obtained from the conversion of β-carotene, the orange pigment found in many plants including carrots, into vitamin A in our bodies.**
- **Vitamin A is water insoluble because it contains only one OH group and 20 carbon atoms.**

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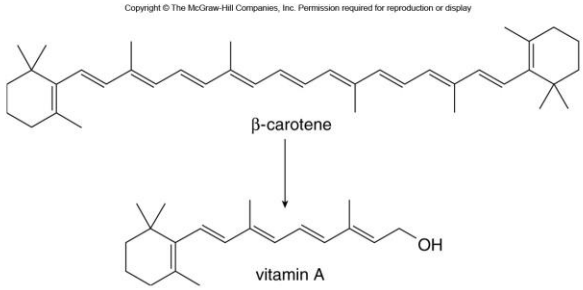

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Vitamin C

- Vitamin C, ascorbic acid, is important in the formation of collagen.
- Most animals can synthesize vitamin C.
- Humans must obtain this vitamin from dietary sources, such as citrus fruits.
- Each carbon atom is bonded to an oxygen which makes it capable of hydrogen bonding, and thus, water soluble.

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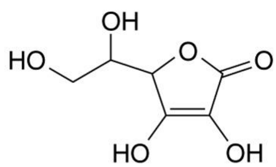

vitamin C
(ascorbic acid)

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Soap Structure

•Soap molecules have two distinct parts:

- There is a hydrophilic portion composed of ions called the polar head.
- There is a hydrophobic carbon chain of nonpolar C-C and C-H bonds, called the nonpolar tail.

Figure 3.6

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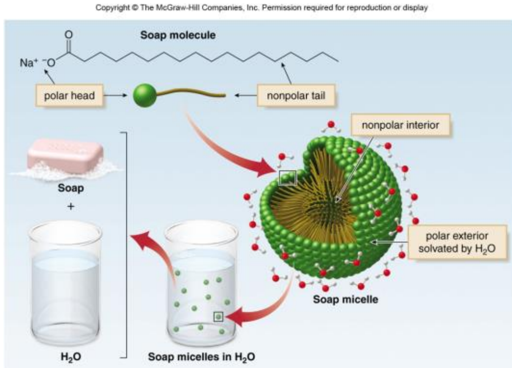

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Structure of the Cell Membrane

- Phospholipids contain an ionic or polar head, and two long nonpolar hydrocarbon tails.
- In an aqueous environment, phospholipids form a lipid bilayer, with the polar heads oriented toward the aqueous exterior and the nonpolar tails forming a hydrophobic interior.

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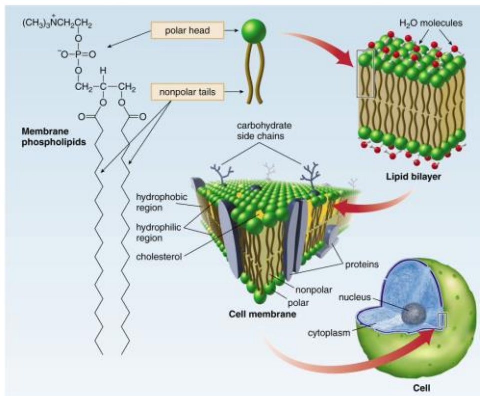
Figure 3.7



Transport Across the Cell Membrane:

- **Ionophores** are organic molecules that complex cations.
- They have a hydrophobic exterior that makes them soluble in the nonpolar interior of the cell membrane, and a central cavity with several oxygens whose lone pairs complex with a given ion.

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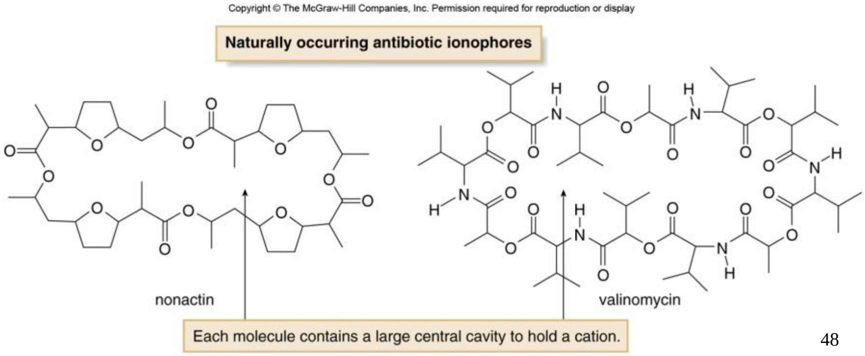

Transport Across The Cell Membrane

- **An ionophore transports an ion across a cell membrane (from the side of higher concentration of the ion to a side of lower ion concentration).**

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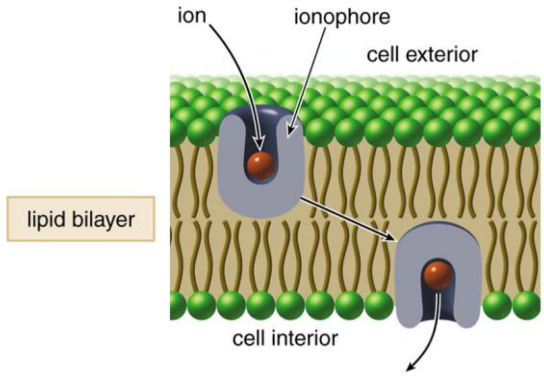
Figure 3.8



Crown Ethers

- **Several synthetic ionophores have also been prepared, including one group called crown ethers.**
- **Crown ethers are cyclic ethers containing several oxygen atoms that bind specific cations depending on the size of their cavity.**

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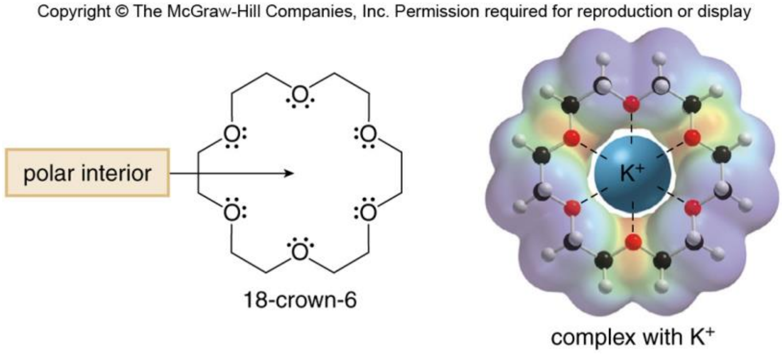

Functional Groups and Electrophiles

- **All functional groups contain a heteroatom, a π bond or both.**
- **These features create electrophilic sites and nucleophilic sites in a molecule.**
- **Electron-rich sites (nucleophiles) react with electron poor sites (electrophiles).**
- **An electronegative heteroatom like N, O, or X makes a carbon atom electrophilic as shown below.**

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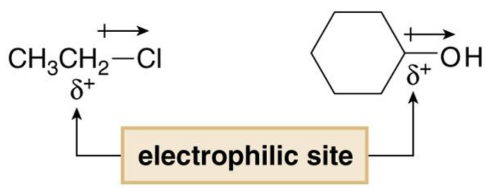

Nucleophilic Sites in Molecules

- **A lone pair on a heteroatom makes it basic and nucleophilic.**

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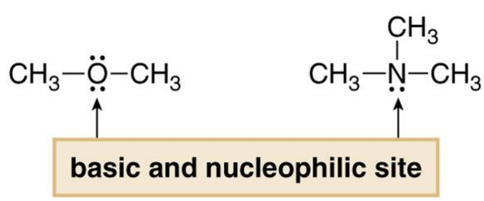

- **π bonds create nucleophilic sites and are more easily broken than σ bonds.**

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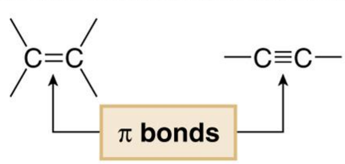

Reaction of π Bonds with Electrophiles

- **An electron-rich carbon reacts with an electrophile, symbolized as E^+.**
- **For example, alkenes contain an electron-rich double bond, and so they react with electrophiles E^+.**

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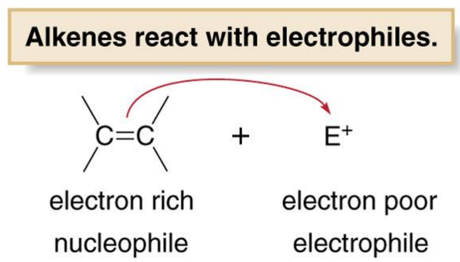

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Reaction of Nucleophiles with Electrophiles

Alkyl halides possess an electrophilic carbon atom, so they react with electron-rich nucleophiles.

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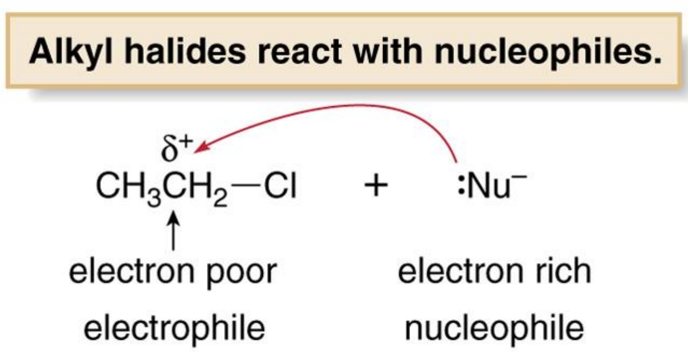

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Biomolecules

- Biomolecules are organic compounds found in biological systems.
- Many are relatively small with molecular weights of less than 1000 g/mol.
- Biomolecules often have several functional groups.

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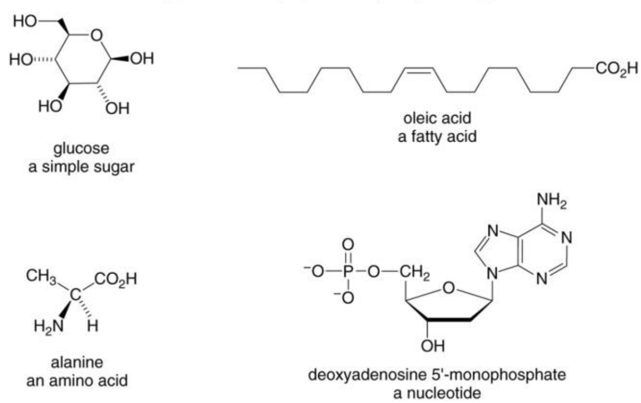

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Families of Biomolecules

- There are four main families of small biomolecules:
    - Simple sugars—combine to form complex carbohydrates like starch and cellulose (Covered in Chapter 28)
    - Amino acids—join together to form proteins (Chapter 29)
    - Nucleotides—combine to form DNA (Chapter 28)
    - Lipids—commonly form from fatty acids and alcohols (Chapters 10, 22, and 30)

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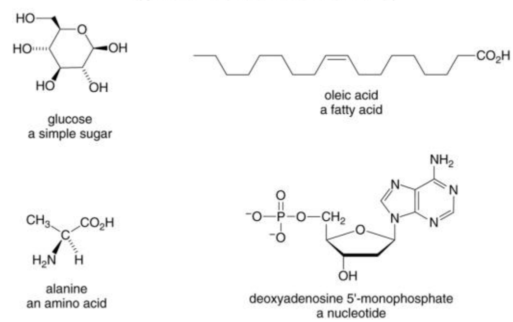

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DNA Double Helix

- DNA is contained in the chromosomes in the nucleus of the cell
  - Stores all the genetic information in an organism
  - Consists of two long strands of polynucleotides held together by hydrogen bonding

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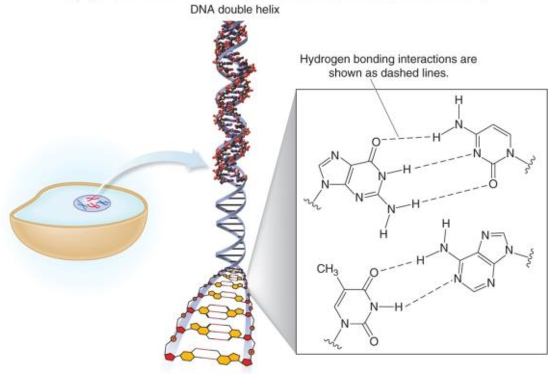
Figure 3.9



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