

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
- 3.3 Intermolecular Forces
- 3.4 Physical Properties
- 3.5 Application: Vitamins
- 3.6 Application of Solubility: Soap
- 3.7 Application: The Cell Membrane
- 3.8 Functional Groups and Reactivity
- Biomolecules

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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.

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Functional Groups

- Functional groups distinguish one organic molecule from another.
- They determine a molecule's:
 - **geometry**
 - **physical properties**
 - **reactivity**

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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.

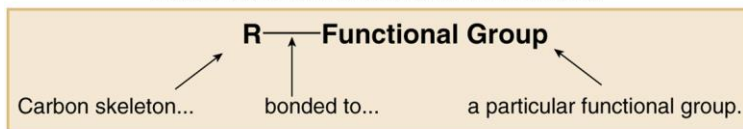
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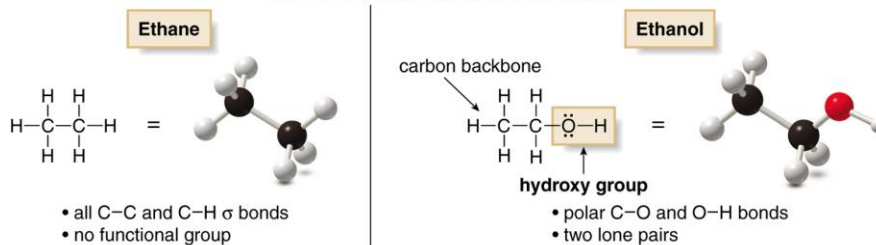
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Parts of a Functional Group

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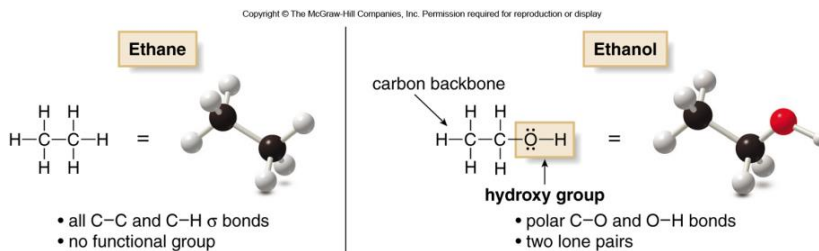
Ethane, a Molecule with No Functional Group

- 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.

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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			double bond
Alkyne	$-C\equiv C-$	$H-C\equiv C-H$	triple bond
Aromatic compound			phenyl group

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Aliphatic Hydrocarbons

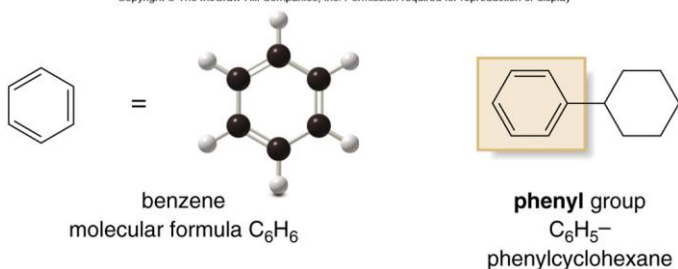
- Aliphatic hydrocarbons have three subgroups.
 - Alkanes have only $C-C$ σ bonds and no functional group.
 - Alkenes have a $C-C$ double bond.
 - Alkynes have a $C-C$ triple bond.

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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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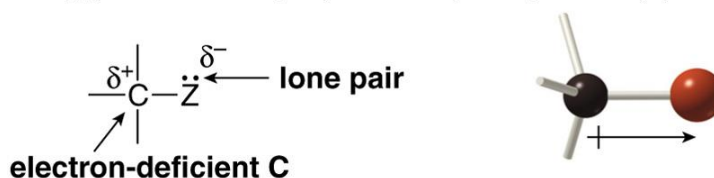


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Functional Groups with Carbon-Heteroatom (C-Z) σ bonds

- 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	$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}$ (X = F, Cl, Br, I)	$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}$		-X halo group
Alcohol	$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H$	$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H$		-OH hydroxy group
Ether	$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-R$	$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH_3$		-OR alkoxy group
Amine	$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}H_2$ or $R_2\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}H$ or $R_3\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}$	$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}H_2$		-NH ₂ amino group
Thiol	$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}H$	$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}H$		-SH mercapto group
Sulfide	$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-R$	$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-CH_3$		-SR alkylthio group

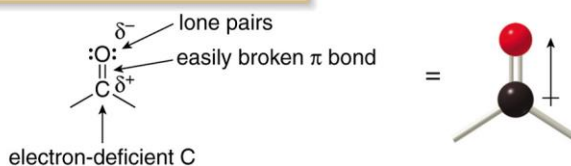
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Functional Groups with C=O Group

- 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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Reactive features of a carbonyl group



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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	$\text{R}-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{H}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{H}$		C=O carbonyl group
Ketone	$\text{R}-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{R}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{CH}_3$		C=O carbonyl group
Carboxylic acid	$\text{R}-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{OH}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{OH}$		-COOH carboxy group
Ester	$\text{R}-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{OR}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{OCH}_3$		-COOR
Amide	$\text{R}-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{N}(\text{H or R})_2$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{NH}_2$		-CONH ₂ , -CONHR, or -CONR ₂
Acid chloride	$\text{R}-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{Cl}$	$\text{CH}_3-\overset{\text{:O:}}{\underset{\text{ }}{\text{C}}}-\text{Cl}$		-COCl

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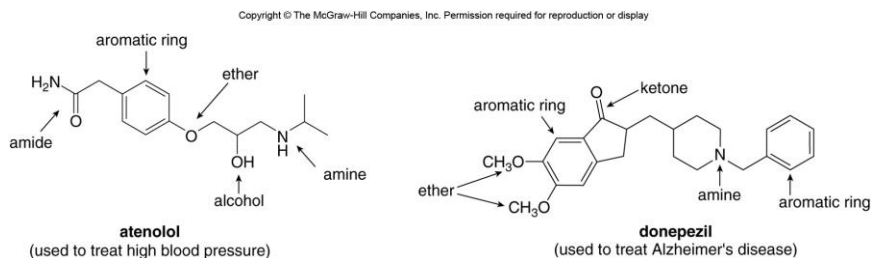
Importance of Functional Groups

A functional group determines all of the following properties of a molecule:

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

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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

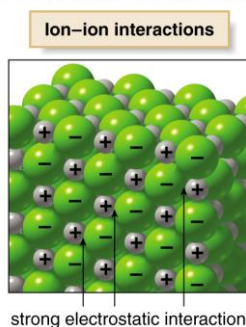
- **Intermolecular forces** are interactions that exist between molecules.
- Functional groups determine the type and strength of these interactions.
- Ionic and covalent compounds have very different intermolecular interactions.

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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

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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.

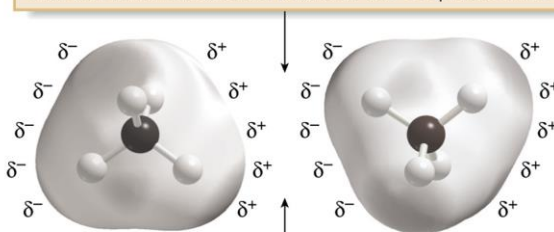
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van der Waals Forces in Methane

- 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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van der Waals interaction between two CH_4 molecules



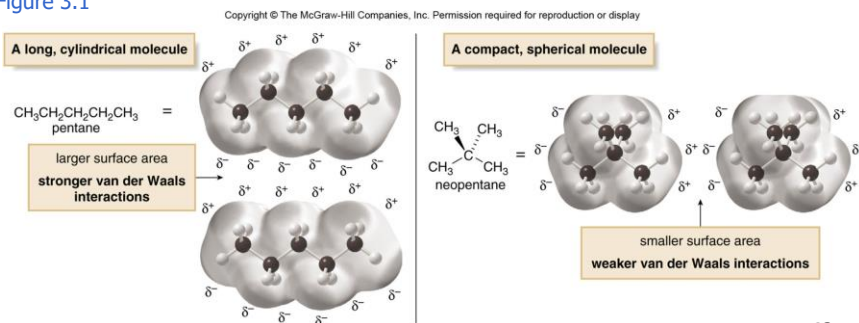
Unsymmetrical electron density creates a temporary dipole.

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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

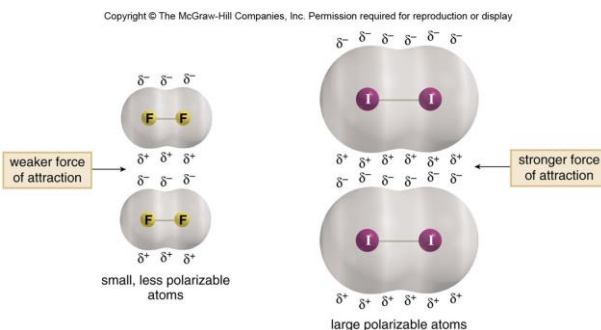


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van der Waals Forces and Polarizability

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

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.

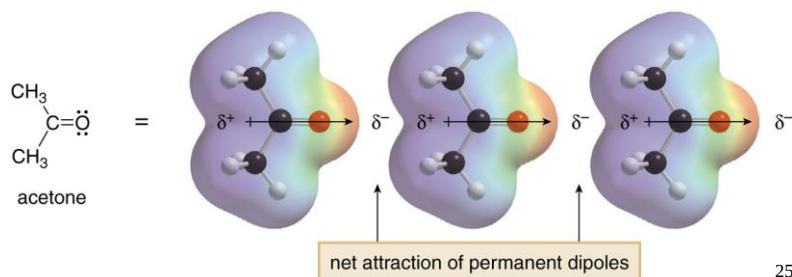


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Dipole-Dipole Interactions

- **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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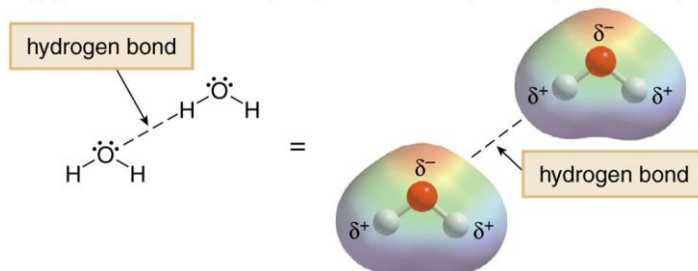


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Hydrogen Bonding

- **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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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

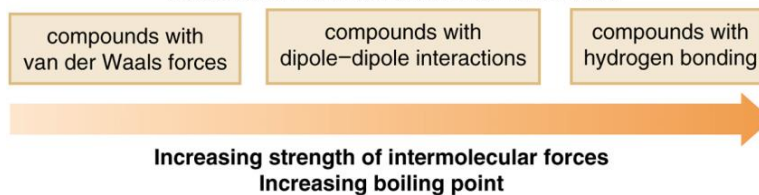
Type of force	Relative strength	Exhibited by	Example
van der Waals	weak	all molecules	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃ CH ₃ CH ₂ CH ₂ CHO CH ₃ CH ₂ CH ₂ CH ₂ OH
dipole–dipole	moderate	molecules with a net dipole	CH ₃ CH ₂ CH ₂ CHO CH ₃ CH ₂ CH ₂ CH ₂ OH
hydrogen bonding	strong	molecules with an O–H, N–H, or H–F bond	CH ₃ CH ₂ CH ₂ CH ₂ OH
ion–ion	very strong	ionic compounds	NaCl, LiF

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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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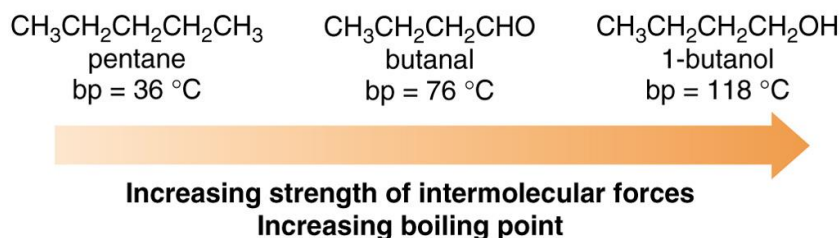


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Boiling Point and Intermolecular Forces

- 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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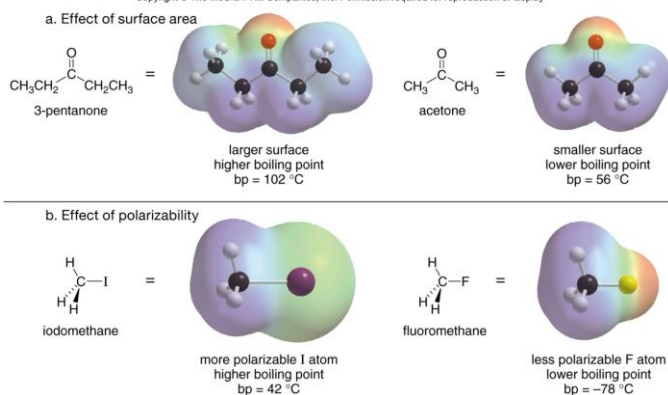
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Other Factors Affecting Boiling Points

- 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

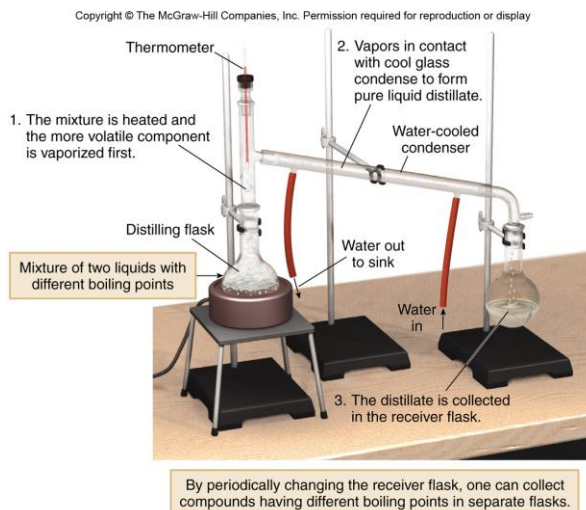
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Separation of Liquids Having Different Boiling Points

Figure 3.3
Distillation Apparatus



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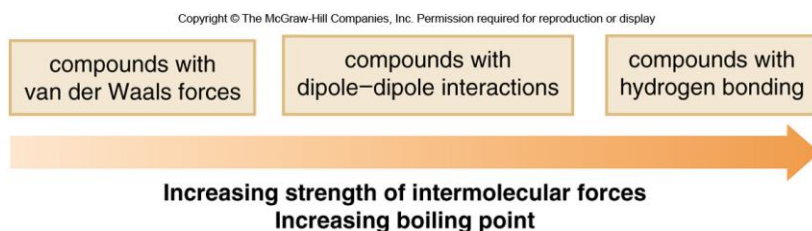
Melting Point

- 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).

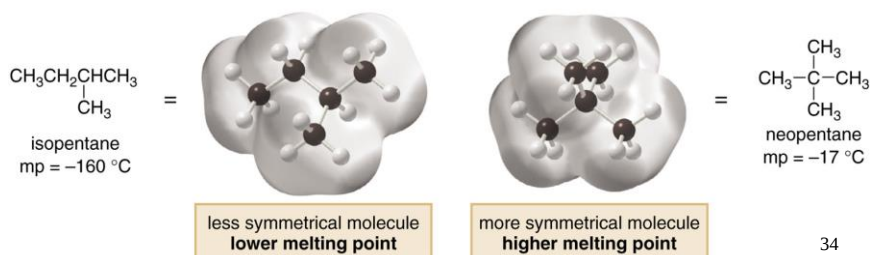


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Effect of Symmetry on Melting Points

- 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.

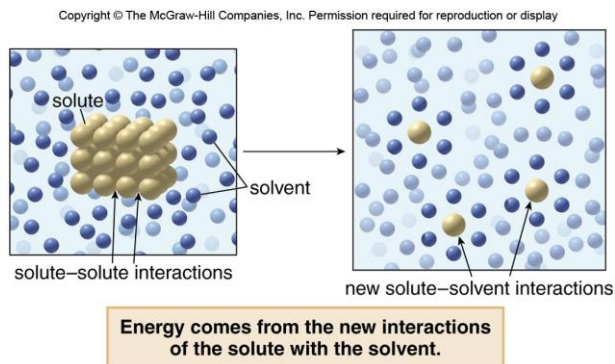
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Solubility

- **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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Solubility Trends

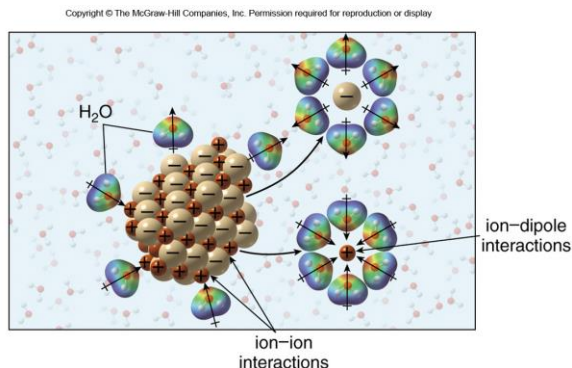
- Compounds dissolve in solvents having similar kinds of intermolecular forces -- “Like dissolves like.”
 - Polar compounds dissolve in polar solvents like water or alcohols capable of hydrogen bonding with the solute.
 - Nonpolar or weakly polar compounds dissolve in:
 - nonpolar solvents (e.g., carbon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

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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.

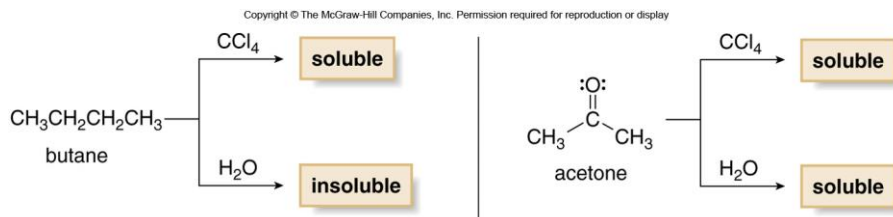
Figure 3.4



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Solubility of Organic Molecules

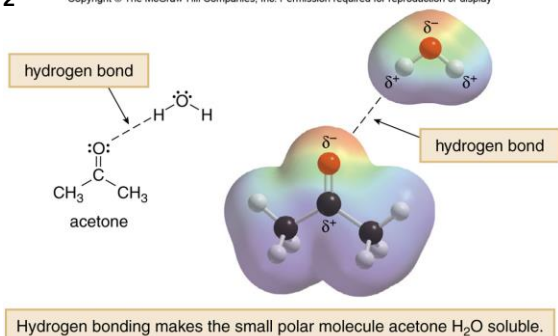
- An organic compound is water soluble only if it contains one polar functional group capable of hydrogen bonding with the solvent for every five C atoms it contains.
- For example, compare the solubility of butane and acetone in H₂O and CCl₄.



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Butane and Acetone Solubility

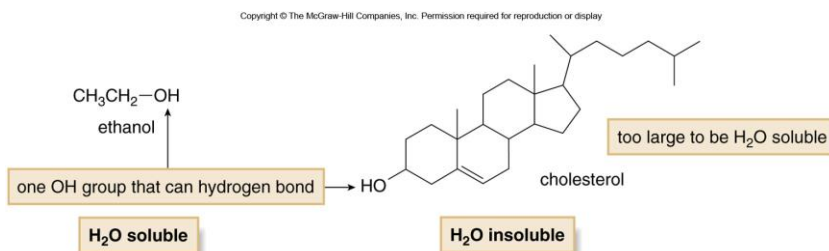
- Since butane and acetone are both organic compounds, they are soluble in the organic solvent CCl_4 .
- Butane, which is nonpolar, is insoluble in H_2O .
- Acetone is soluble in H_2O because it contains only three C atoms and its O atom can hydrogen bond with an H atom of H_2O .



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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.

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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 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	insoluble (no N or O atom to hydrogen bond to H_2O)	soluble
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	soluble (≤ 5 C's and an O atom for hydrogen bonding to H_2O)	soluble
$\text{CH}_3(\text{CH}_2)_{10}\text{OH}$	insoluble (> 5 C's; too large to be soluble even though it has an O atom for hydrogen bonding to H_2O)	soluble

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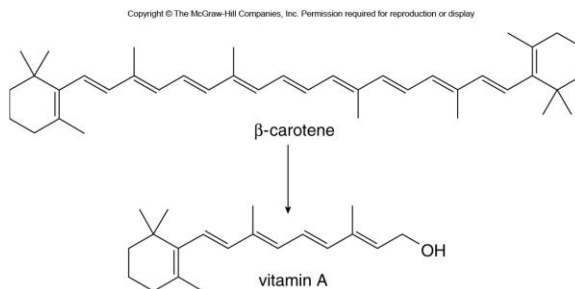
Application—Vitamins

- **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 B₁, B₂, and B₁₂.
- 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.

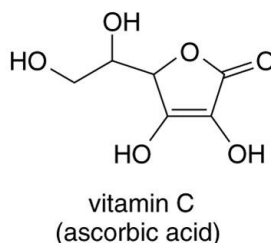


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Vitamin C

- 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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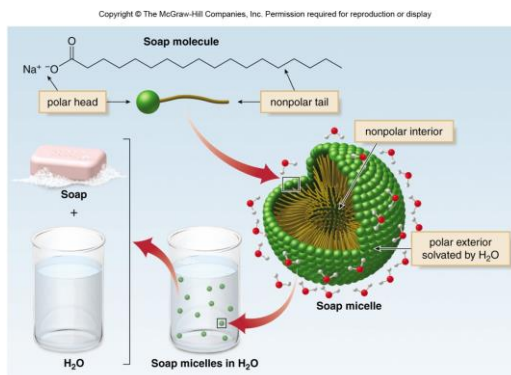


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Soap Structure

- 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

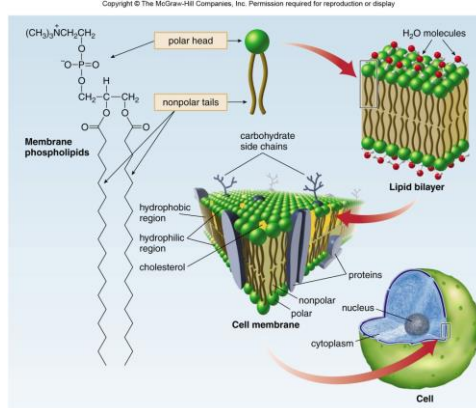


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Structure of the Cell Membrane

- 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.

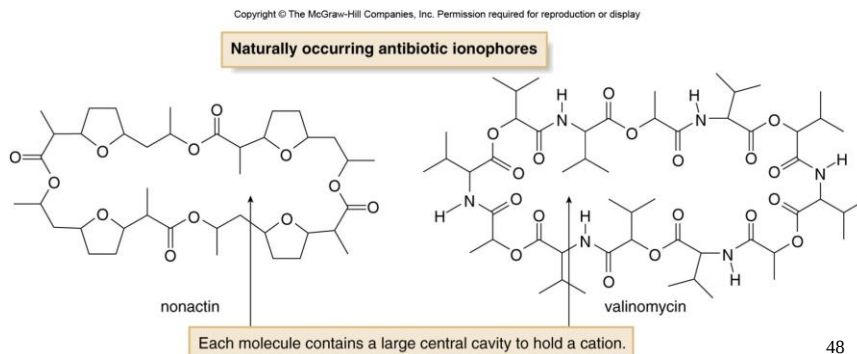
Figure 3.7



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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.

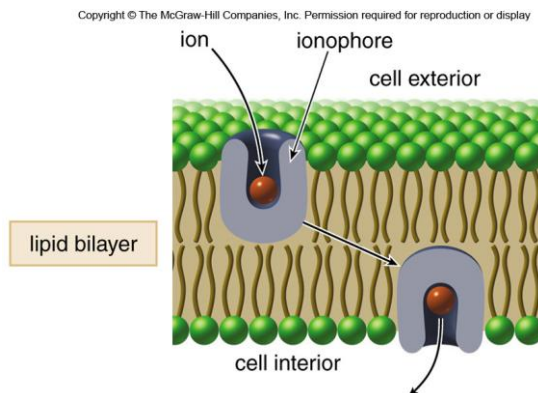


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Transport Across The Cell Membrane

- 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).

Figure 3.8

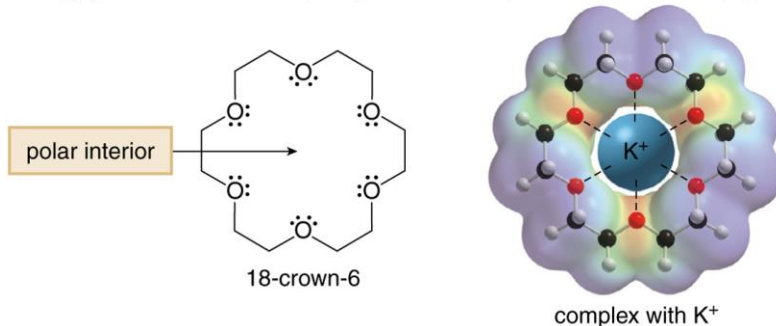


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Crown Ethers

- 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.

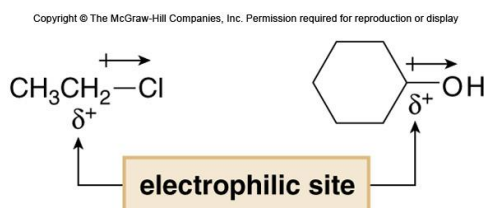
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Functional Groups and Electrophiles

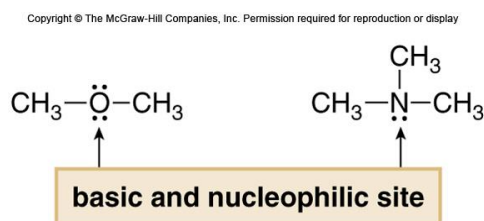
- All functional groups contain a heteroatom, a π bond or both.
- These features create electrophilic sites and nucleophilic sites in a molecule.
- Electron-rich sites (nucleophiles) react with electron poor sites (electrophiles).
- An electronegative heteroatom like N, O, or X makes a carbon atom electrophilic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



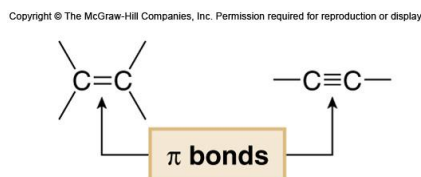
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Nucleophilic Sites in Molecules

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



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



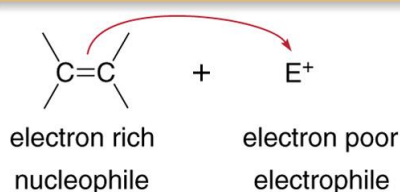
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Reaction of π Bonds with Electrophiles

- 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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Alkenes react with electrophiles.



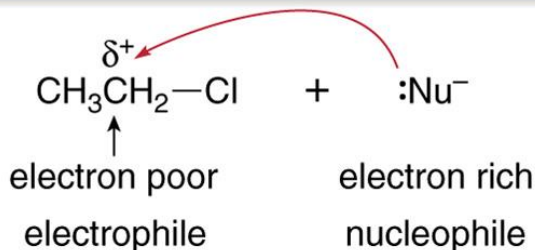
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Reaction of Nucleophiles with Electrophiles

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

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Alkyl halides react with nucleophiles.

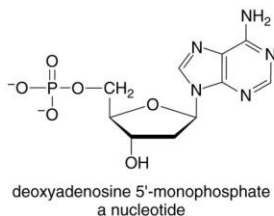
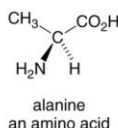
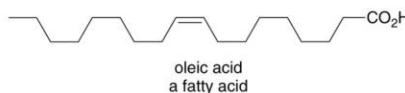
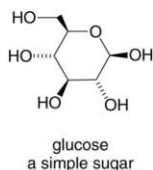


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Biomolecules

- 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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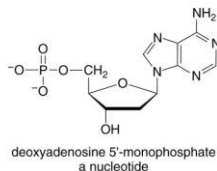
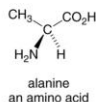
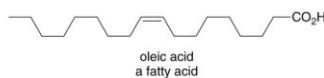
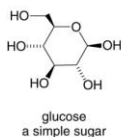


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Families of Biomolecules

- 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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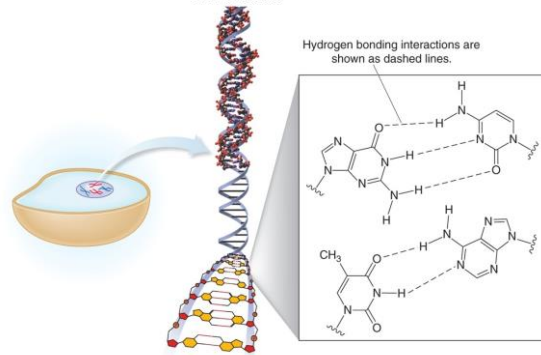
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DNA Double Helix

- 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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DNA double helix

Figure 3.9



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