

Lecture Notes
Chem 51A
S. King

Chapter 3 Introduction to Organic Molecules and Functional Groups

I. Functional Groups

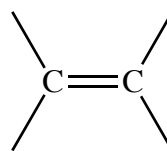
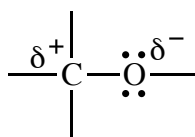
A functional group is an atom or group of atoms with characteristic chemical and physical properties. A functional group contains either heteroatoms or π -bonds.

Heteroatom: An atom other than carbon or hydrogen. Common heteroatoms are nitrogen, oxygen, sulfur, phosphorous, and halogens.

π -bonds: The most common π -bonds occur in C–C and C–O double bonds, and C–C and C–N triple bonds.

How do heteroatoms and π -bonds confer reactivity on a molecule?

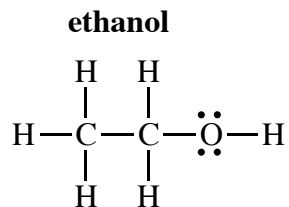
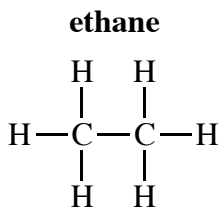
- Heteroatoms have lone pairs and create electron deficient or electron rich sites on a molecule.
- π -bonds are easily broken in chemical reactions. C–C double bonds create electron rich sites in a molecule. A C–C double bond makes a molecule a base and a nucleophile.



C–C and C–H σ -bonds in organic molecules form the carbon backbone to which functional groups are bonded. C–C and C–H σ -bonds are typically unreactive, and, as a result, they are not considered functional groups. They are often designated as R, especially when the focus is on the functional group.

R — Functional group

Compare:



A. An Overview of Functional groups

Most functional groups can be divided into three categories:

- Hydrocarbons containing π -bonds
- Compounds containing a C-Z σ -bond where Z = an electronegative element
- Compounds containing a C=O group or a C \equiv N group

1. Hydrocarbons:

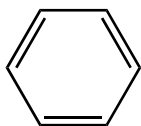
Hydrocarbons are compounds that only contain hydrogen and carbon. They can be **aliphatic** or **aromatic**.

a. **Aliphatic** hydrocarbons can be divide into three categories:

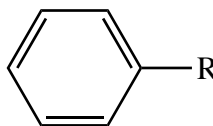
- Alkanes have only C-C σ -bonds and no functional groups.
- Alkenes have a C-C double bond as a functional group.

- Alkynes have a C–C triple bond as a functional group.

- b. **Aromatic** hydrocarbons have a ring containing alternating single and double bonds. The aromatic ring is considered to be a single functional group.



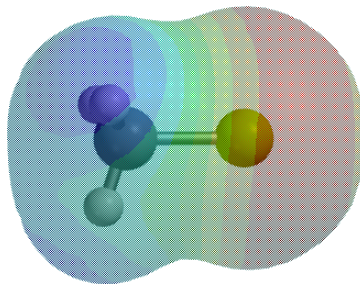
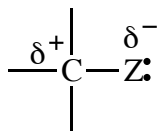
Benzene
molecular formula: C₆H₆



Phenyl group
C₆H₅–

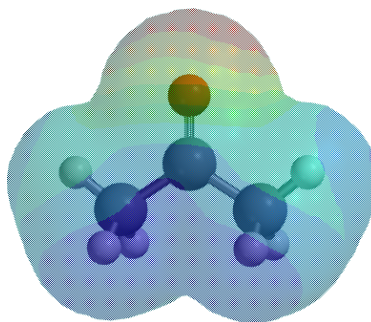
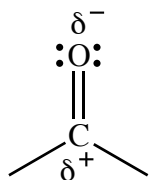
2. Compounds containing C–Z single bonds (**Table 1**):

These compounds contain an electronegative heteroatom **Z** that creates a polar bond, making carbon electron deficient. The lone pairs on **Z** are also available for reaction with protons and other electrophiles, especially when **Z** = N or O.



3. Compounds containing C=O double bonds & C≡N triple bonds (**Table 2**):

- a. Compounds containing C=O double bonds very important in organic chemistry. The polar C=O double bond (**a carbonyl group**) makes the carbonyl carbon electron-deficient (electrophilic). The lone pairs on oxygen are nucleophilic and basic. The carbonyl group also contains a π -bond that is easily broken.



- b. Compounds containing C–N triple bonds are also important in organic chemistry. The C–N triple bond (a **nitrile** or **cyano group**) is very polar and makes the C of the cyano group electrophilic. The nitrile group also contains a π -bond that is easily broken.

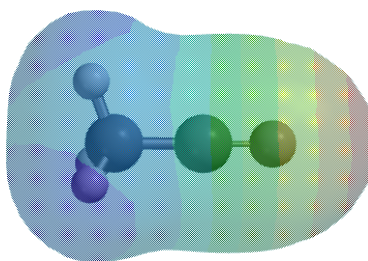
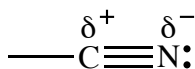


TABLE 1: Compounds Containing Polar C-Z σ -bonds

Compound	Structure	Functional group
alkyl halide	R—X	ξ —X (halo group)
alcohol	R—OH	ξ —OH (hydroxyl group)
ether	R—O—R'	ξ —OR (alkoxy group)
amine	R—NH ₂ , R ₂ NH, R ₃ N	ξ —NH ₂ , ξ —NHR, ξ —NR ₂ (amino group)
thiol	R—SH	ξ —SH (thio group)
sulfide <i>or</i> thioether	R—S—R'	ξ —SR (alkylthio group)

TABLE 2: Compounds Containing a Polar C=O, C≡N, or NO₂ Group

Compound	Structure	Functional group
aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	
ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$	
carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \xi-\text{C}-\text{OH} \end{array} \text{ (carboxy group)}$
ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array}$	
amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{H (or R)} \\ \\ \text{H (or R)'} \end{array}$	
acid chloride	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$	
anhydride	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R}' \end{array}$	
nitrile	$\text{R}-\text{C}\equiv\text{N}$	$\xi-\text{C}\equiv\text{N} \text{ (cyano group)}$
nitro compound	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N}^{\oplus}-\text{O}^{\ominus} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---N}^{\oplus}-\text{O}^{\ominus} \end{array} \text{ (nitro group)}$

Functional groups are *extremely* important. They determine all the following properties of a molecule:

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

II. Intermolecular Forces

Intermolecular forces are the interactions that exist ~~between~~ molecules. Functional groups determine the type and strength of these 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.

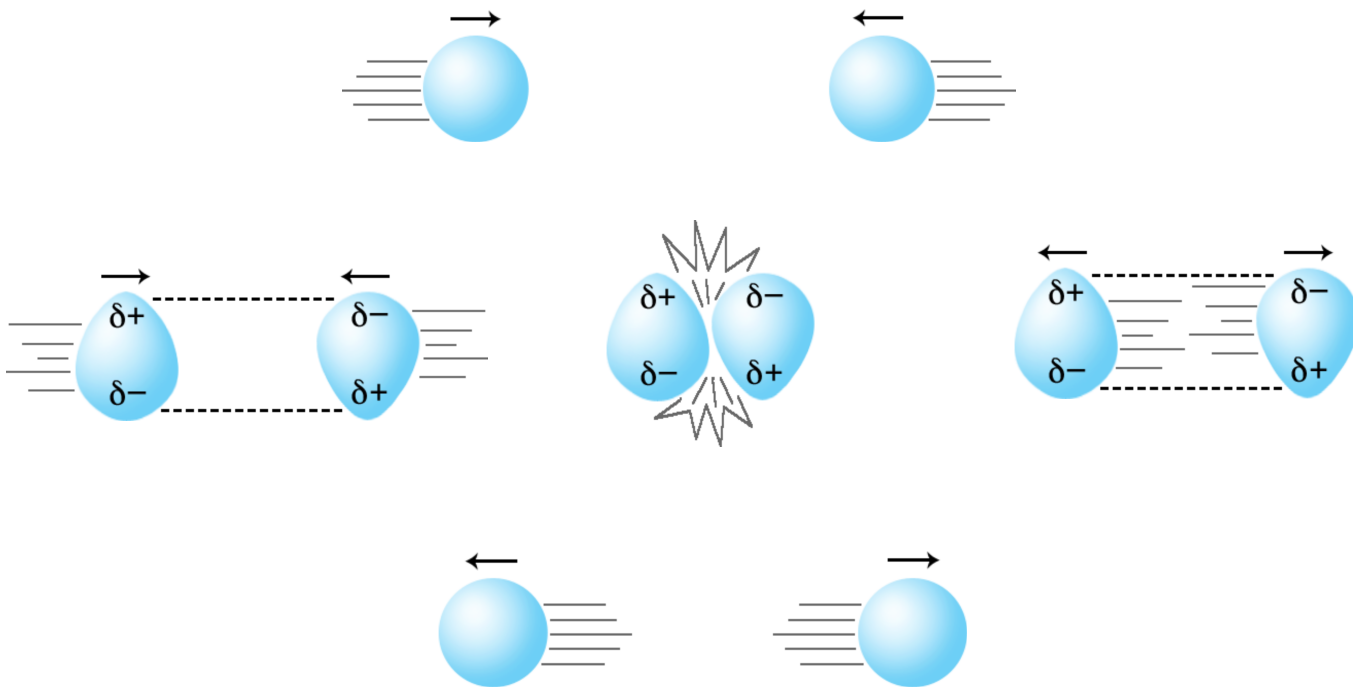
There are ~~three~~ types of intermolecular forces between covalent compounds:

- van der Waals forces
- dipole-dipole interactions
- hydrogen bonding

A. van der Waals Forces

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

How does this attractive force work? Small temporary dipoles induce opposite attractive dipoles in surrounding molecules:



There are two important factors that affect the strength of van der Waals forces.

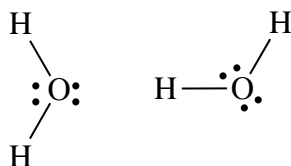
1. **Surface area:** The larger the surface area, the larger the attractive force between two molecules, and the stronger the intermolecular forces.
2. **Polarizability:** This is a measure of how the electron cloud around an atom responds to changes in its electronic environment. Larger atoms, like iodine, which have more loosely held valence electrons, are more polarizable than smaller atoms, like fluorine, which have tightly held electrons.

B. Dipole-Dipole Interactions

Molecules with permanent dipole moments are attracted to one another because they can align themselves in such a way that the (+)-end of one dipole is close to the (-)-end of another dipole. These electrostatic forces, called *dipole-dipole interactions*, are *stronger than van der Waals forces, but not as strong as ionic or covalent bonds*.

C. Hydrogen Bonding

Hydrogen bonding occurs when a hydrogen atom bonded to an O, N, or F, is electrostatically attracted to a lone pair of electrons on an O, N, or F atom in another molecule. Hydrogen bonds are the strongest type of intermolecular attraction in covalent molecules, though they are still much weaker than any covalent bond.



- Formation of a hydrogen bond requires two partners, the hydrogen-bond donor (*the atom to which the hydrogen is fully bonded*), and the H-bond acceptor (*the atom to which the hydrogen is partially bonded*).
- The strongest hydrogen bonds are linear: (the two electronegative atoms and the hydrogen between them lie in a straight line.)

IV. Physical Properties

The strength of a compound's intermolecular forces determines many of its physical properties, including its boiling point, melting point, and solubility.

A. Boiling Point (bp)

The boiling point of a compound is the temperature at which a liquid is converted to a gas. In order for a compound to vaporize, the forces that hold the molecules close to each other must be disrupted. This means that the boiling point of a compound depends on the attractive forces between individual molecules.

If molecules are held together by strong forces:

If molecules are held together by weak forces:

Because ionic compounds are held together by extremely strong interactions, they have very high boiling points.

With covalent molecules, the boiling point depends on the functional groups present, the size, the surface area, and the polarizability of any heteroatoms present.

For compounds of *approximately the same molecular weight*:

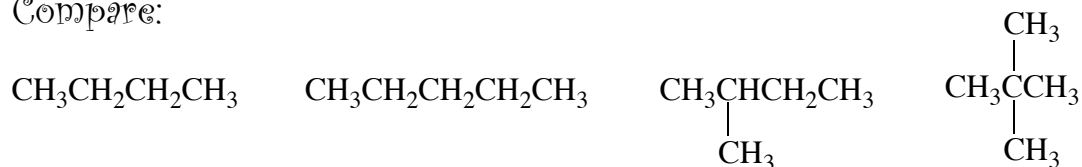
compounds w/
van der Waals forces

compounds with dipole-
dipole interactions

compounds with
hydrogen bonding

Simple hydrocarbons are held together by relatively weak van der Waals forces, and therefore they typically have very low boiling points, unless they are high molecular weight:

Compare:



Notice:

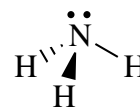
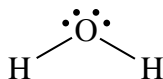
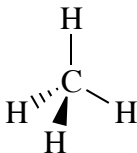
- There is a regular increase in b.p. with increasing molecular weight. *Why?*
- Branching makes a molecule more compact, which reduces surface area and van der Waals attractions.

Ethers generally have higher boiling points than alkanes of comparable molecular weight because both van der Waals forces *and* dipole-dipole-interactions in an ether must be overcome for the ether to boil.



Alcohols and **amines** have much higher boiling points than alkanes or ethers of similar molecular weight, because in addition to van der Waals forces and dipole-dipole interactions they can form hydrogen bonds.

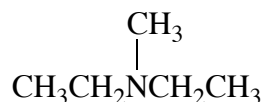
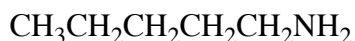
Compare:



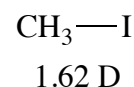
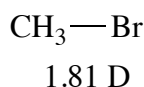
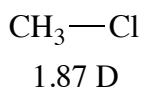
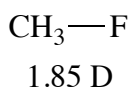
- Nitrogen is not as electronegative as oxygen, so H-bonds between amine molecules are weaker than hydrogen bonds between alcohol molecules.

Because primary amines have two N-H bonds, hydrogen bonding is more important for primary amines than secondary amines. Tertiary amines don't H-bond! **Why?**

Compare:



Both van der Waals forces and dipole-dipole interactions must be overcome for an **alkyl halide** to boil:



Q. Why does methyl fluoride boil at a lower temperature than methyl iodide, even though it has a larger dipole moment?

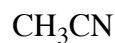
A. *Two reasons:*

1. Iodine is much larger than fluorine.

2. Iodine is more polarizable. *The farther electrons are from the nucleus, the more polarizable they are.*

The following example shows that the rule of hydrogen bonds always being stronger than dipole-dipole attractions isn't always true.

Compare:

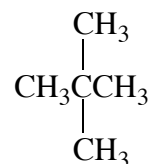
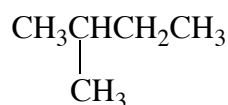


B. Melting Point (mp)

The melting point is the temperature at which a solid is converted into a liquid.

- The stronger the intermolecular forces, the higher the melting point.
- Given the same functional group, the more symmetrical the molecule, the higher the melting point. *Why?*

Compare:



Because ionic compounds are held together by extremely strong interactions, they have very high melting points. With covalent molecules, the melting point once again depends on the identity of the functional group.

For compounds of *approximately the same molecular weight*:

compounds w/
van der Waals forces

compounds with dipole-
dipole interactions

compounds with
hydrogen bonding

C. Solubility

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

Rule of Thumb:

****LIKE DISSOLVES LIKE****

- polar and ionic compounds are soluble in polar solvents.
- nonpolar compounds are soluble in nonpolar or weakly polar solvents

Hydrogen bonding is important in determining the solubility of organic compounds in H₂O.

- Molecules that can participate in hydrogen bonding with water will dissolve in water if the nonpolar part of the molecule (the part made up of C-H bonds) is not too large.

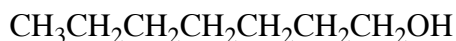
General guidelines:

- An organic compound is water soluble if it contains one hydrogen bond acceptor (O, N or F) for every five carbon atoms.
- A compound is considered soluble when 3 g solute dissolves in 100 mL solvent.

Compare:



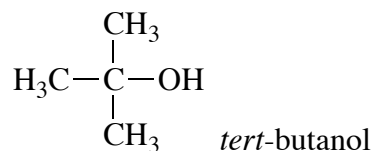
ethanol



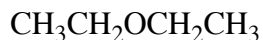
1-hexanol



1-butanol



- Compounds that contain O, N or F but lack O–H, N–H or F–H bonds can participate in hydrogen bonding as hydrogen bond acceptors. *They are less soluble in water than compounds that are both hydrogen bond donors and acceptors.*



7.9g dissolves in
100 ml H₂O

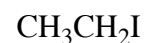


1.9g dissolves in
100 ml H₂O



0.036g dissolves in
100ml H₂O

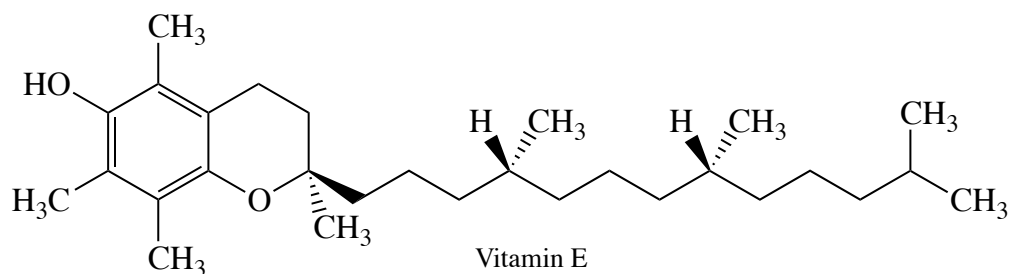
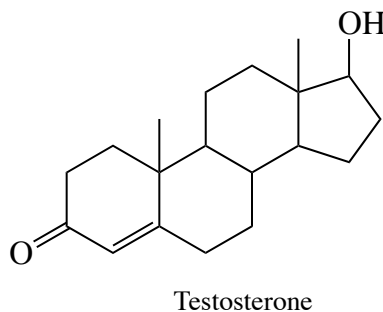
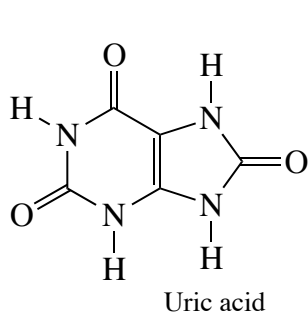
Alkyl halides have some polar character, but only the alkyl fluorides have an atom that can form a hydrogen bond. This means that alkyl fluorides are the most water soluble of the alkyl halides. The other alkyl halides are considerably less soluble than ethers or alcohols with the same number of carbons.



V. Applications

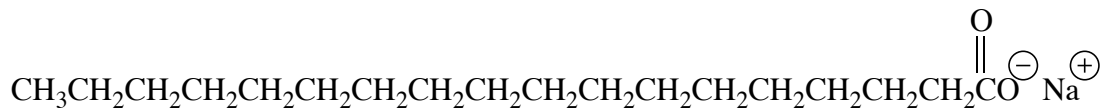
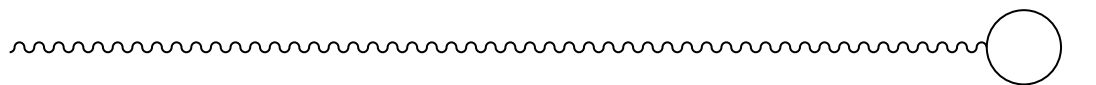
A. Biomolecules

Solubility principals can be applied to biomolecules to determine if they are water soluble or fat soluble.



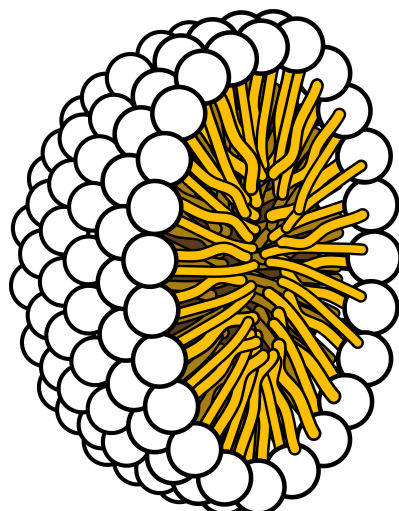
B. Soap

Soap is an example of a surface-active compound (*surfactant*.) Surfactants are molecules with hydrophilic (*ionic*) heads and hydrophobic tails (*greater than 12 carbons in chain*).



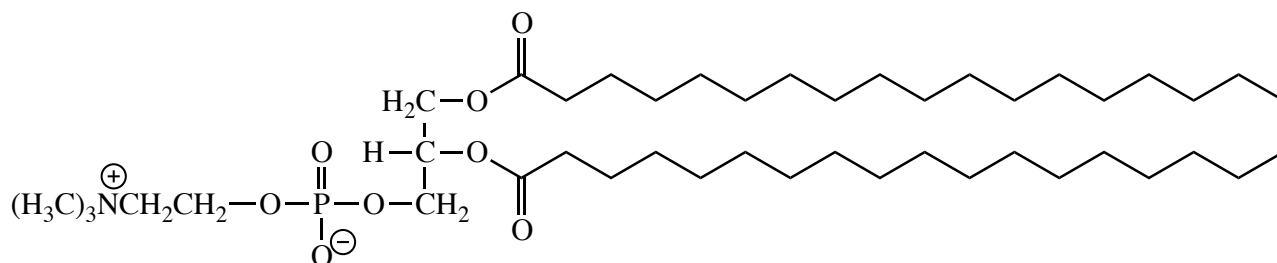
sodium stearate
(sodium octadecanoate)
a soap

Dissolving soap in water forms micelles, spherical droplets having the ionic heads on the surface and the nonpolar tails packed together in the interior.

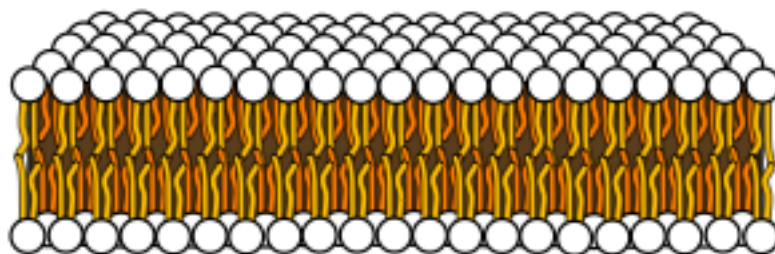


C. Structure of the Cell Membrane

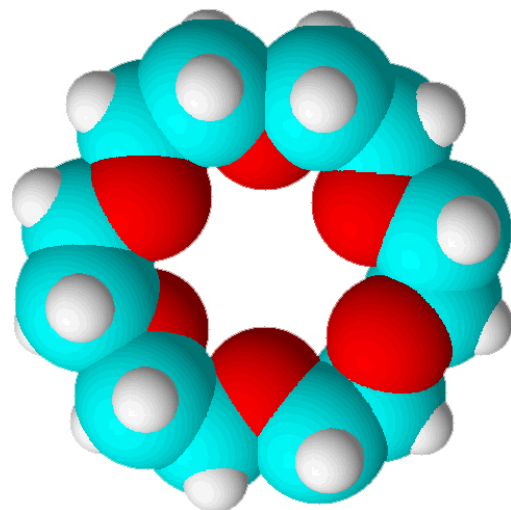
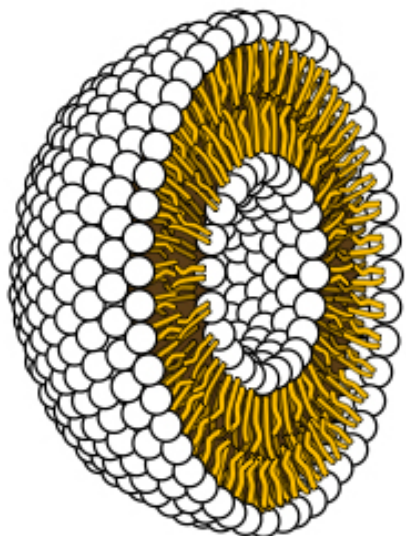
A major component of the cell membrane is a group of organic molecules called phospholipids. Like soap, they contain a hydrophilic ionic portion and a hydrophobic hydrocarbon portion.



When phospholipids are mixed with water, they assemble in an arrangement called a lipid bilayer, with the ionic heads oriented on the outside and the nonpolar tails on the inside. The polar heads interact with the polar solvent water, while the nonpolar tails are held in close proximity by van der Waals attractions:

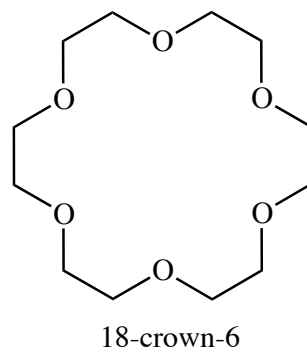
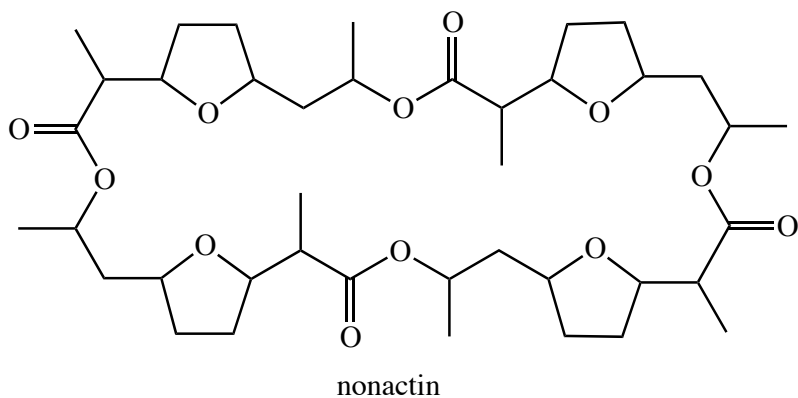


Lipid bilayers can be manipulated in the laboratory to create liposomes, which are similar to micelles, but they have an inner cavity that is hydrophilic. Liposomes can be used to deliver drugs that are hydrophilic in the central cavity and hydrophobic in the lipid interior.



D. Transport Across a Cell Membrane

How are ions transported across the cell membrane? Some ions are transported across the membrane with the help of **ionophores**. 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 oxygen atoms whose lone pairs complex with a given ion.



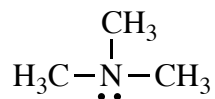
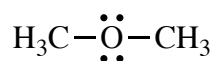
VI. Functional Groups and Reactivity

Functional groups determine the reactivity of a molecule: All functional groups contain a heteroatom, a π -bond, or both, and these features make electron deficient (electrophilic) sites and electron-rich (nucleophilic) sites in the molecule. Molecules react at these sites.

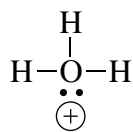
An electronegative heteroatom like N, O, or X makes carbon electrophilic:



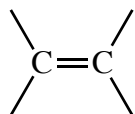
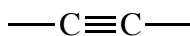
A lone pair on a heteroatom makes it basic and nucleophilic:



An important *EXCEPTION* to this rule: Hydronium ion! The oxygen in hydronium ion is not nucleophilic! *Why not?*



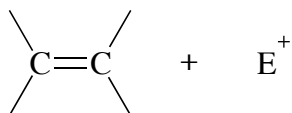
C—C π -bonds create nucleophilic sites and are more easily broken than σ -bonds.



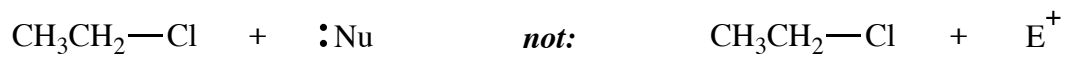
electron rich sites react with electron poor sites

COMMON REACTIVITY WE WILL SEE:

Alkenes react with electrophiles:



Alkyl halides mostly react with nucleophiles, but they can also react with Lewis acids to form unstable intermediates:



Attributions

Page 67, 68: Micelle, Lipid bilayer, Liposome (Micelle modified from original drawing):

http://upload.wikimedia.org/wikipedia/commons/c/c6/Phospholipids_aqueous_solution_structures.svg

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Page 68: Crown ether:

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