Universiti Malaysia PAHANG
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Organic Chemistry

Introduction to Organic Molecules and Functional Groups

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Expected Outcomes

In the completion of this chapter, student will have the ability to:

- Identify IUPAC nomenclature and draw functional groups [hydrocarbon, compound containing C-Z bonds (alkyl halide, alcohol, ether, amine, thiol, sulfide) and C=O group (aldehyde, ketone, carboxylic acid, ester, amide)]
- Identify strength of intermolecular forces (ionic and covalent) of compounds
- Predict physical properties (boiling point, melting point and solubility) of a compound
- Label electrophilic and nucleophilic sites in a molecule.

Contents

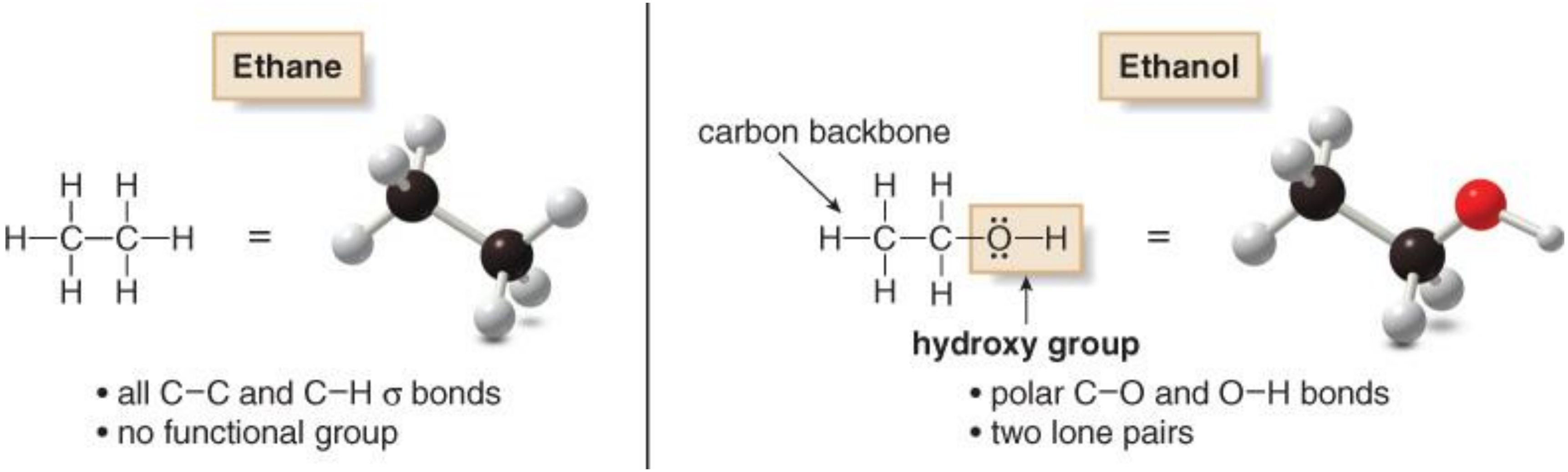
- Functional groups
- Intermolecular forces
- Physical properties
- Functional group & reactivity

Functional Groups

Functional Groups

- A functional group is an atom or a group of atoms with characteristic chemical and physical properties. It is the reactive part of the molecule.
- Most organic compounds have C—C and C—H bonds. However, many organic molecules possess other structural features:
  - **Heteroatoms**—atoms other than carbon or hydrogen. These structural features distinguish one organic molecule from another. They determine a molecule's geometry, physical properties,
  - Pyridine , Oxirane, Furan

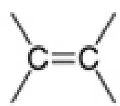
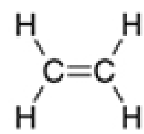
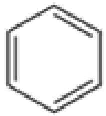
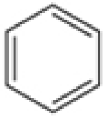
Functional Groups



Functional Groups

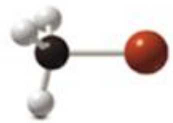
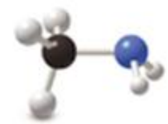
Hydrocarbons are compounds made up of only the elements carbon and hydrogen**. They may be aliphatic or aromatic.**

Hydrocarbons

Type of compound	General structure	Example	Functional group
Alkane	R—H	CH_3CH_3	– –
Alkene			double bond
Alkyne	—C≡C—	H—C≡C—H	triple bond
Aromatic compound			phenyl group

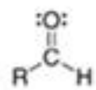
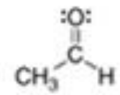
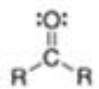
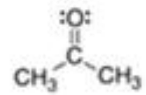
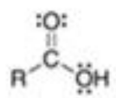
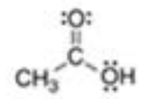
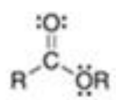
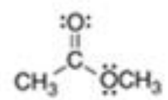
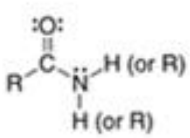
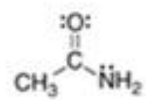
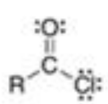
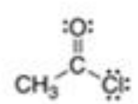
Functional Groups

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

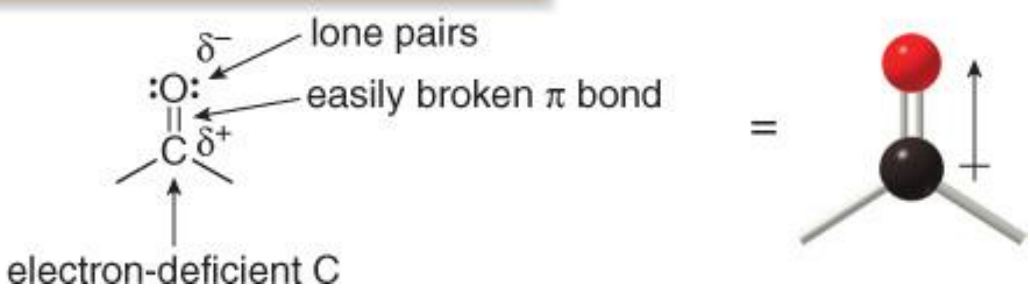
Compounds Containing a C=O Group

Type of compound	General structure	Example	3-D structure	Functional group
Aldehyde				(aldehyde group) C=O carbonyl group
Ketone				(ketone group) C=O carbonyl group
Carboxylic acid				(carboxylic group) −COOH carboxy group
Ester				(ester group) −COOR
Amide				(amide group) $-CONH_2$, −CONHR, or $-CONR_2$
Acid chloride				(acid chloride group) −COCl

Compounds Containing the 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.**

Reactive features of a carbonyl group



Functional Groups

It should be noted that the importance of a functional group cannot be overstated.

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

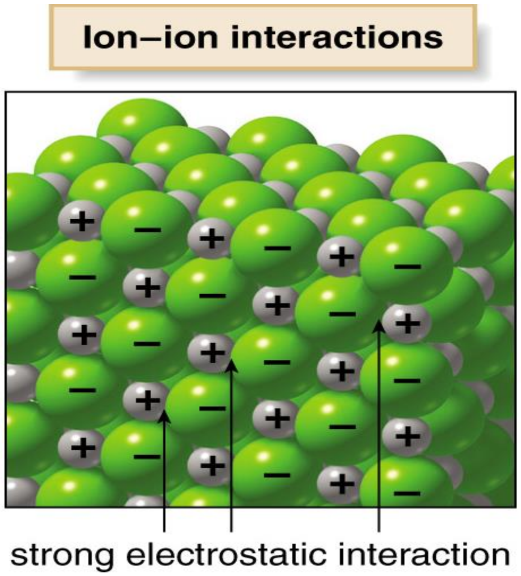
- **Bonding and shape**
- **Type and strength of intermolecular forces**
- **Physical properties**
- **Nomenclature**
- **Chemical reactivity**

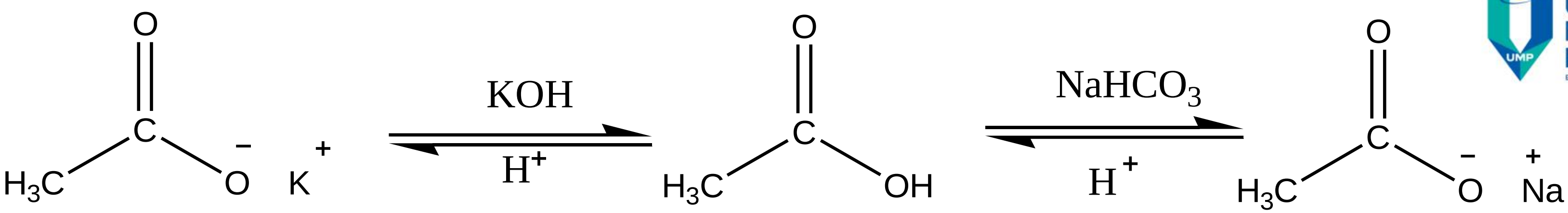
Ion-Ion Interactions

Ion – Ion interactions are strong intramolecular forces between oppositely charged ions. e.g.

$Na^{+}Cl^{-}$ (oppositely charged particles or ions): The attractive forces between these oppositely charged ions or particles are extremely strong. These are Ion – Ion interactions or electrostatic interactions.

Ion – Ion interactions are much stronger than the intermolecular forces in covalent molecules.

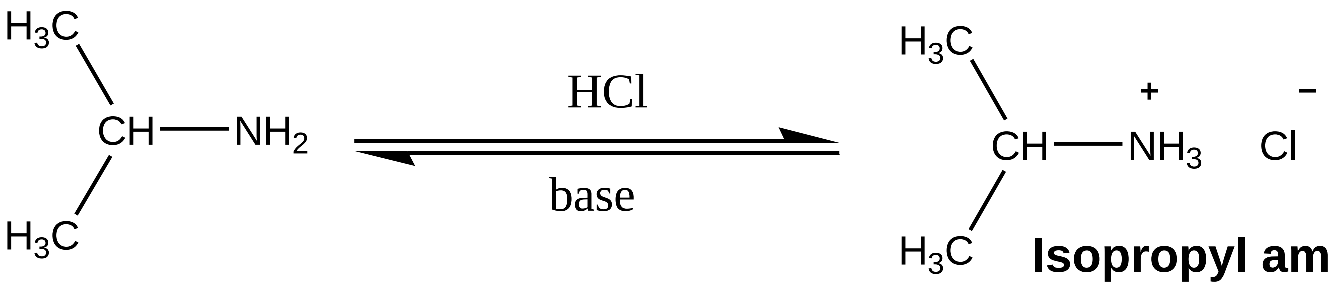




potassium acetate
mp 306

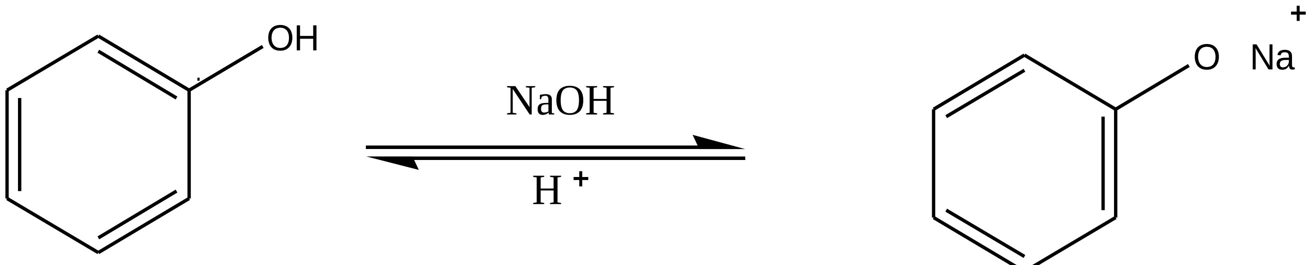
Acetic acid
mp 17

Sodium acetate
mp > 300



Isopropyl amine
mp -95

Isopropyl amine hydrochloride
mp -162



phenol
mp 41 C

Sodium phenolate
mp 382

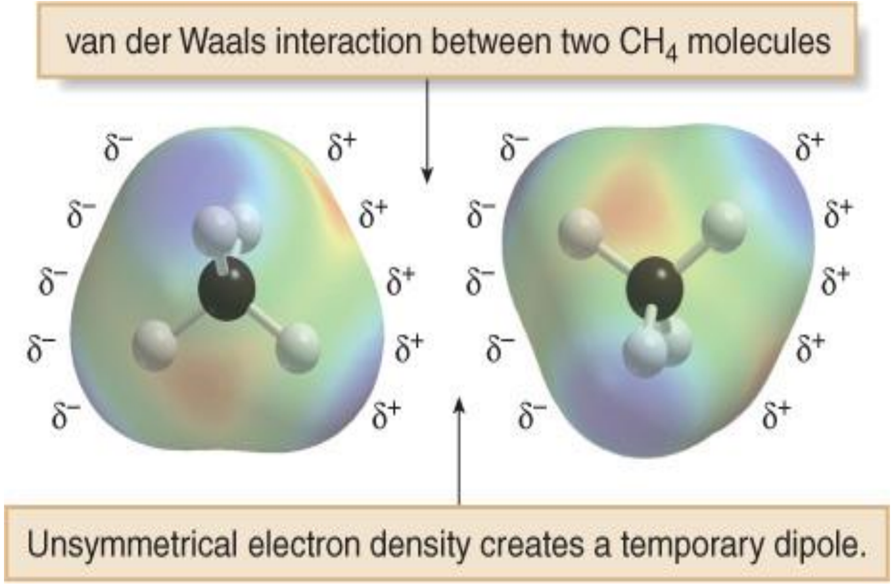
Intermolecular Forces

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

Intermolecular Forces

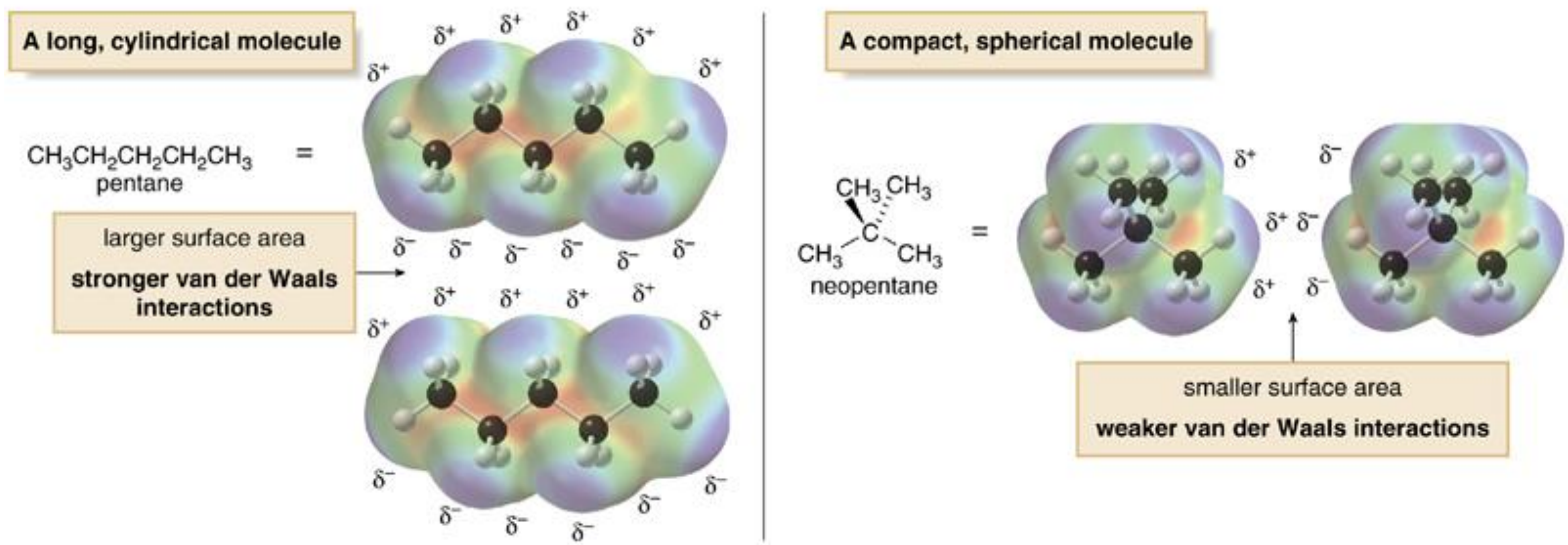
Intermolecular Forces—van der Waals Forces

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



Intermolecular Forces-Van der Waals Forces

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



Intermolecular Forces—van der Waals Forces

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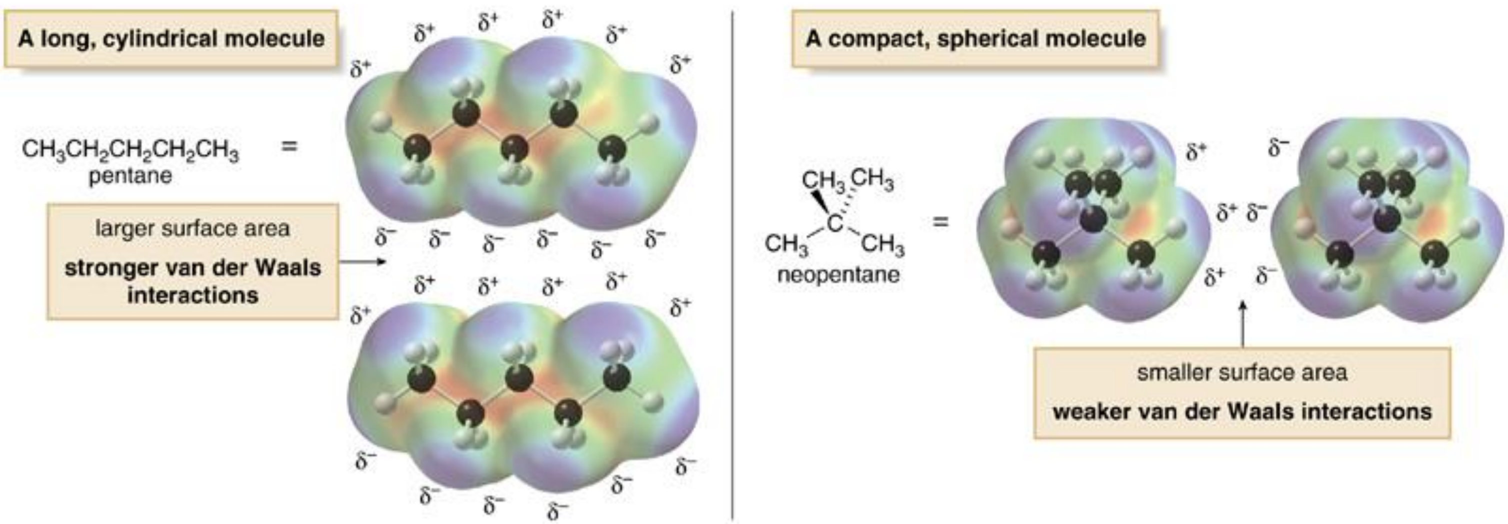
Surface area and van der Waals forces



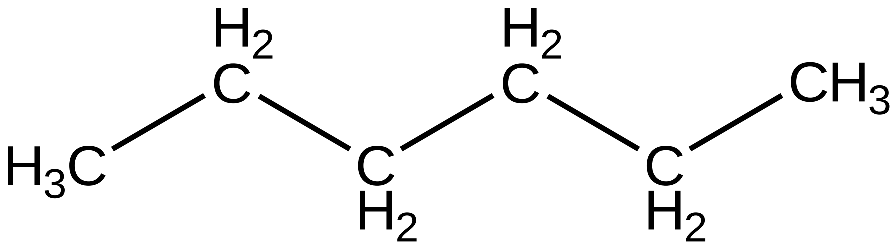
Intermolecular Forces-Van der Waals Forces

- Organic compound that contain only carbon and hydrogen (hydrocarbon) are weekly attracted to each other by Van Der Waals forces

- These attractive forces increase as molecular size increases.

CH_4

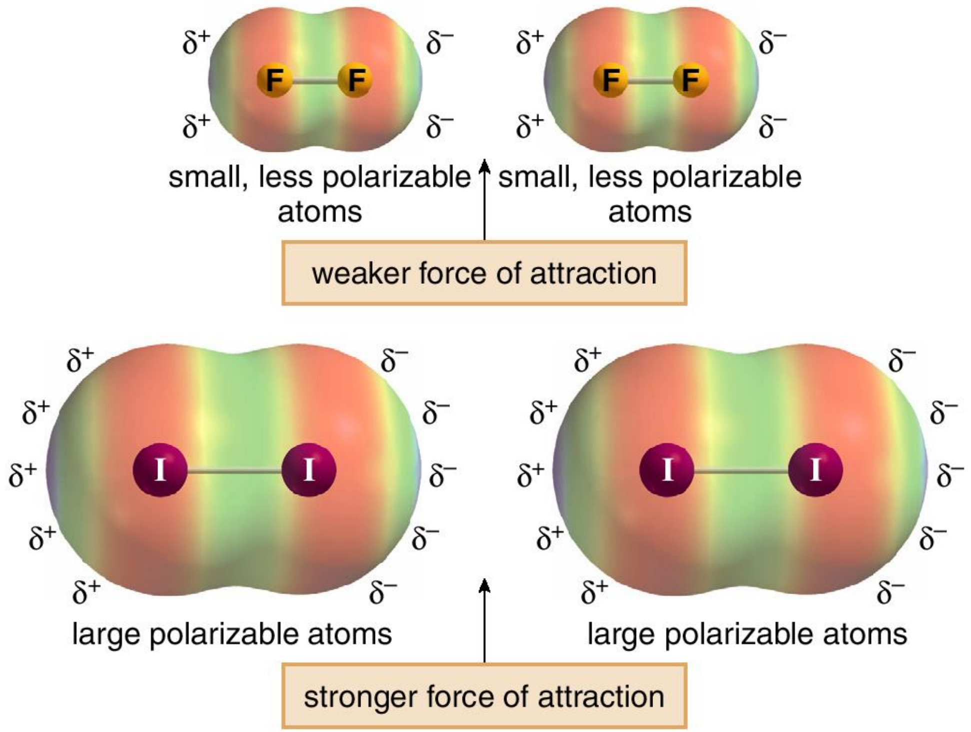
Methane
Mp -180
Bp -162



Hexane
Mp -95
Bp +69

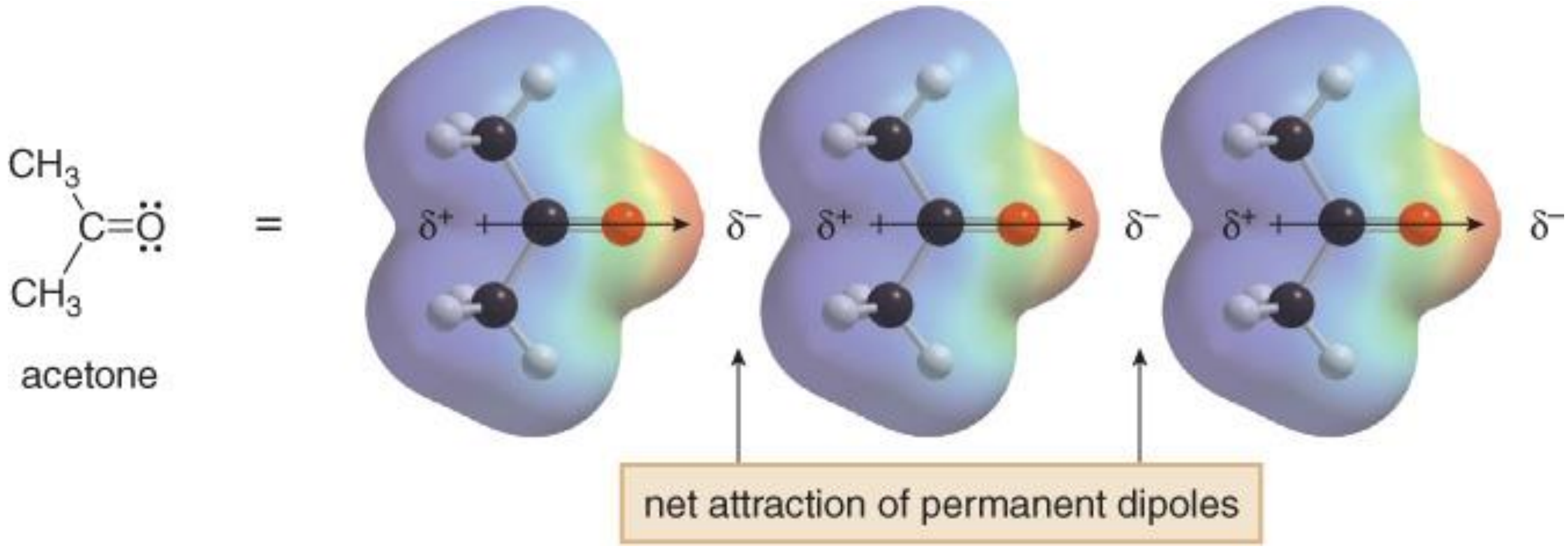
Intermolecular Forces—van der Waals Forces

- **van der Waals forces are also affected by polarizability.**
- **Polarizability is a measure of how the electron cloud around an atom responds to changes in its electronic environment.**
- **Larger atoms (more loosely held valence e$^-$) are more polarizable than smaller atoms (more tightly held e$^-$).**



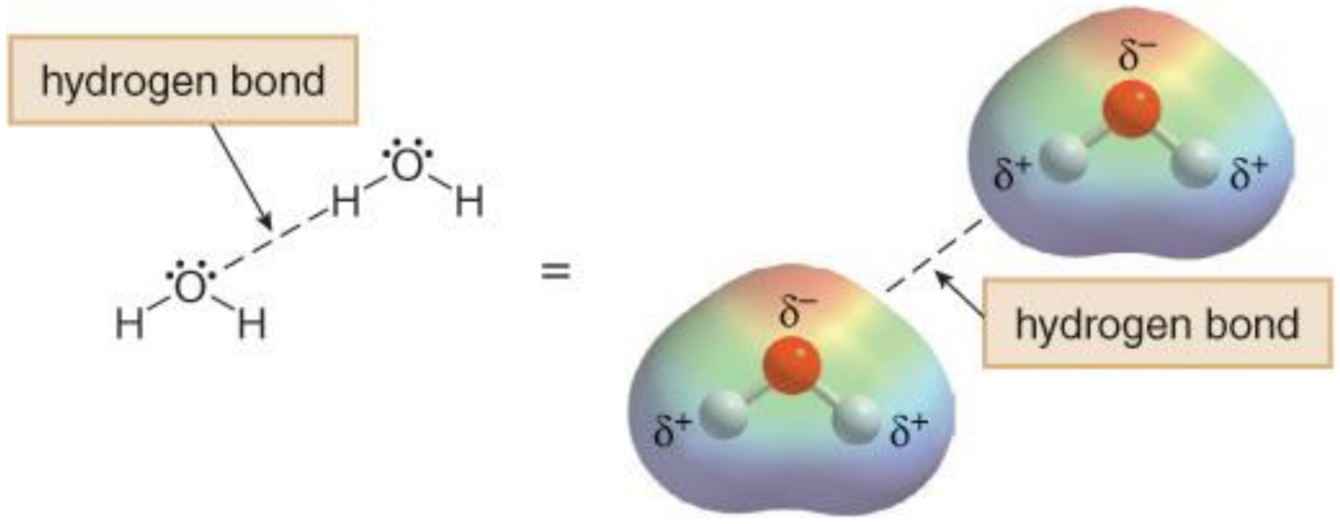
Intermolecular Forces—Dipole-Dipole Interactions

- **Dipole—dipole interactions are the attractive forces between the permanent dipoles of two polar molecules.**
- **Consider acetone (below). The dipoles in adjacent molecules 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.**



Intermolecular Forces—Hydrogen Bonding

- Very strong interactions.
- **Between H bonded to electronegative elements (O, N, X) and a lone pair ($2e^-$) on an electronegative element.**
- **Hydrogen bond occurs among organic molecules containing OH group (alcohol and carboxylic acid) and N-H group**



Summary

As the polarity of a molecule increases, the strength of its intermolecular forces increases.

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

Physical Properties—boiling point & melting point

- Boiling point (bp): the temperature at which liquid molecules are converted into gas.
- Melting point (mp): the temperature at which a solid is converted to its liquid phase.

The stronger the intermolecular forces, the higher the bp & mp.

Physical properties

compounds with van der Waals forces	compounds with dipole–dipole interactions	compounds with hydrogen bonding

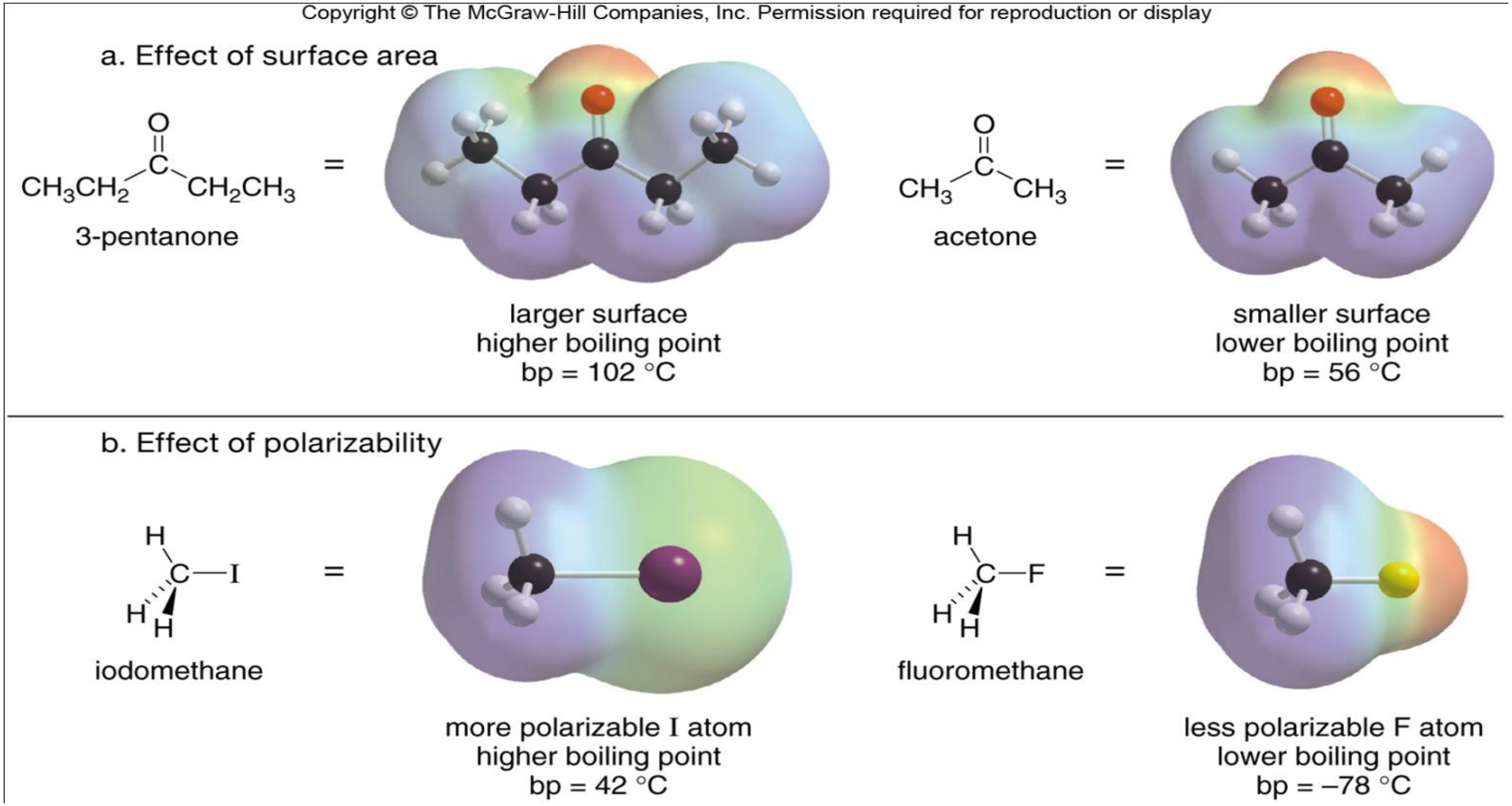
Increasing strength of intermolecular forces
Increasing boiling point

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

Increasing strength of intermolecular forces
Increasing boiling point

Other Factors Affecting Boiling Points

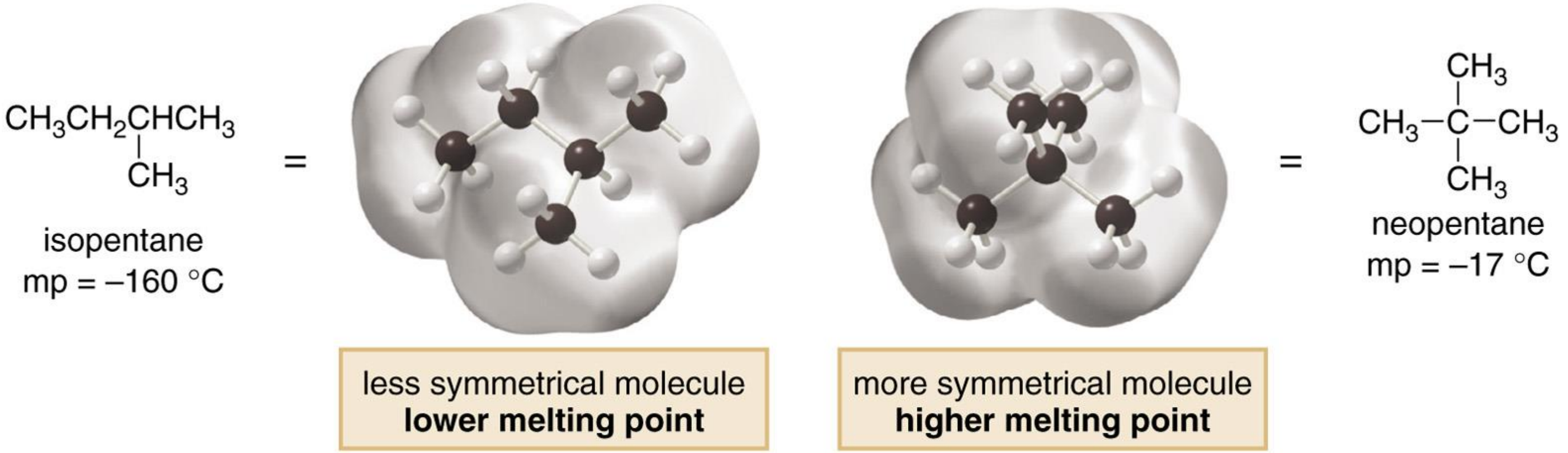
- **For compounds with similar functional groups:**
  - **The larger the surface area, the higher the boiling point.**
  - **The more polarizable the atoms, the higher the boiling point.**



Effect of Symmetry on Melting Points

- **The more compact and symmetrical the shape (a crystalline lactice), the higher the melting point.**

For e.g. Neopentane has a much higher mp than isopentane.



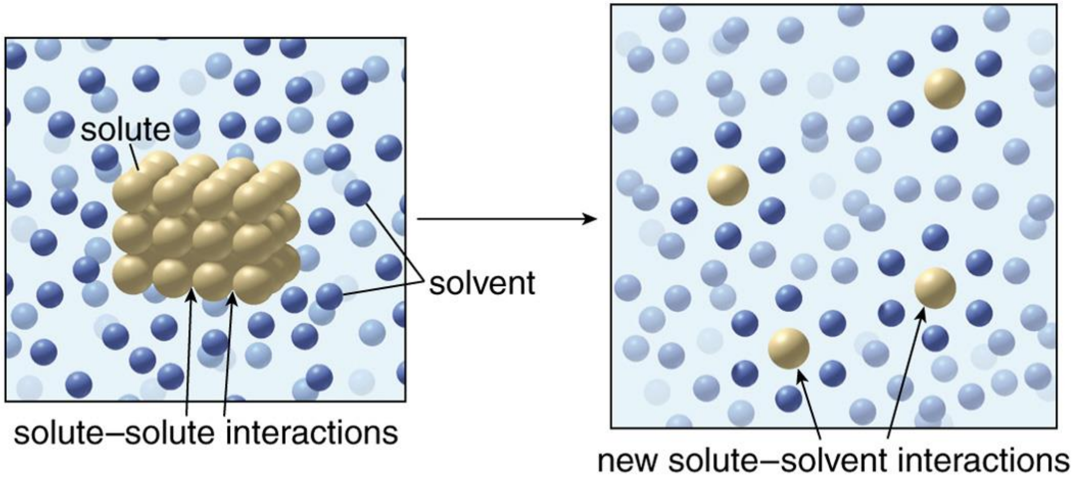
Solubility

- **Solubility:** **the extent of solute dissolution in a solvent.**

- **Hydrophobic and Hydrophilic**

  Hydrophobic: Nonpolar part of a molecule, water-insoluble (not attracted to H_2O).

  Hydrophilic: Polar part of a molecule, water-soluble (H-bond to H_2O).



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

Solubility Trends

- "Like dissolves like"

1) Ionic compounds & polar compounds dissolve in polar solvents.
2) Nonpolar or weakly polar compounds dissolve in:
   - nonpolar solvents (e.g., CCl_4 , hexane).
   - weakly polar solvents (e.g., diethyl ether)
3) Solubility of organic molecules
   - Relative size of non-polar portion to a polar portion
   - Water soluble: ≤ 5 C for one functional group

Competing intermolecular forces and solubility

The sum of attractive forces tend to work together to raise melting and boiling points as

- **the size of molecule's hydrocarbon skeleton increases polar, incorporated into molecule**

- **hydrogen bonded, incorporated into molecule**

- **ionic function group is incorporated into molecule**

Solubility involves the interaction of two different molecules, which may have different types of attractive forces

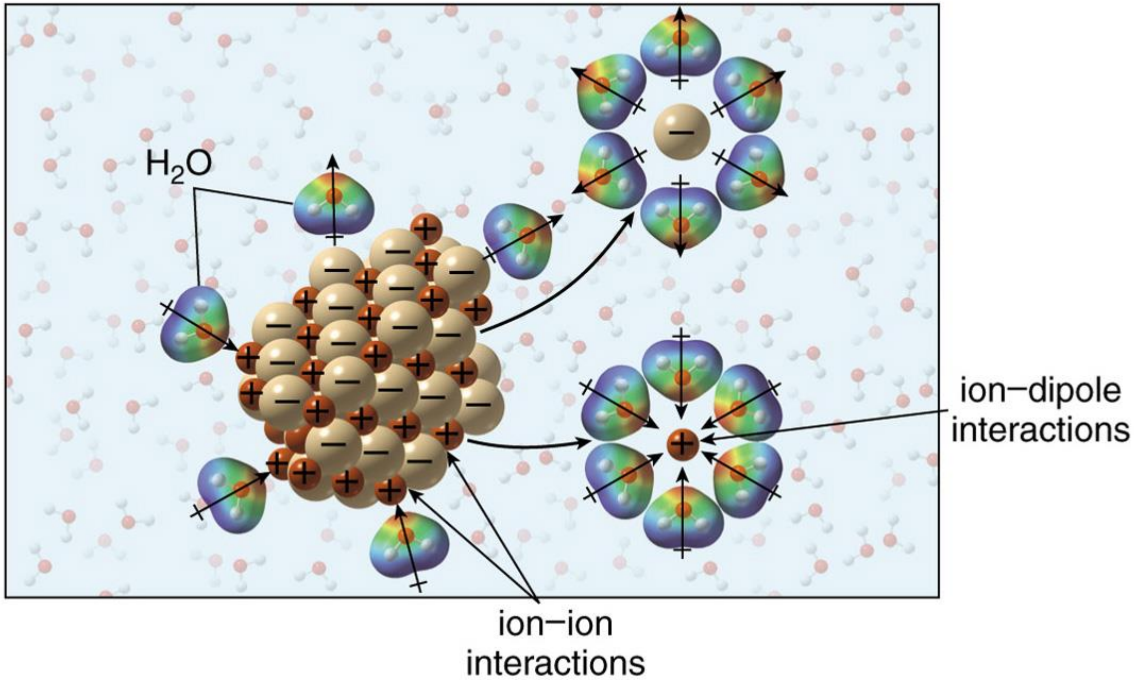
For e.g. Adding hydrocarbon to water (oil and water do not mix)

Water have hydrogen bond

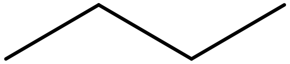
Hydrocarbon is nonpolar and no hydrogen bond

Solubility of Ionic Compounds

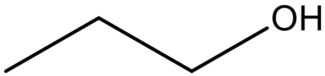
- **Dissolve in water by many ion–dipole interactions.**



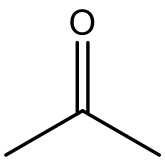
number of carbon less than 5



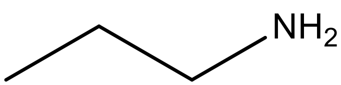
butane
mp -138
insolube in water



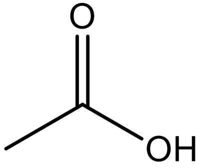
mp -127
solube in water



ketone
mp -94
solube in water

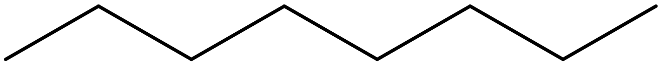


amine
mp -43
solube in water

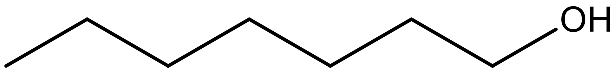


acid
mp -17
solube in water

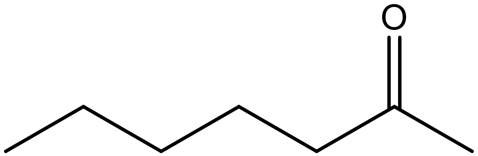
number of carbon mor than 5



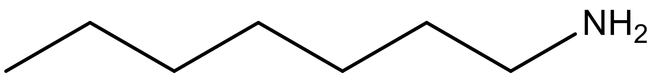
mp -57 insoluble



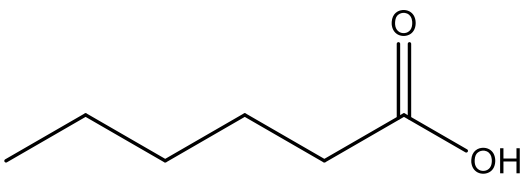
mp -34 insoluble



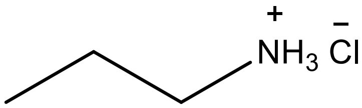
mp -35 insoluble



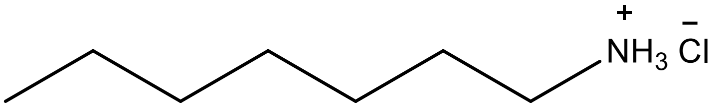
mp -18 insoluble



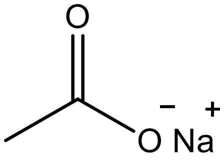
mp -2 insoluble



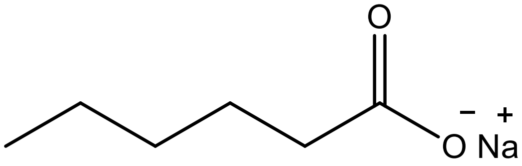
amine hydrochloride
mp 161
solube in water



amine hydrochloride
mp 242
solube in water



sodium salt of carboxlic acid
solube in water



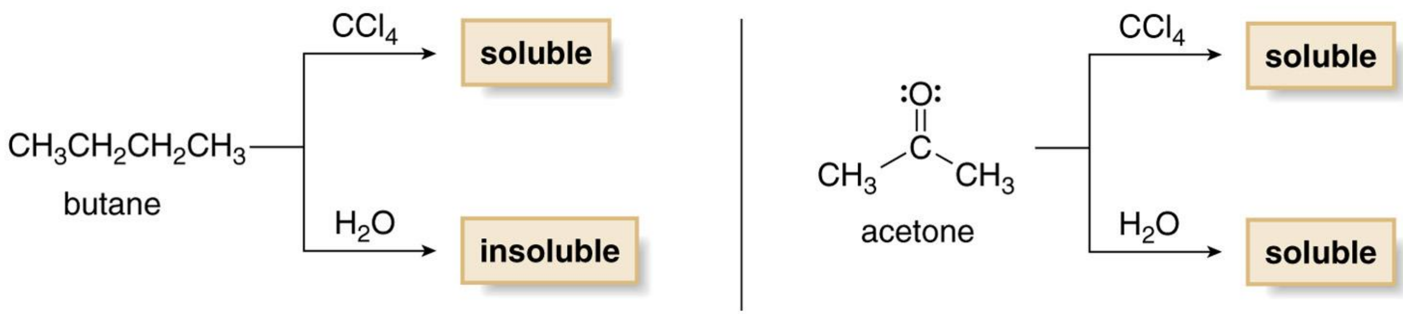
soluble in water

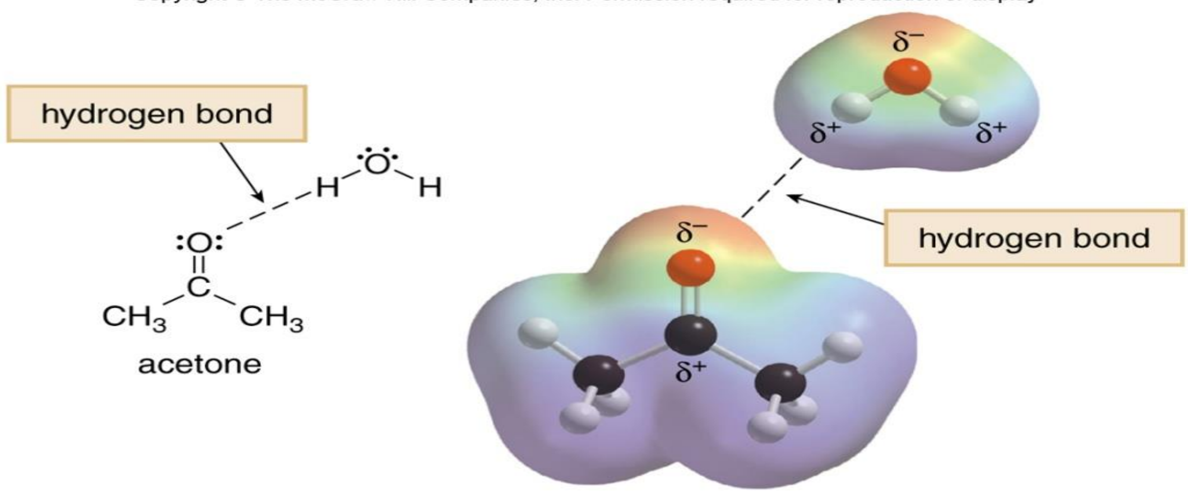
Solubility of Organic Molecules

- **Relative size of non-polar portion to a polar portion**

  Water soluble when; ≤ 5 C for one functional group

For example,





Hydrogen bonding makes the small polar molecule acetone H_2O soluble.

Solubility Properties of Representative Compounds

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** ($\leq$ 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**

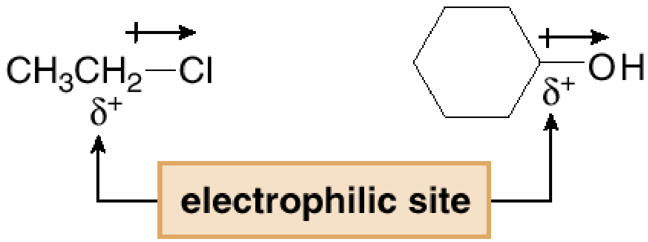
Influence of Functional Groups on Reactivity

Recall that:

- **Functional groups create reactive sites in molecules.**
- **Electron-rich sites react with electron poor sites.**

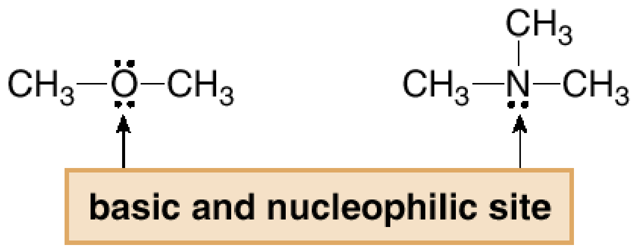
All functional groups contain a heteroatom, a π bond or both, and these features create electron-deficient (or electrophilic) sites and electron-rich (or nucleophilic) sites in a molecule. Molecules react at these sites.

- An electronegative heteroatom like N, O, or X makes a carbon atom *electrophilic.*

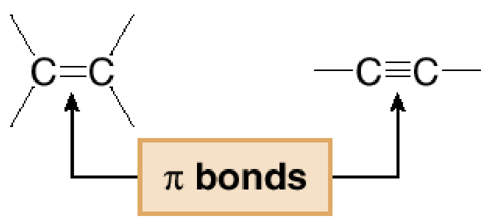


Influence of Functional Groups on Reactivity

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



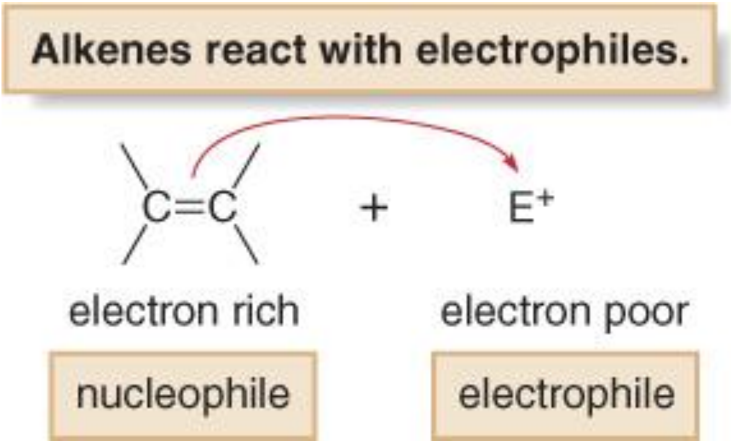
- π Bonds create *nucleophilic* sites and are more easily broken than σ bonds.



Influence of Functional Groups on Reactivity

- An electron-deficient carbon reacts with a nucleophile, symbolized as $:Nu^{-}$.
- 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^{+}.



Influence of Functional Groups on Reactivity

On the other hand, alkyl halides possess an electrophilic carbon atom, so they react with electron-rich nucleophiles.