

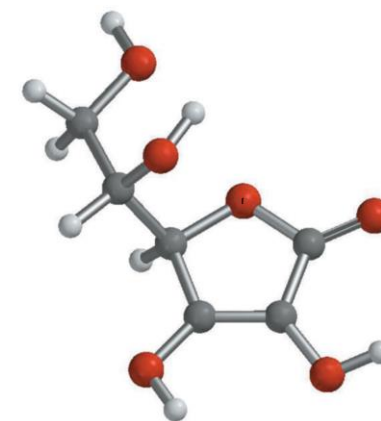
**CHEM 244**

# **PRINCIPLES OF ORGANIC CHEMISTRY I**

FOR CHEMISTRY' STUDENTS, COLLEGE OF ENGINEERING

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 2 (2+0)



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## **CHAPTER 1. INTRODUCTION**

# LEARNING OUTCOMES

*At the end of this chapter, students will be able to:*

- ✖ Recognize the definition and importance of organic chemistry.
- ✖ Arrange the electrons in atoms.
- ✖ Differentiate between ionic and covalent bonds in chemical compounds.
- ✖ Identify the hybridization of carbon atom.
- ✖ Know dipole moment & inductive effect in chemical compounds.
- ✖ Classify the organic compounds according to functional groups.
- ✖ Define the types of organic reactions.

# IMPORTANCE OF ORGANIC CHEMISTRY

- ✖ **Organic chemistry** touches our daily lives. We are made of and surrounded by **organic compounds**.
- ✖ Almost all of the reactions in living matter involve **organic** compounds.
- ✖ The major constituents of living matter e.g. proteins, carbohydrates, fats, nucleic acid (DNA and RNA), enzymes and hormones are **organic**.
- ✖ Other organic materials include the gasoline, oil, tires, clothing we wear, wood for our furniture, the paper for our books, the medicines we take and plastic containers, camera film, perfume, carpeting and fabrics.
- ✖ In short, **organic chemistry** is more than just a branch of science for the professional chemist or for student preparing to become a physician, dentist, pharmacist, nurse or agriculturist. **It is part of our technological culture.**

# DEFINITION OF ORGANIC CHEMISTRY

- The word **Organic** can be a biological or chemical term, in biology it means anything that is living or has lived. The opposite is Non-Organic.
- **Organic Chemistry** is unique in that it deals with vast numbers of substances, both natural and synthetic.

*The clothes, the petroleum products, the paper, rubber, wood, plastics, paint, cosmetics, insecticides, and drugs*

- But, from the chemical makeup of organic compounds, it was recognized that one constituent common to all was **the element carbon**.
- **Organic chemistry** is defined as *the study of carbon/hydrogen-containing compounds and their derivatives*.

# THE UNIQUENESS OF CARBON

- What is unique about the element **carbon**?
- Why does it form so many compounds?
  - **The answers lie in**
    - The **structure** of the *carbon* atom.
    - The **position** of *carbon* in the periodic table.
- These factors enable it to form strong bonds with
  - other carbon atoms
  - and with other elements (hydrogen, oxygen, nitrogen, halogens,...etc).
- Each **organic compound** has its own characteristic set of physical and chemical properties which depend on the *structure of the molecule*.

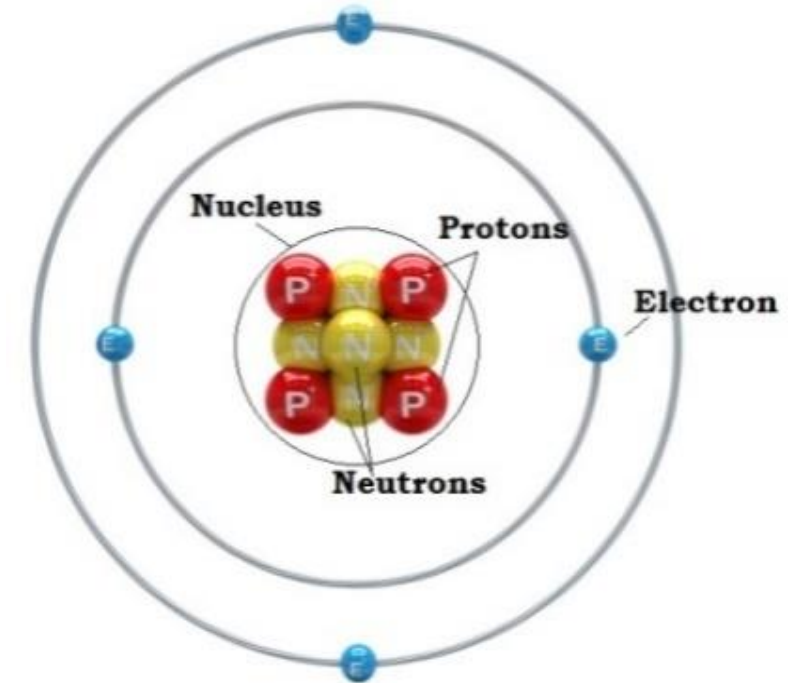
IA	IIA							Zero
H								He
Li	Be							Ne
Na	Mg							Ar
K	Ca	Transition Elements						Kr
Rb	Sr							Xe
Cs	Ba							Rn
Fr	Ra							
		IIIA	IVA	VA	VIA	VIIA		
		B	C	N	O	F		
		Al	Si	P	S	Cl		
		Ga	Ge	As	Se	Br		
		In	Sn	Sb	Te	I		
		Tl	Pb	Bi	Po	At		

# ATOMIC STRUCTURE

- **Atoms** consist of three main particles: **neutrons** (have no charge), **protons** (positively charged) and **electrons** (negatively charged).

- Neutrons and protons are found in the nucleus.
- Electrons are found outside the nucleus.

Electrons are distributed around the nucleus in successive **shells** (*principal energy levels*).



- **Atom** is electrically neutral.  
i.e. Number of electrons = Number of protons
- **Atomic number** of an element is the number of protons.
- The **atomic weight** is approximately equal to the sum of the number of protons and the number of neutrons in the nucleus

# ATOMIC STRUCTURE

- **The energy levels** are designated by capital letters (K, L, M, N, ..) or whole numbers (n).

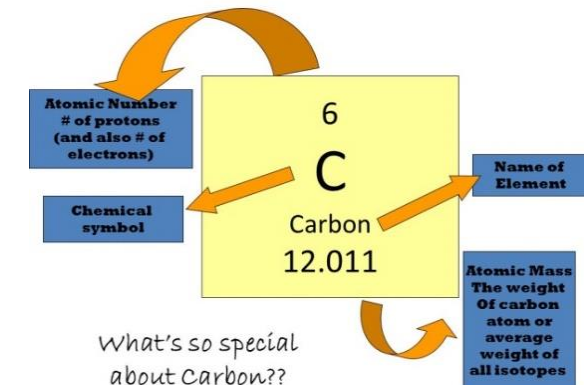
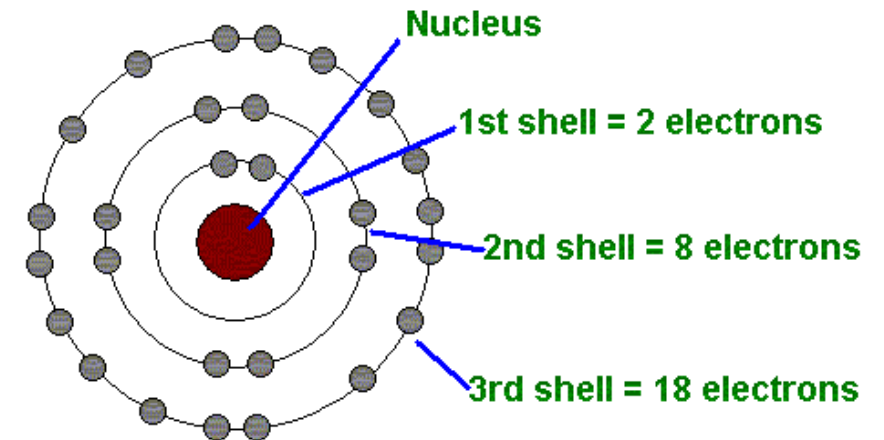
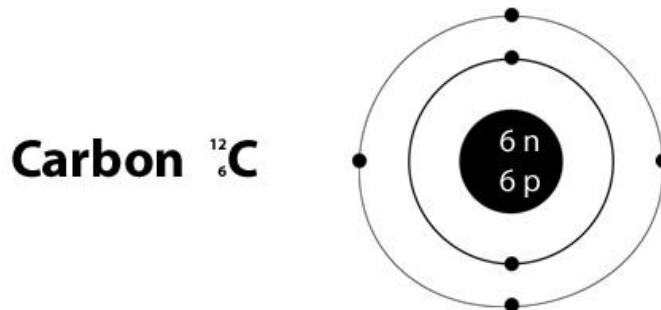
- **The maximum capacity of a shell =  $2n^2$  electrons.**

**$n$  = number of the energy level.**

- **For example,** the element carbon (atomic number 6)

**6 electrons are distributed about the nucleus as**

Shell	K	L	M	N
Number of electrons	2	4	0	0

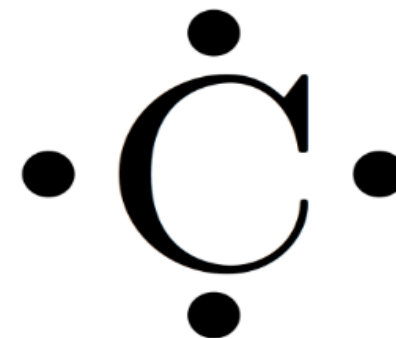


# ATOMIC STRUCTURE



## Electron-dot structures

- **Valance Electrons** are those electrons located in the *outermost energy level (the valance shell)*.
- **Electron-dot structures**
  - The symbol of the element represents the core of the atom.
  - The valance electrons are shown as dots around the symbol.



Valence and Covalence of Common Elements						
Elements	H·	·C·	·N:	·Ö:	:F:	:Cl:
Valence	1	4	5	6	7	7
Covalence	1	4	3	2	1	1



# CHEMICAL BONDS

- In 1916 G.N. Lewis pointed out that:

*The noble gases were stable elements and he described their lack of reactivity to their having their valence shells filled with electrons.*

➤ 2 electrons in case of helium.      ➤ 8 electrons for the other noble gases.

- According to Lewis,

*in interacting with one another atoms can achieve a greater degree of stability*

by rearrangement of the valence electrons  
to acquire the outer-shell structure of the closest noble gas in the  
periodic table.

- Types of Chemical Bonds

A) Ionic Bonding

B) Covalent Bonding

## A) IONIC BOND

- **Ionic bonds** are formed by the transfer of one or more valence electrons from one atom to another.
  - The atom that **gives up electrons** becomes positively charged, a **cation**.
  - The atom that **receives electrons** becomes negatively charged, an **anion**.
- Ionic Bond** is the electrostatic force of attraction between oppositely charged ions.*
- The majority of ionic compounds are **inorganic substances**.

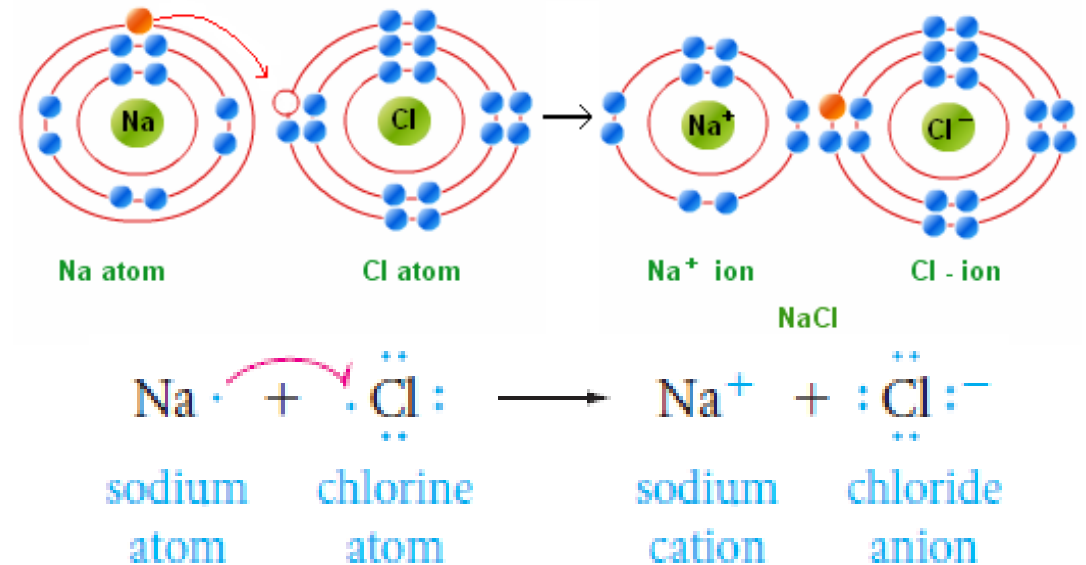
# TYPES OF CHEMICAL BONDS

## A) IONIC BOND

Increasing Electronegativity							
H							
2.1							
Li	Be		B	C	N	O	F
1	1.5		2	2.5	3	3.5	4
Na	Mg		Al	Si	P	S	Cl
0.9	1.2		1.5	1.8	2.1	2.5	3
K							Br
0.8							2.8

Increasing Electronegativity

### Example



# TYPES OF CHEMICAL BONDS

## B) COVALENT BOND

- A **covalent bond** is formed when two atoms share one or more electron pairs.

*Elements that are neither strongly electronegative nor strongly electropositive, or that have similar electronegativities, tend to form bonds by sharing electron pairs rather than completely transferring electrons.*

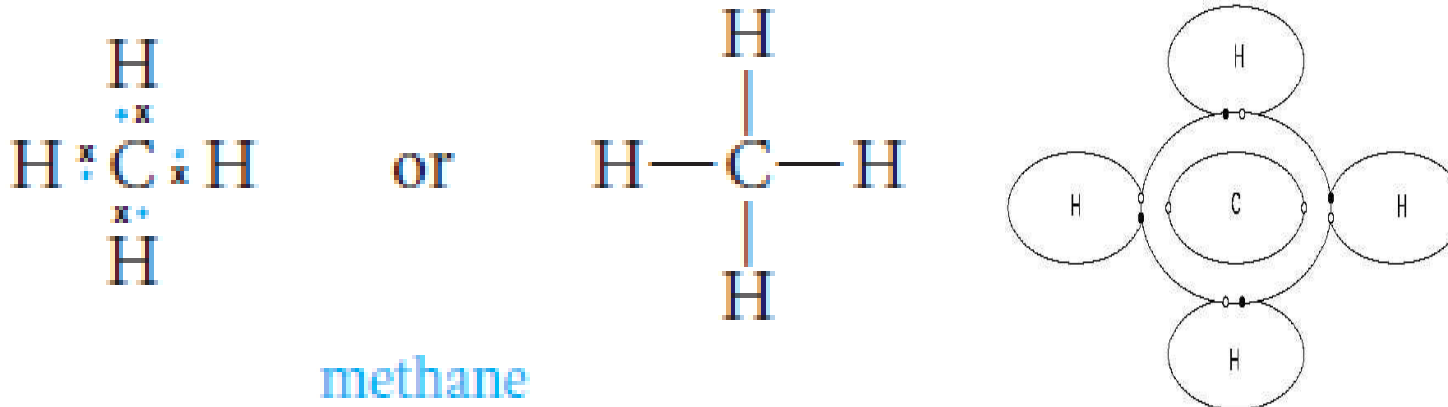
- A **molecule** consists of two or more atoms joined by covalent bonds.
  - When the **two atoms are identical or have equal electronegativities**, the electron pairs are shared **equally**.



# TYPES OF CHEMICAL BONDS

## B) COVALENT BOND

- **For example**, carbon combines with four hydrogen atoms (each of which supplies one valence electron) by sharing four electron pairs. The substance formed is known as **methane**.



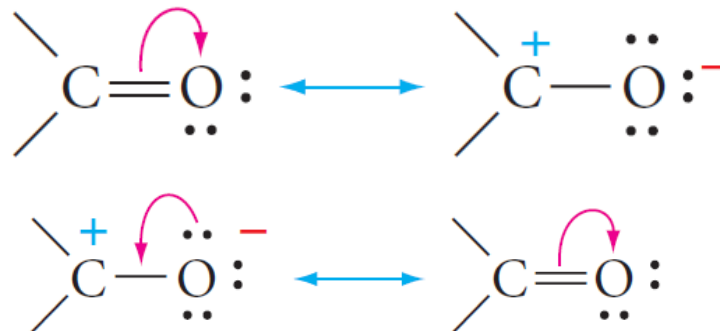
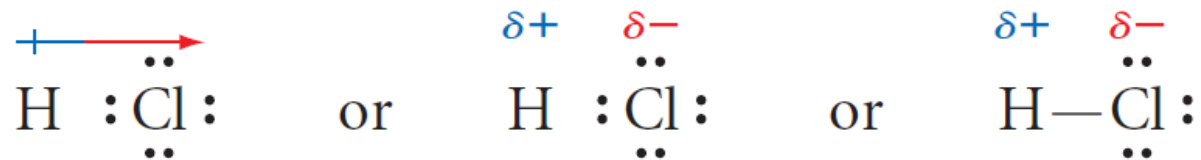
# TYPES OF CHEMICAL BONDS

## B) COVALENT BOND

### 1) POLAR COVALENT BONDS

- A **polar covalent bond** is a covalent bond in which the electron pair is not shared equally between the two atoms.

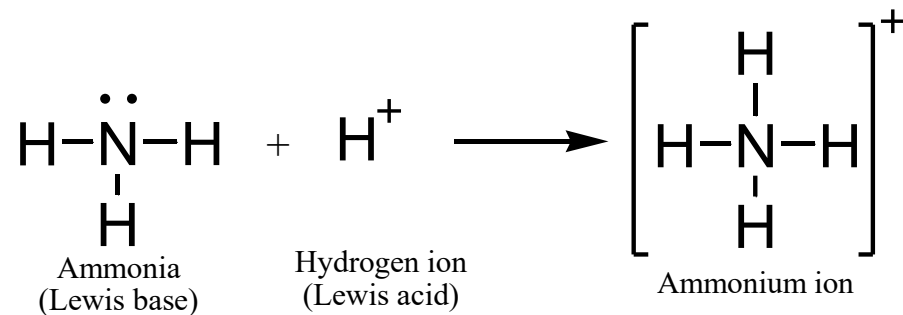
*The more electronegative atom assumes a partial negative charge and the less electronegative atom assumes a partial positive charge.*



## B) COVALENT BOND

### 2) COORDINATE COVALENT BONDS

- There are molecules in which one atom supplies both electrons to another atom in the formation of a covalent bond.
- For example;



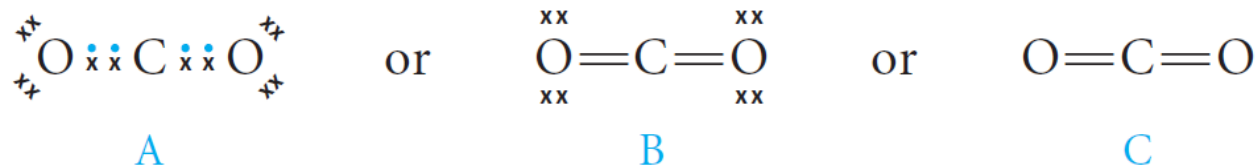
- **Lewis base;** *The species that furnishes the electron pair to form a coordinate covalent bond.*
- **Lewis acid;** *The species that accepts the electron pair to complete its valance shell.*

# TYPES OF CHEMICAL BONDS

## MULTIPLE COVALENT BONDS

- In a **double bond**, two electron pairs are shared between two atoms.

**Example;** Carbon dioxide, CO<sub>2</sub>

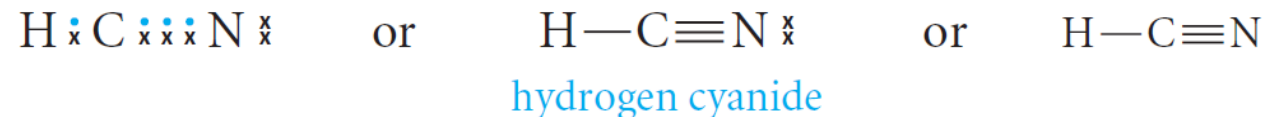


**Structure A**, the **dots** represent the electrons from carbon, and the **x's** are the electrons from the oxygens.

**Structure B** shows the **bonds'** and oxygens' **unshared electrons** (nonbonding electrons).

**Structure C** shows only the covalent **bonds**.

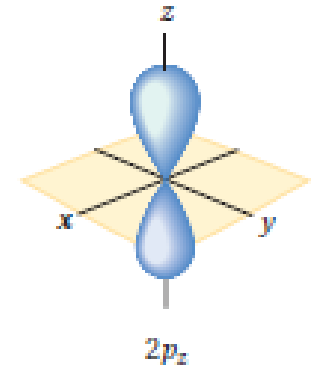
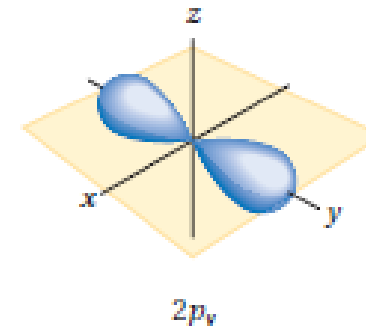
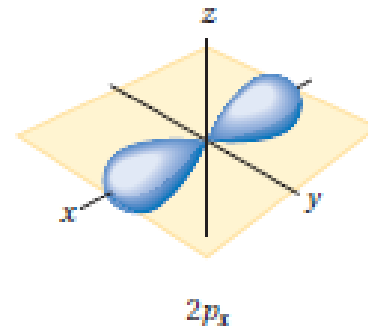
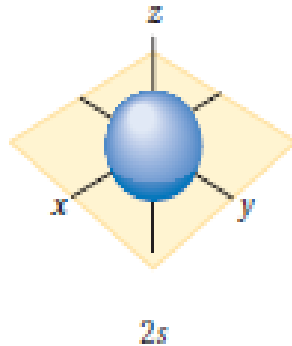
- In a **triple bond**, three electron pairs are shared between two atoms.





# ATOMIC ORBITALS

- An **atomic orbital** represents a specific region in space in which an electron is most likely to be found.
- **Atomic orbitals** are designated in the order in which they are filled by the letters **s**, **p**, **d**, and **f**.
  - An **s orbital** is **spherically shaped** electron cloud with the atom's nucleus and its center.
  - A **p orbital** is a **dumbbell-shaped** electron cloud with the nucleus between the two lobes.



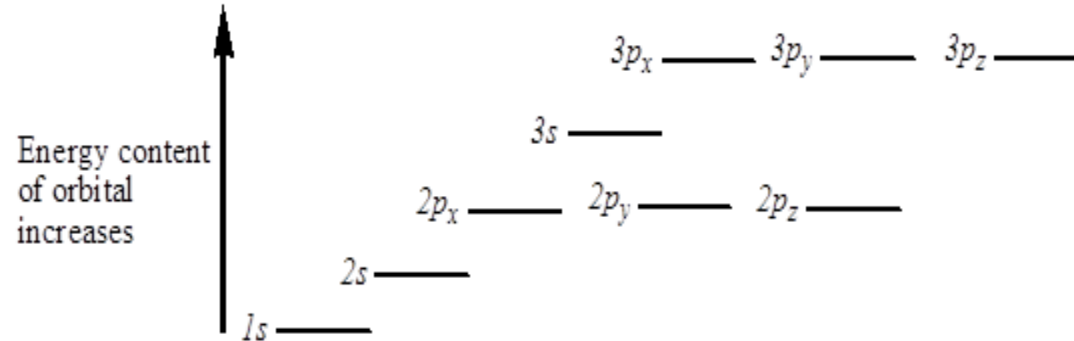
- **Examples:**

*K shell* has only **one 1s** orbital.

*L shell* has **one 2s** and **three 2p** (**2p<sub>x</sub>**, **2p<sub>y</sub>** and **2p<sub>z</sub>**).

# ATOMIC ORBITALS

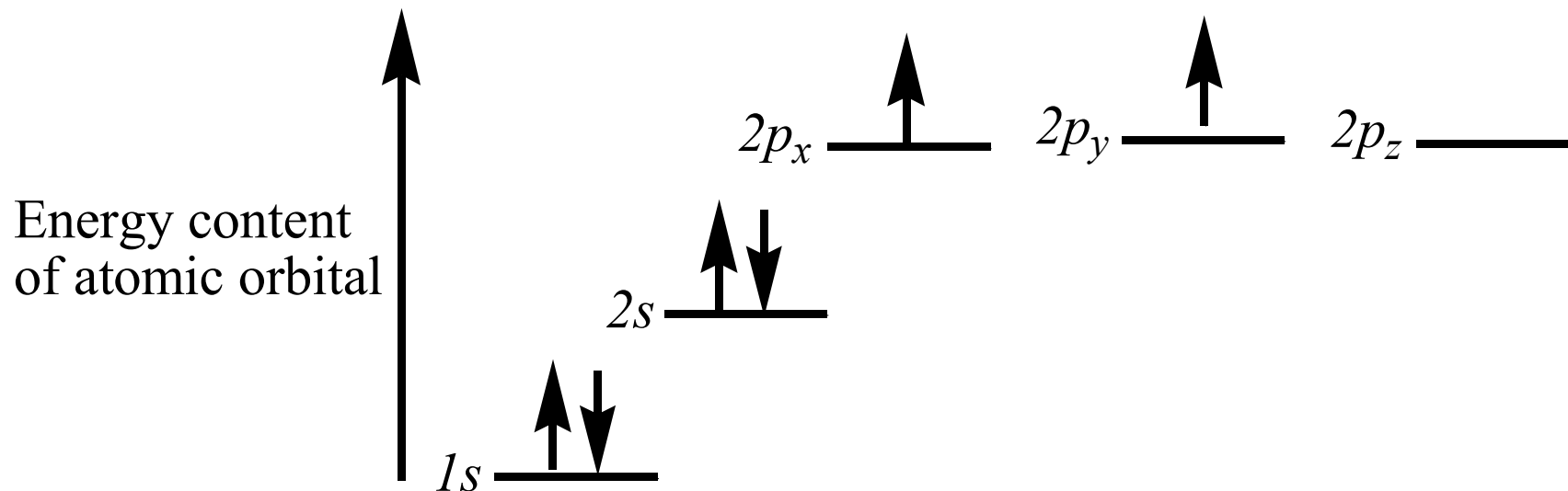
- An energy level diagram of atomic orbitals.



- The electronic configuration of **carbon** (*atomic number 6*) can be represented as
- **When filling the atomic orbitals, keep in mind that**
  - (1)** An atomic orbital contain no more 2 electrons.
  - (2)** Electrons fill orbitals of lower energy first.
  - (3)** No sub-orbital is filled by 2 electrons until all the sub-orbitals of equal energy have at least one electron.

# ATOMIC ORBITALS

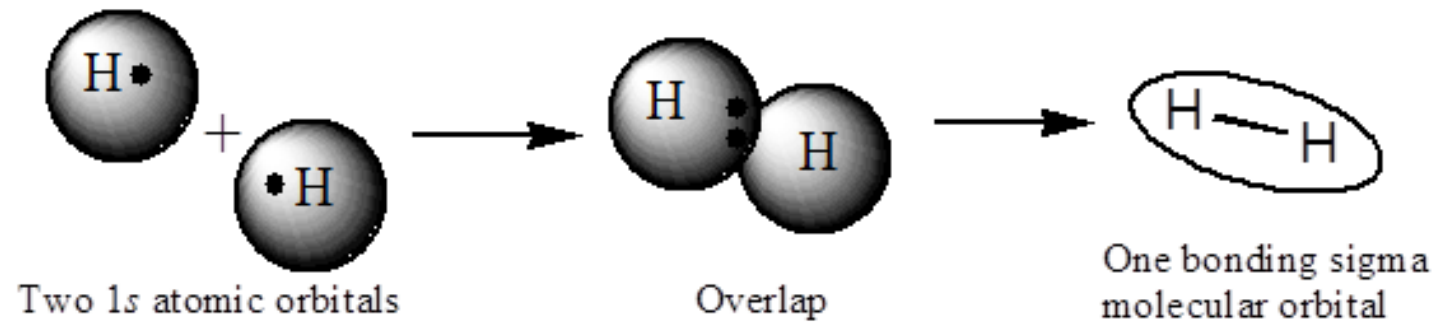
- The electronic configuration of **carbon** (atomic number 6) can be represented as



Energy level diagram for carbon.

# MOLECULAR ORBITALS

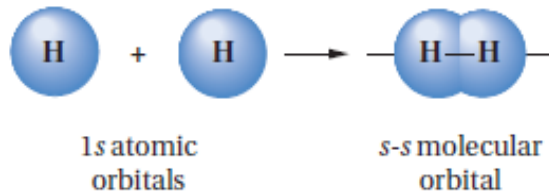
- A covalent bond consists of the overlap between two atomic orbitals to form a **molecular orbital**.
- **Example:** Molecular orbital of  $H_2$



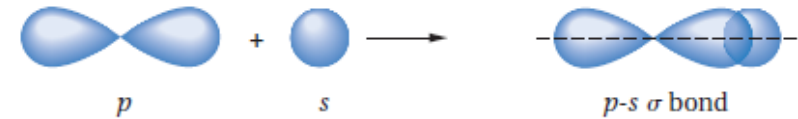
# SIGMA ( $\sigma$ ) AND pi ( $\pi$ ) BONDS

## ○ Sigma bonds ( $\sigma$ bonds) can be formed from

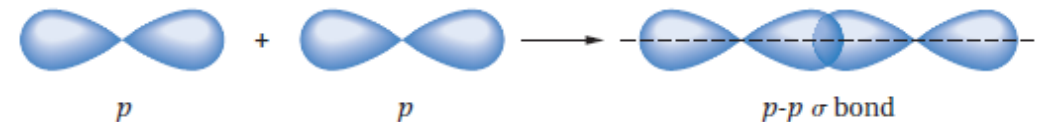
- The overlap of two s atomic orbitals.



- The overlap of two an s atomic orbital with a p atomic orbital.

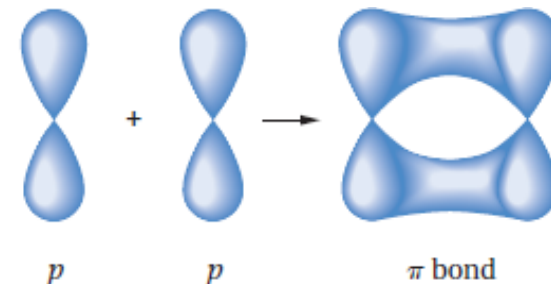


- The end-on overlap of two p atomic orbitals.



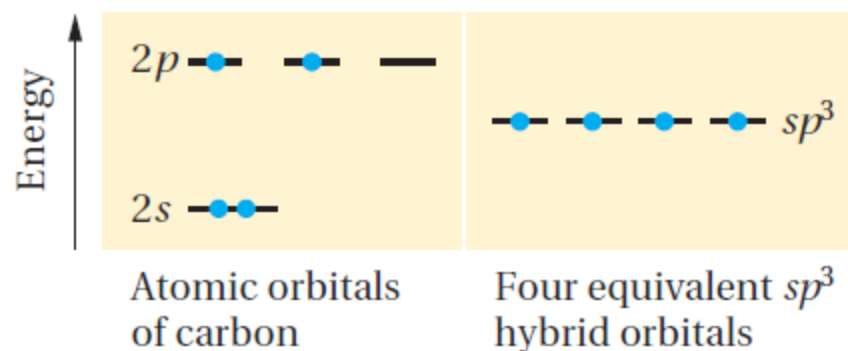
## ○ pi bonds ( $\pi$ bonds) can be formed from

- The side-side overlap between two p atomic orbitals.



## CARBON $sp^3$ HYBRID ORBITALS

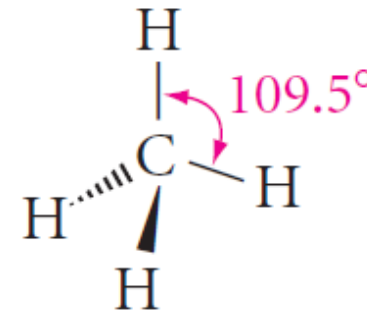
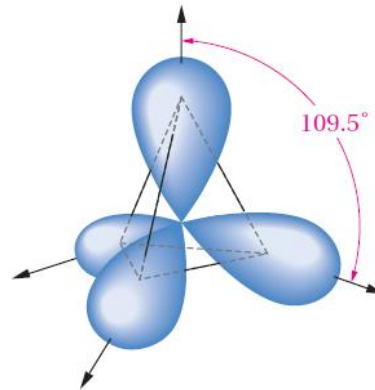
- The electronic configuration of the isolated or ground-state carbon



- Mix or combine the four atomic orbitals of the valence shell to form four identical hybrid orbitals, each containing one valence electron. In this model, the hybrid orbitals are called  **$sp^3$  hybrid orbitals** because each one has one part s character and three parts p character
- Each  $sp^3$  orbital has the same energy: less than that of the 2p orbitals but greater than that of the 2s orbital.

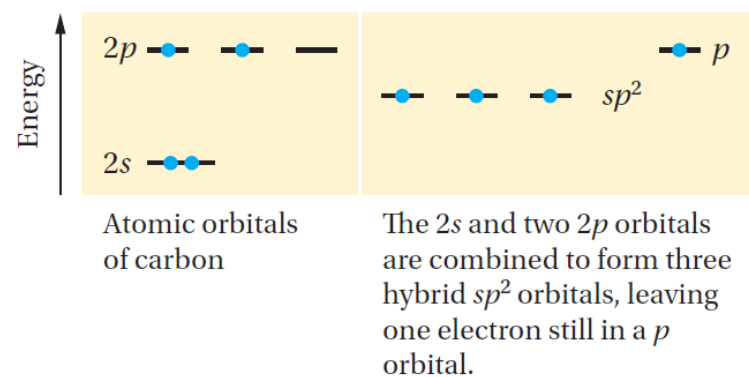
## CARBON $sp^3$ HYBRID ORBITALS

- The angle between any two of the four bonds formed from  $sp^3$  orbitals is approximately  $109.5^\circ$ .
- Regular tetrahedral geometry
- The tetrahedral is a pyramid-like structure with the carbon atom at the center and the four attached atoms located at a corner.

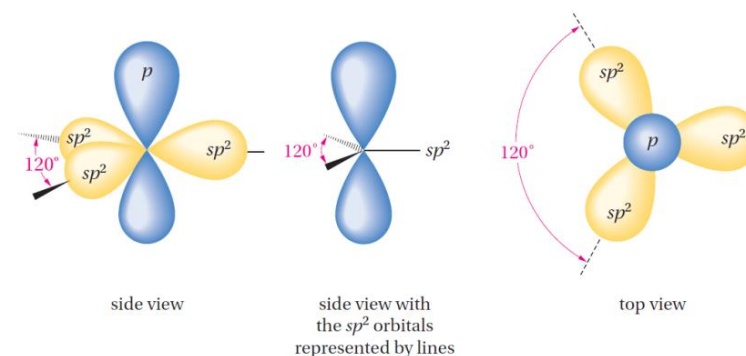


## CARBON $sp^2$ HYBRID ORBITALS

- Combine only three of the orbitals, to make three equivalent  $sp^2$ -hybridized orbitals (called  $sp^2$  because they are formed by combining one s and two p orbitals)

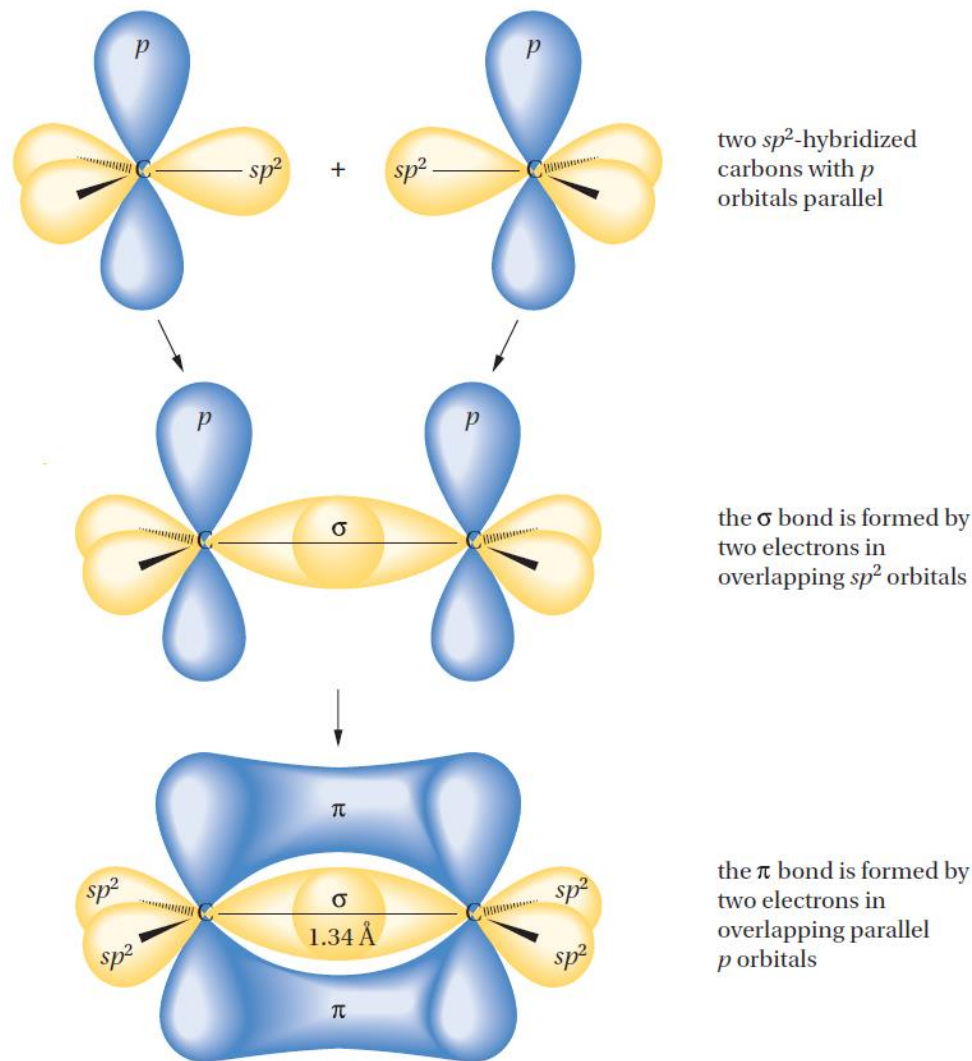


- Three valence electrons are placed in the three  $sp^2$  orbitals. The fourth valence electron is placed in the remaining 2p orbital, whose axis is perpendicular to the plane formed by the three  $sp^2$  hybrid orbitals
- The angle between them is  $120^\circ$ .
- A trigonal carbon





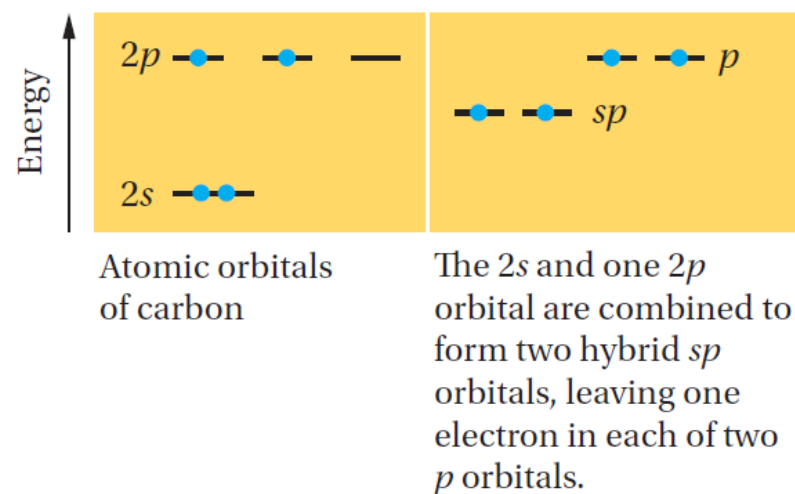
## CARBON $sp^2$ HYBRID ORBITALS



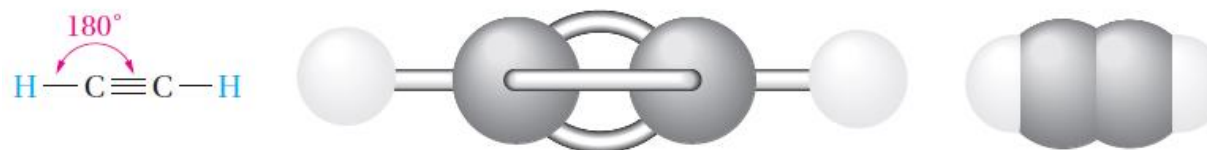
Schematic formation of a carbon-carbon double bond. Two  $sp^2$  carbons form a sigma ( $\sigma$ ) bond (end-on overlap of two  $sp^2$  orbitals) and a pi ( $\pi$ ) bond (lateral overlap of two properly aligned  $p$  orbitals).

## CARBON $sp$ HYBRID ORBITALS

- The carbon atom of an acetylene is connected to only two other atoms. Therefore, we combine the 2s orbital with only one 2p orbital to make two  $sp$ -hybrid orbitals

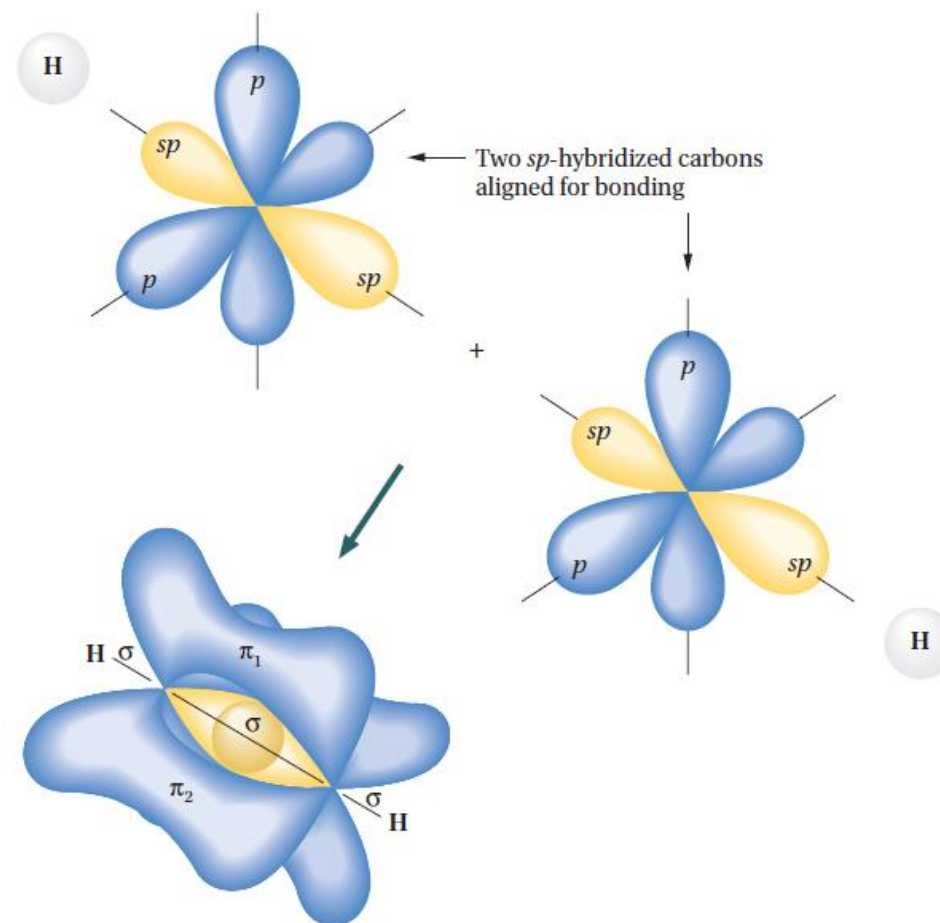


- The angle between the two hybrid orbitals is  $180^\circ$
- Linear



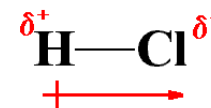
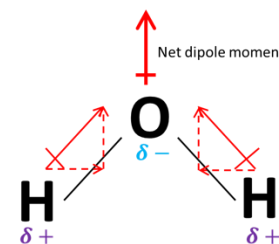
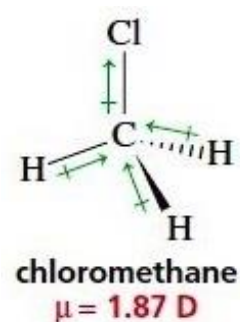
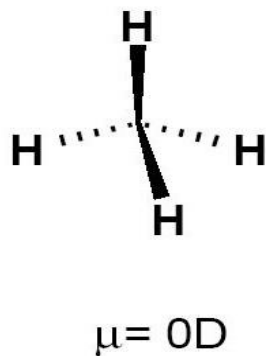
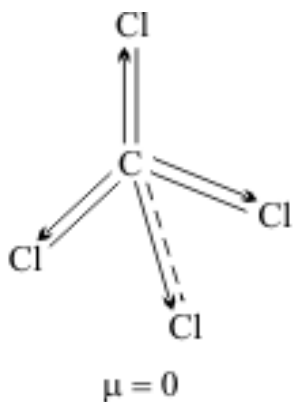
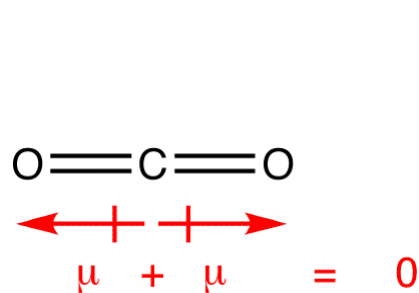
## CARBON $sp$ HYBRID ORBITALS

A triple bond consists of the end-on overlap of two  $sp$ -hybrid orbitals to form a  $\sigma$  bond and the lateral overlap of two sets of parallel-oriented  $p$  orbitals to form two mutually perpendicular  $\pi$  bonds.



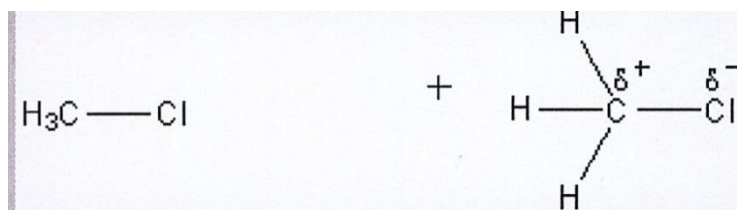
# BOND POLARITY AND DIPOLE MOMENT ( $\mu$ )

- A **polar bond** is a covalent bond between two atoms where the electrons forming the bond are **unequally** distributed.
- A **nonpolar bond** is a covalent bond between two atoms where the electrons forming the bond are **equally** distributed.
- A **dipole moment** is a measurement of the separation of two oppositely charged.
- Dipole moments are a **vector** quantity.
- The **magnitude** is equal to the charge multiplied by the distance between the charges and the direction is from negative charge to positive charge.



# INDUCTIVE EFFECT

- An **inductive effect** is an electronic effect due to the polarization of  $\sigma$  bonds within a molecule or ion.
- This is typically due to an electronegativity difference between the atoms at either end of the bond.
  - This is the electron-withdrawing inductive effect, also known as the **-I effect**
  - This is electron releasing character and is indicated by the **+I effect**



$-\text{CH}_3, -\text{C}_2\text{H}_5, -\text{NH}_2, -\text{OH}, -\text{OCH}_3, \dots$  (+ I) electron-donating substituent

$-\text{NO}_2, -\text{CN}, -\text{SO}_3\text{H}, \text{C}(=\text{O})\text{R}, \dots$  (- I) electron-withdrawing substituent

# ACID-BASE CONCEPT

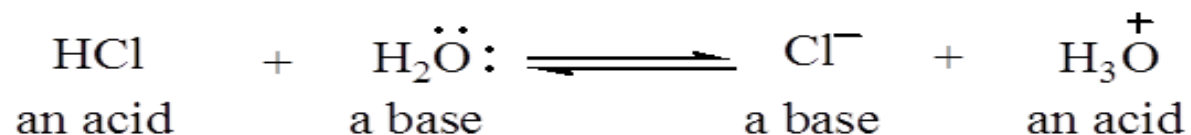
- In the Brønsted–Lowry definitions (1923),

*An acid is a species that donates a proton, and a base is a species that accepts a proton* (or any compound possessing a lone pair).

- Example:

*Hydrogen chloride (HCl)* meets the Brønsted–Lowry definition of *an acid* because it donates a proton to water.

*Water (H<sub>2</sub>O)* meets the definition of *a base* because it accepts a proton from HCl.



Acid-Base reactions are often called proton-transfer reactions.

*In the reverse reaction, H<sub>3</sub>O<sup>+</sup> is an acid because it donates a proton to Cl<sup>-</sup>, and Cl<sup>-</sup> is a base because it accepts a proton from H<sub>3</sub>O<sup>+</sup>.*

# ACID-BASE CONCEPT

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- When a compound loses a proton, the resulting species is called its conjugate base.

*Thus,  $\text{Cl}^-$  is the conjugate base of  $\text{HCl}$ , and  $\text{H}_2\text{O}$  is the conjugate base of  $\text{H}_3\text{O}^+$*

*Thus,  $\text{HCl}$  is the conjugate acid of  $\text{Cl}^-$  and  $\text{H}_3\text{O}^+$  is the conjugate acid of  $\text{H}_2\text{O}$*

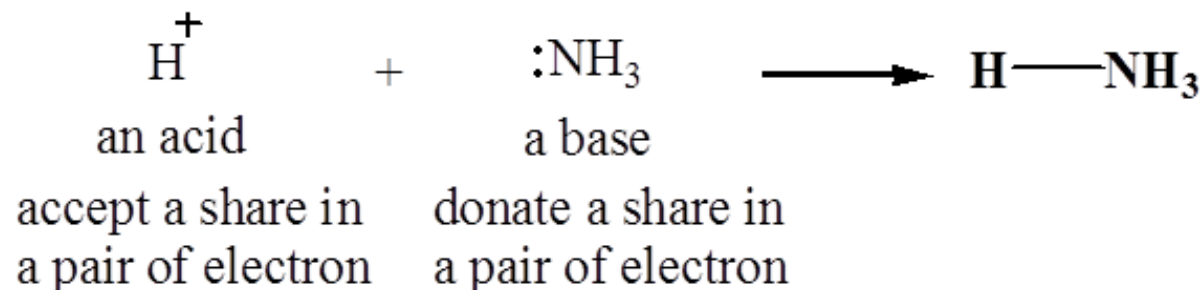
- **Acidity** is a measure of the tendency of a compound to give up a proton.
- **Basicity** is a measure of a compound's affinity for a proton.

# ACID-BASE CONCEPT

- In 1923, G. N. Lewis offered new definitions for the terms “acid” and “base.”

An acid as a species that accepts a share in an electron pair.

A base as a species that donates a share in an electron pair.



- **Lewis acid** such as aluminum chloride (AlCl<sub>3</sub>) boron trifluoride (BF<sub>3</sub>) and borane (BH<sub>3</sub>).

*The term “**acid**” is used to mean a proton-donating acid, and the term “**Lewis acid**” is used to refer to non-proton-donating acids such as AlCl<sub>3</sub> or BF<sub>3</sub>.*

- All bases are **Lewis bases** because they have a pair of electrons that they can share, either with an atom such as aluminum or boron or with a proton.



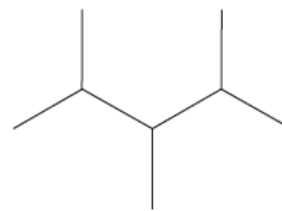
# CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

## a) Acyclic Compounds

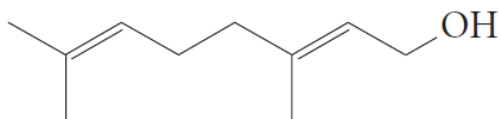
*Acyclic organic molecules* have chains of carbon atoms but no rings.



unbranched chain of  
eight carbon atoms



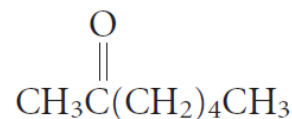
branched chain of  
eight carbon atoms



geraniol  
(oil of roses)  
bp 229–230°C



heptane  
(petroleum)  
bp 98.4°C



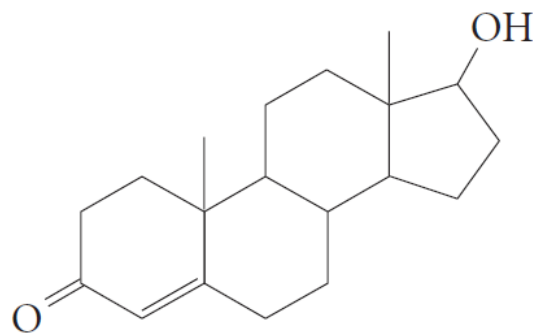
2-heptanone  
(oil of cloves)  
bp 151.5°C

# CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

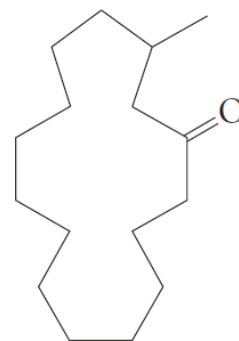
## b) Carbocyclic Compounds

*Carbocyclic compounds contain rings of carbon atoms.*

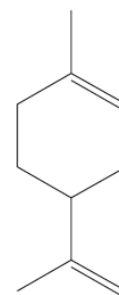
- The **smallest** possible carbocyclic ring has **three carbon atoms**.
- **Five- and six-membered rings** are most common, but smaller and larger rings are also found.
- Many compounds with more than one carbocyclic ring are known.



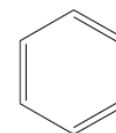
testosterone  
(testes)  
mp 155°C



muscone  
(musk deer)  
bp 327–330°C



limonene  
(citrus fruit oils)  
bp 178°C

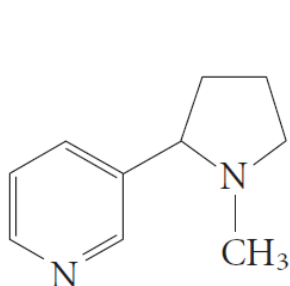


benzene  
(petroleum)  
mp 5.5°C, bp 80.1°C

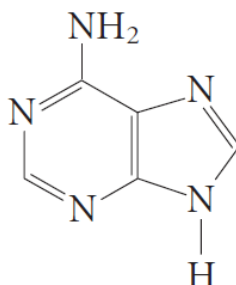
# CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

## c) Heterocyclic Compounds

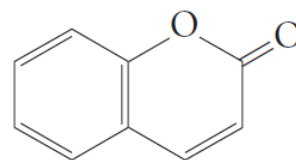
- **Heterocyclic compounds** make up the third and largest class of molecular frameworks for organic compounds.
- In **heterocyclic compounds**, at least one atom in the ring must be a heteroatom, an atom that is not carbon.
- The most common heteroatoms are **oxygen**, **nitrogen**, and **sulfur**, but heterocyclics with other elements are also known.



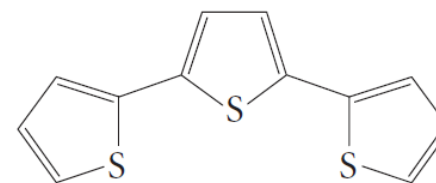
nicotine  
bp 246°C



adenine  
mp 360–365°C  
(decomposes)



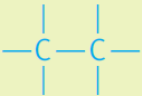
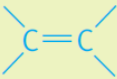

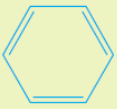
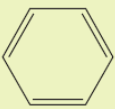
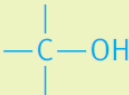
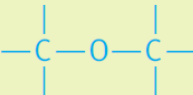
coumarin  
mp 71°C



$\alpha$ -terthienyl  
mp 92–93°C

# CLASSIFICATION ACCORDING TO FUNCTIONAL GROUP

## The Main Functional Groups

	Structure	Class of compound	Specific example	Common name of the specific example
<i>A. Functional groups that are a part of the molecular framework</i>		alkane	$\text{CH}_3\text{—CH}_3$	ethane, a component of natural gas
		alkene	$\text{CH}_2\text{=CH}_2$	ethylene, used to make polyethylene
		alkyne	$\text{HC}\equiv\text{CH}$	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
<i>B. Functional groups containing oxygen</i>				
<i>1. With carbon–oxygen single bonds</i>				
		alcohol	$\text{CH}_3\text{CH}_2\text{OH}$	ethyl alcohol, found in beer, wines, and liquors
		ether	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	diethyl ether, once a common anesthetic

# CLASSIFICATION ACCORDING TO FUNCTIONAL GROUP

continued

	Structure	Class of compound	Specific example	Common name of the specific example
2. With carbon-oxygen double bonds*	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	aldehyde	$\text{CH}_2=\text{O}$	formaldehyde, used to preserve biological specimens
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{C}-\text{C}- \\   \quad   \quad   \end{array}$	ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \end{array}$	acetone, a solvent for varnish and rubber cement
3. With single and double carbon-oxygen bonds	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OH} \end{array}$	acetic acid, a component of vinegar
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{C}- \\   \quad   \end{array}$	ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OCH}_2\text{CH}_3 \end{array}$	ethyl acetate, a solvent for nail polish and model airplane glue
C. Functional groups containing nitrogen**	$\begin{array}{c}   \\ -\text{C}-\text{NH}_2 \\   \end{array}$	primary amine	$\text{CH}_3\text{CH}_2\text{NH}_2$	ethylamine, smells like ammonia
	$-\text{C}\equiv\text{N}$	nitrile	$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	acrylonitrile, raw material for making Orlon

# CLASSIFICATION ACCORDING TO FUNCTIONAL GROUP

continued

	Structure	Class of compound	Specific example	Common name of the specific example
D. Functional group with oxygen and nitrogen	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}_2 \end{array}$	primary amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{NH}_2 \end{array}$	formamide, a softener for paper
E. Functional group with halogen	$-\text{X}$	alkyl or aryl halide	$\text{CH}_3\text{Cl}$	methyl chloride, refrigerant and local anesthetic
F. Functional groups containing sulfur <sup>†</sup>	$\begin{array}{c}   \\ -\text{C}-\text{SH} \\   \end{array}$	thiol (also called mercaptan)	$\text{CH}_3\text{SH}$	methanethiol, has the odor of rotten cabbage
	$\begin{array}{c}   \quad \quad   \\ -\text{C}-\text{S}-\text{C}- \\   \quad \quad   \end{array}$	thioether (also called sulfide)	$(\text{CH}_2=\text{CHCH}_2)_2\text{S}$	diallyl sulfide, has the odor of garlic

\*The  $\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$  group, present in several functional groups, is called a **carbonyl group**. The  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$  group of acids is called a **carboxyl group** (a contraction of *carbonyl* and *hydroxyl*).

\*\*The  $-\text{NH}_2$  group is called an **amino group**.

<sup>†</sup>Thiols and thioethers are the sulfur analogs of alcohols and ethers.