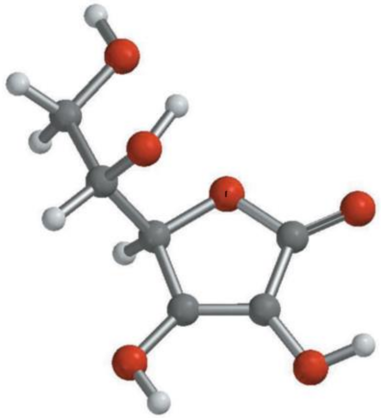
CHEM 240

PRINCIPLES OF ORGANIC CHEMISTRY I

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.

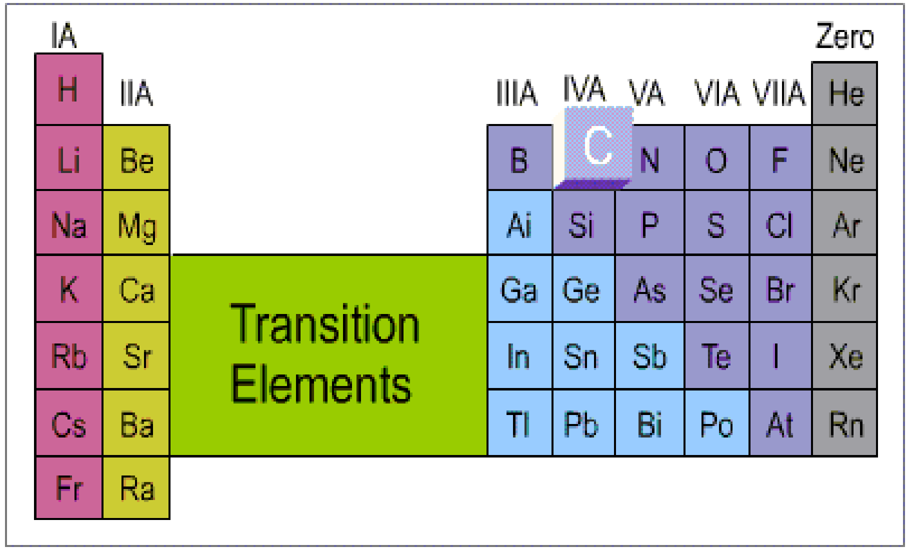
  The clothes, the petroleum products, the paper, rubber, wood, plastics, paint, cosmetics, insecticides, and drugs

- 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.



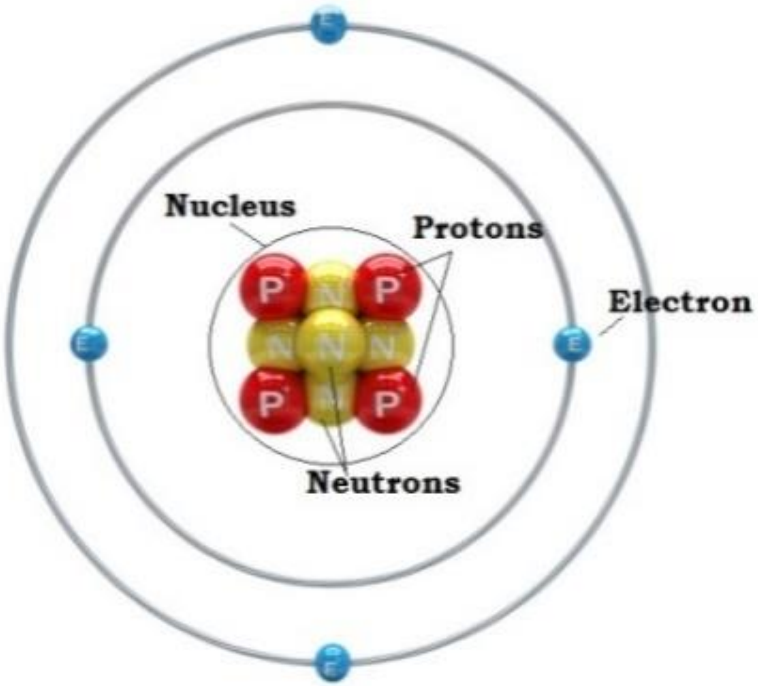
- **These factors enable it to form strong bonds with**
  - other carbon atoms
  - and with other elements (hydrogen, oxygen, nitrogen, halogens,…etc).

- **Each organic compound has its own characteristic set of physical and chemical properties which depend on the *structure of the molecule*.**

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.

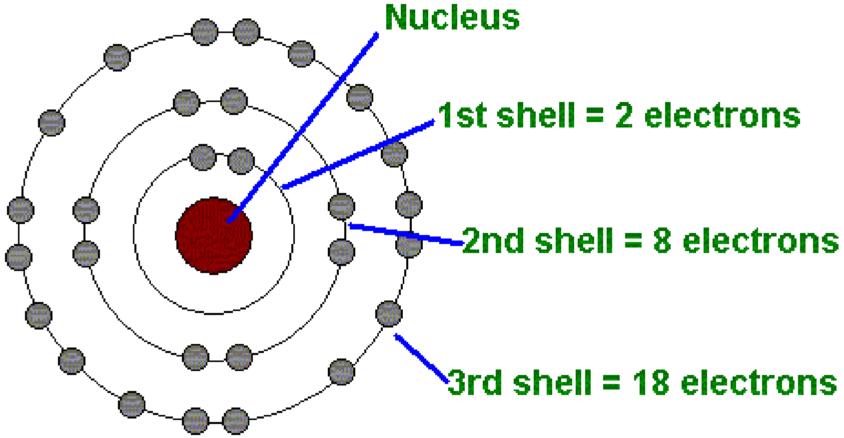
  i.e. Number of electrons = Number of protons

- **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.**

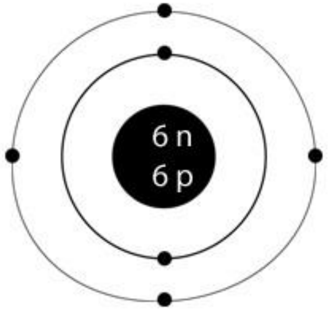


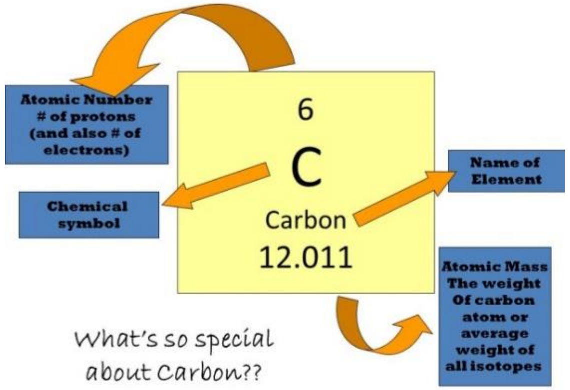
- **For example,** the element carbon (atomic number 6)

  6 electrons are distributed about the nucleus as

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

Carbon $^{12}_{6}C$

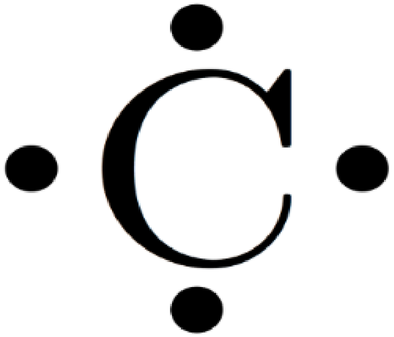




ATOMIC STRUCTURE

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.



Valences of Common Elments						
Element	H·	·C·	·N:	·O:	:F:	:Cl:
Valence	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***.

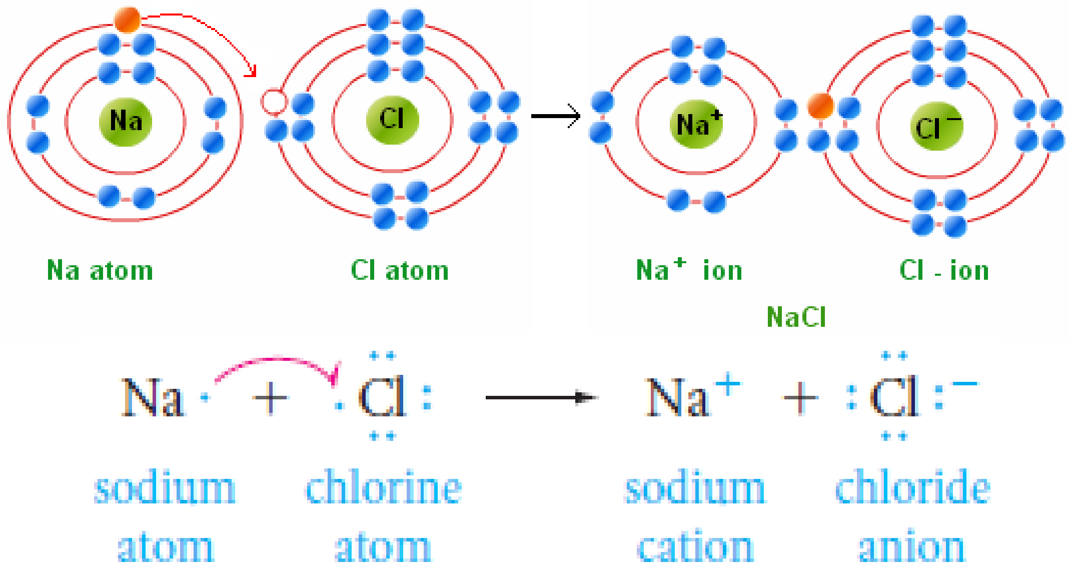
A) IONIC BOND

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



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.*

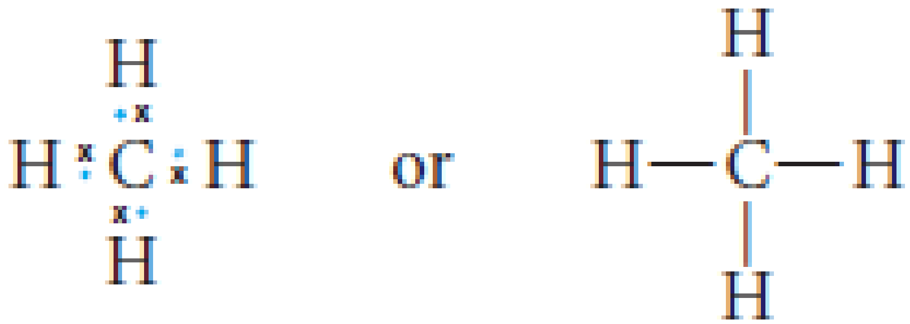
  - When the two atoms are <u>identical or have equal electronegativities</u>, the electron pairs are shared equally.

$$H\cdot + H\cdot \longrightarrow H:H + \text{heat}$$

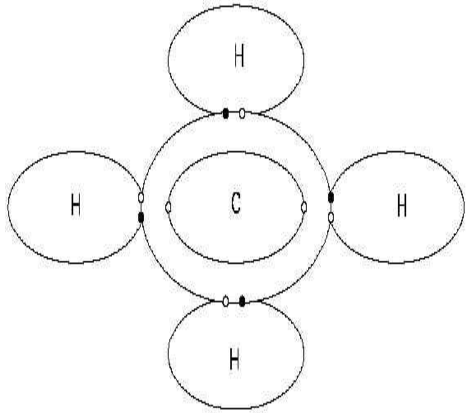
hydrogen atoms → hydrogen molecule

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.



methane

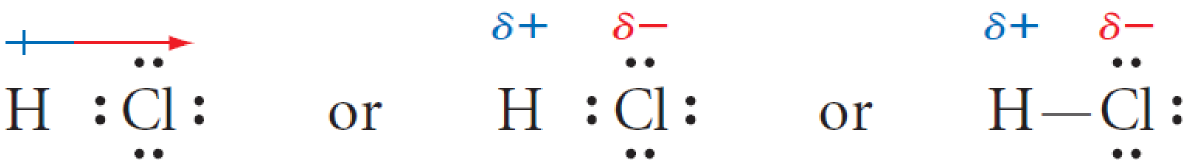


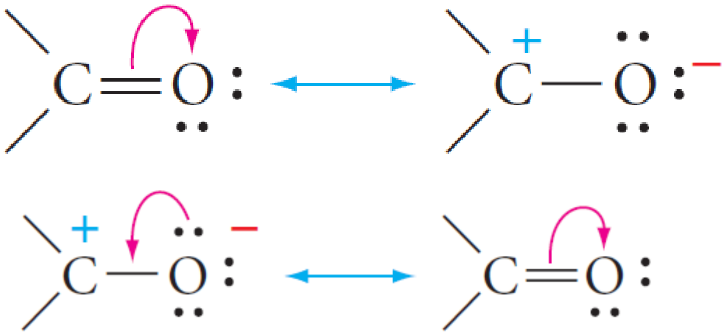
B) COVALENT BOND

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****.*

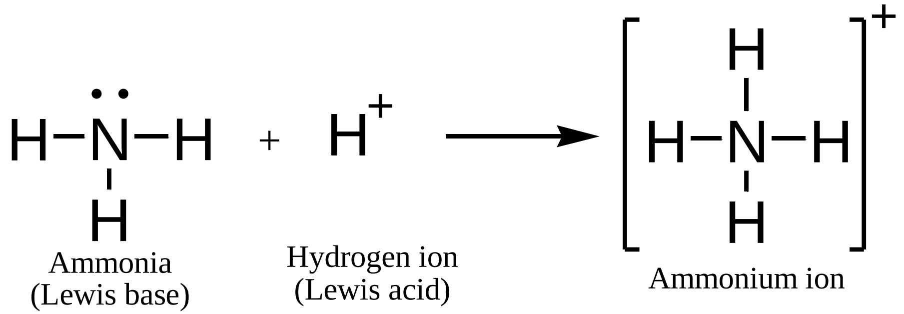




B) COVALENT BOND

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;

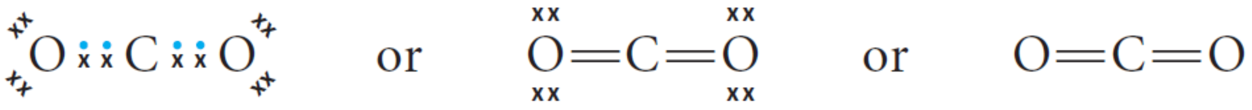


- Lewis base; *The species that furnishes the electron pair to form a coordinate covalent bond.*
- Lewis acid; *The species that accepts the electron pair to complete its valance shell.*

MULTIPLE COVALENT BONDS

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

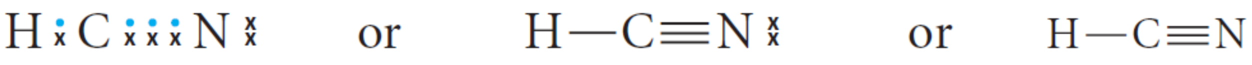
  Example; Carbon dioxide, CO_2



A B C

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.

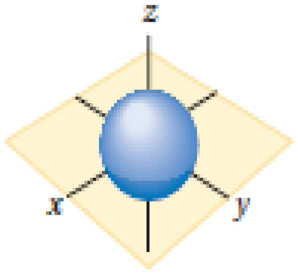
- In a ***triple bond,*** *three electron pairs are shared between two atoms.*



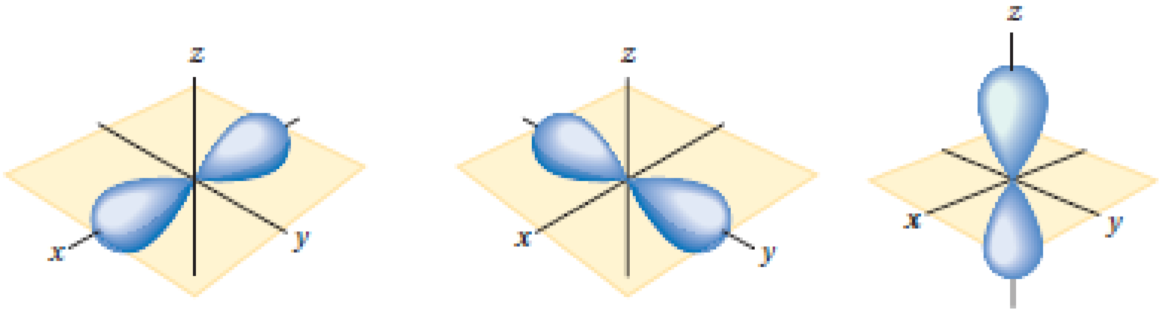
hydrogen cyanide

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.



2s



$2p_x$ $2p_y$ $2p_z$

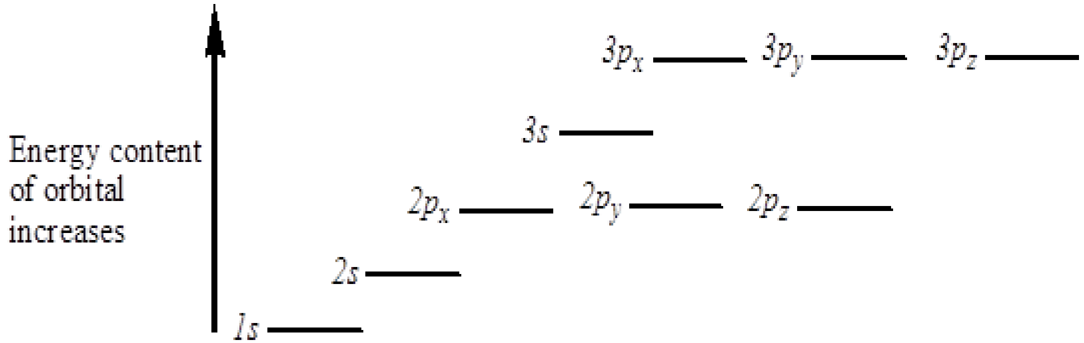
- **Examples:**

K shell has only one 1s orbital.

L shell has one 2s and three 2p ($2p_x$, $2p_y$ and $2p_z$).

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.

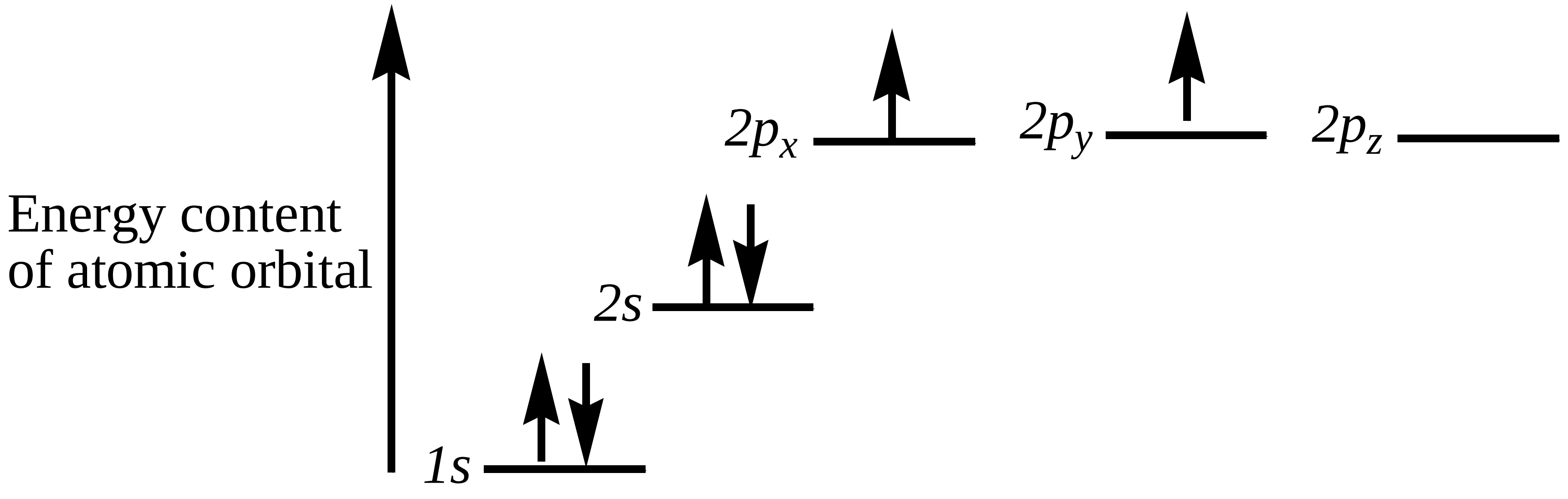
  (2) Electrons fill orbitals of lower energy first.

  (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

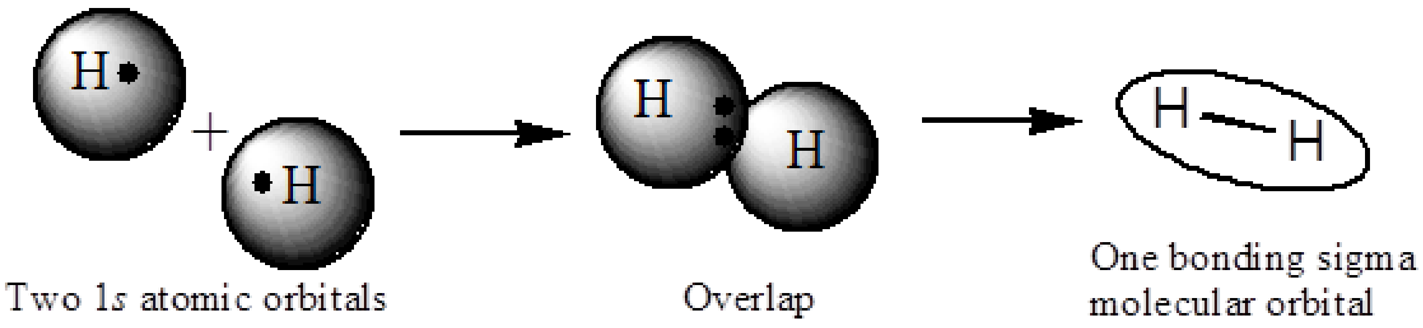
$1s^2 2s^2 2p1x2p1y$ or $1s^2 2s^2 2p^2$



Energy level diagram for carbon.

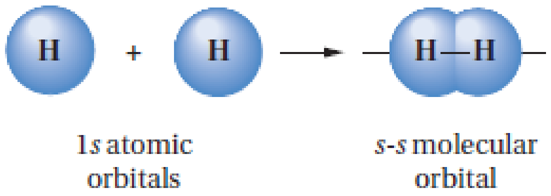
MOLECULAR ORBITALS

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

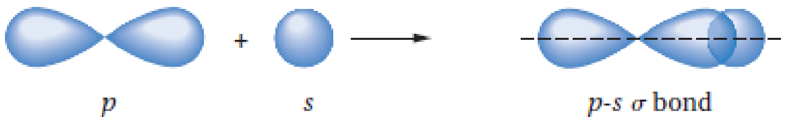


SIGMA (σ) AND pi (π) BONDS

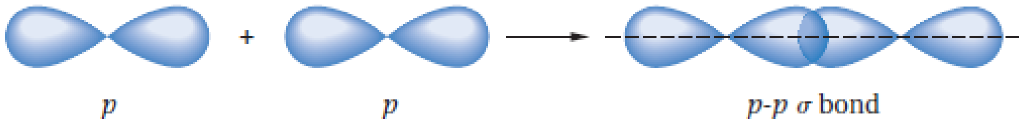
- Sigma bonds (σ bonds) can be formed from
  - The overlap of two s atomic orbitals.



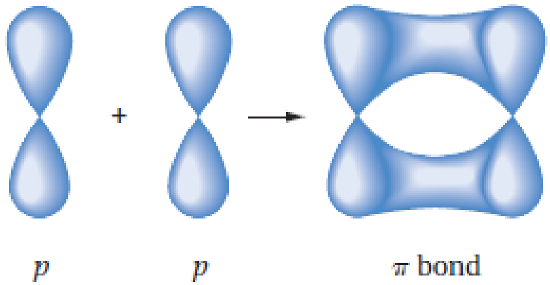
  - The overlap of two an s atomic orbital with a p atomic orbital.



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



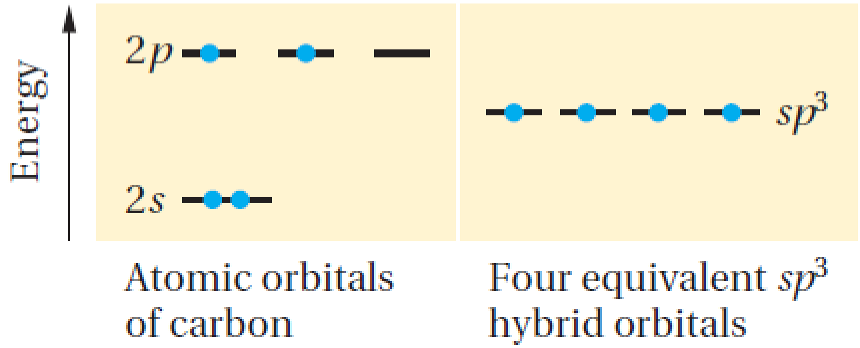
- pi bonds (π bonds) can be formed from
  - The side-side overlap between two p atomic orbitals.



CARBON sp^3 HYBRID ORBITALS

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

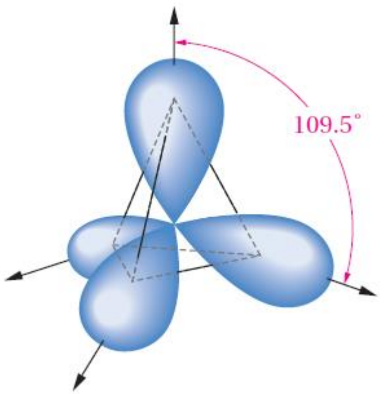
$1s^22s^22p_x^{\ 1}2p_y^{\ 1}$ ***Equivalent to*** :Ċ·

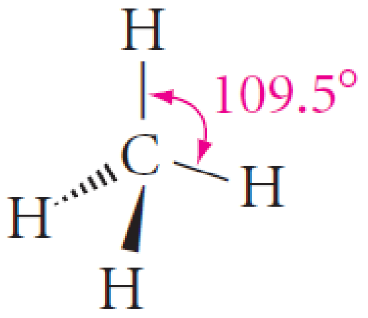


- Mix or combine the four atomic orbitals of the valence shell to form four identical hybrid orbitals, each containing one valence electron. In this model, the hybrid orbitals are called **sp^3 hybrid orbitals** because each one has one part s character and three parts *p* character
- Each sp^3 orbital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

CARBON *sp*^{3} HYBRID ORBITALS

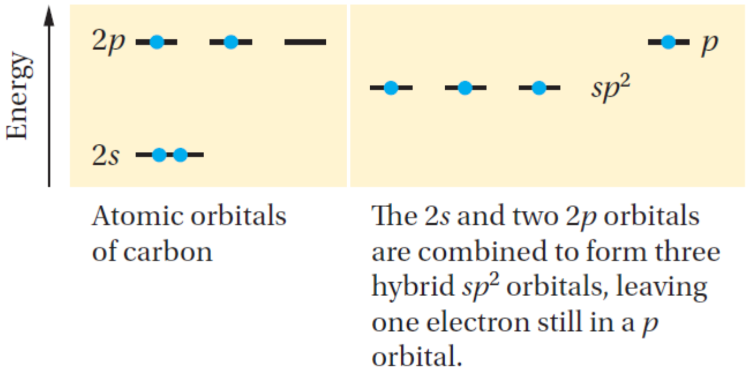
- The angle between any two of the four bonds formed from *sp*^{3} orbitals is approximately 109.5°.
- Regular tetrahedral geometry
- The tetrahedral is a pyramid-like structure with the carbon atom at the center and the four attached atoms located at a corner.





CARBON sp^2 HYBRID ORBITALS

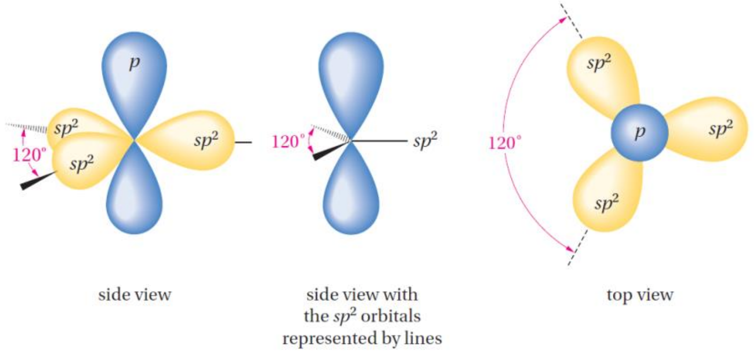
- Combine only three of the orbitals, to make three equivalent sp^2-hybridized orbitals (called sp^2 because they are formed by combining one s and two p orbitals)



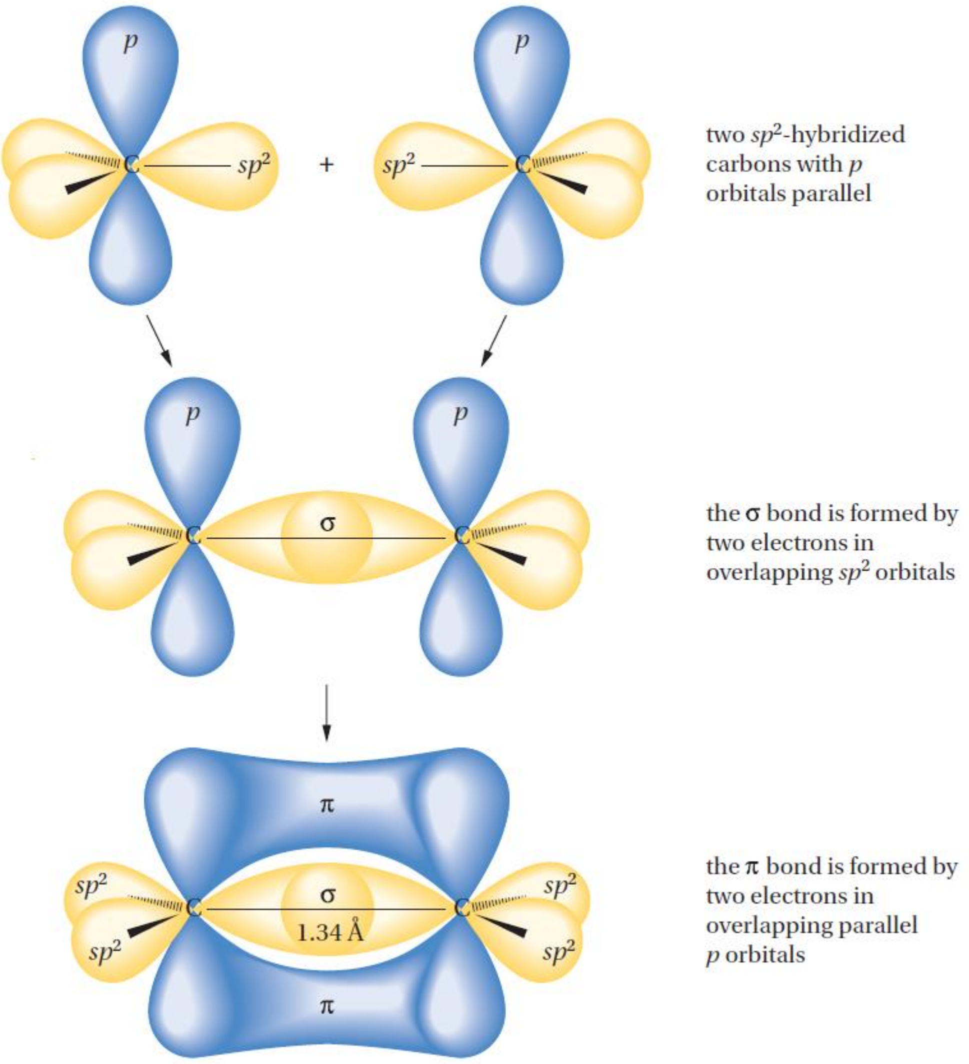
- Three valence electrons are placed in the three sp^2 orbitals. The fourth valence electron is placed in the remaining $2p$ orbital, whose axis is perpendicular to the plane formed by the three sp^2 hybrid orbitals

- The angle between them is 120°.

- A trigonal carbon



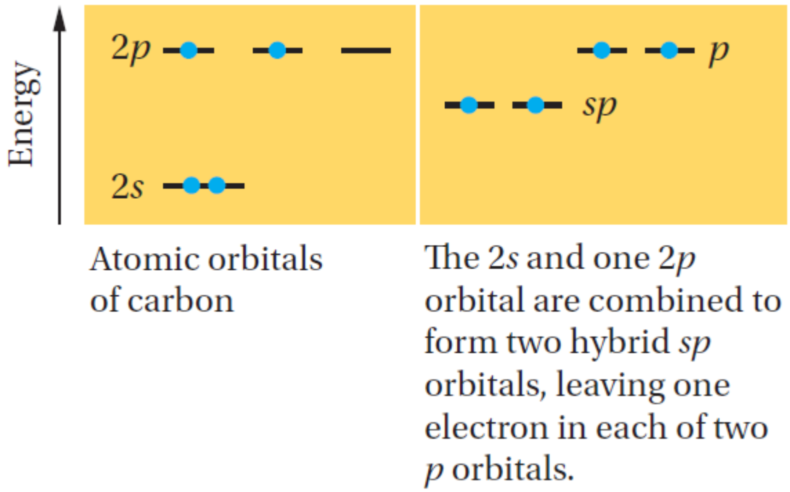
CARBON *sp*^{2} HYBRID ORBITALS



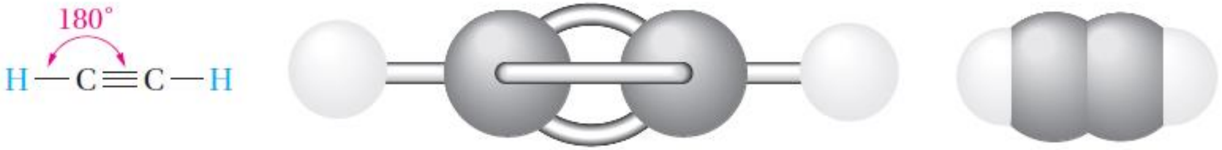
Schematic formation of a carbon–carbon double bond. Two *sp*^{2} carbons form a sigma (s) bond (end-on overlap of two *sp*2 orbitals) and a pi (p) bond (lateral overlap of two properly aligned *p* orbitals).

CARBON *sp* HYBRID ORBITALS

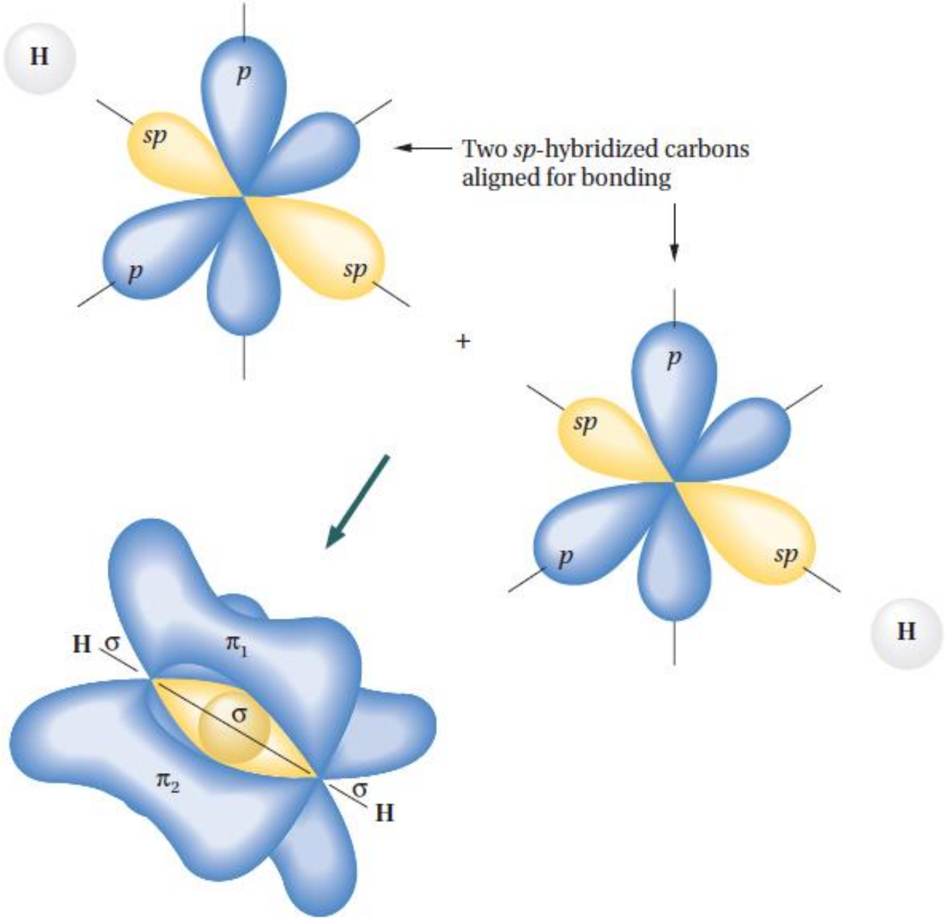
- The carbon atom of an acetylene is connected to only *two* other atoms. Therefore, we combine the 2*s* orbital with only one 2*p* orbital to make two *sp*-hybrid orbitals



- The angle between the two hybrid orbitals is 180°
- Linear



CARBON *sp* HYBRID ORBITALS

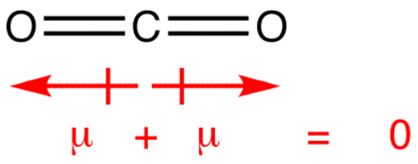


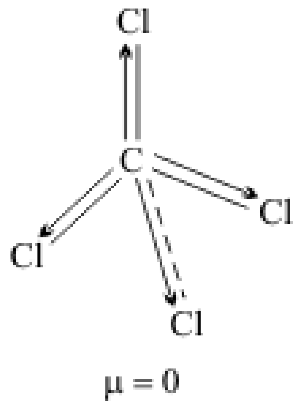
The resulting carbon–carbon triple bond, with a hydrogen atom attached to each remaining *sp* bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

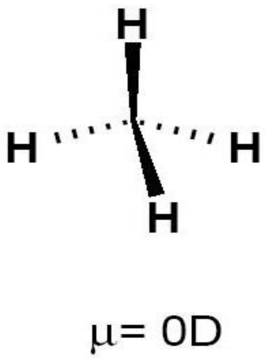
A triple bond consists of the end-on overlap of two *sp*-hybrid orbitals to form a σ bond and the lateral overlap of two sets of parallel-oriented *p* orbitals to form two mutually perpendicular π bonds.

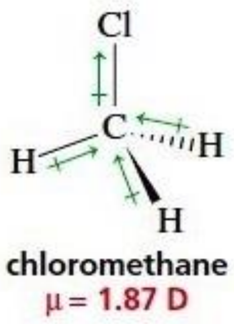
BOND POLARITY AND DIPOLE MOMENT (μ)

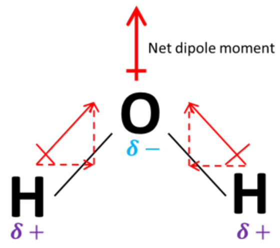
- A polar bond is a covalent bond between two atoms where the electrons forming the bond are unequally distributed.
- A nonpolar bond is a covalent bond between two atoms where the electrons forming the bond are equally distributed.
- A dipole moment is a measurement of the separation of two oppositely 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.

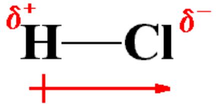






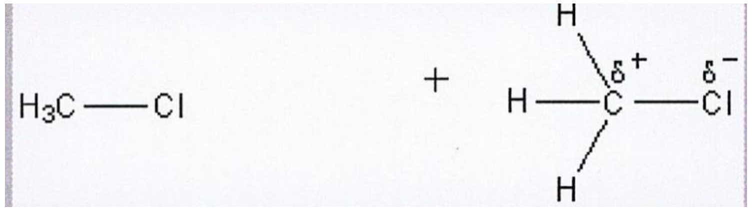




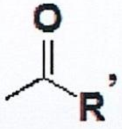


INDUCTIVE EFFECT

- *An* ***inductive effect*** *is an electronic effect due to the polarization of* ***σ 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



- CH_3, -C_2H_5, -NH_2, -OH, -OCH_3,..... (+ I) electron-donating substituent

-NO_2, -CN, -SO_3H,  , ... (- 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_2O) meets the definition of a base because it accepts a proton from HCl.

$$\underset{\text{an acid}}{HCl} + \underset{\text{a base}}{H_2\ddot{O}:} \rightleftharpoons \underset{\text{a base}}{Cl^-} + \underset{\text{an acid}}{H_3\overset{+}{O}}$$

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

In the reverse reaction, H_3O^+ is an acid because it donates a proton to Cl^-, and Cl^- is a base because it accepts a proton from H_3O^+.

ACID-BASE CONCEPT

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

  Thus, Cl^- is the conjugate base of HCl, and H_2O is the conjugate base of H_3O^+

  Thus, HCl is the conjugate acid of Cl^- and H_3O^+ is the conjugate acid of H_2O

- 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.

$$H^{+} \quad + \quad :NH_3 \longrightarrow \mathbf{H{-}NH_3}$$

H⁺	:NH₃
an acid	a base
accept a share in a pair of electron	donate a share in a pair of electron

- Lewis acid such as aluminum chloride ($AlCl_3$) boron trifluoride (BF_3) and borane (BH_3).

  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 $AlCl_3$ or BF_3.

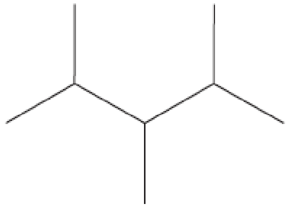
- All bases are Lewis bases because they have a pair of electrons that they can share, either with an atom such as aluminum or boron or with a proton.

CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

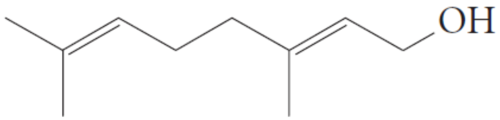
a) Acyclic Compounds

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

$CH_3(CH_2)_5CH_3$

heptane
(petroleum)
bp 98.4°C

$CH_3\overset{\overset{O}{\|}}{C}(CH_2)_4CH_3$

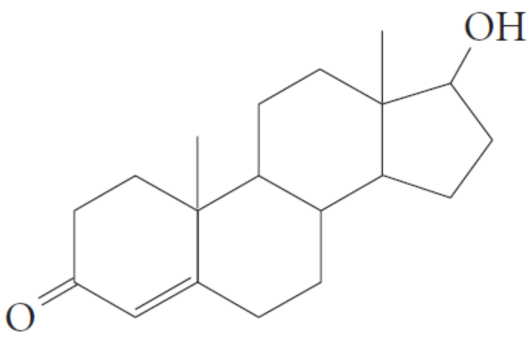
2-heptanone
(oil of cloves)
bp 151.5°C

CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

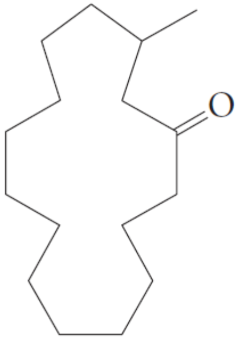
b) Carbocyclic Compounds

Carbocyclic compounds *contain rings of carbon atoms.*

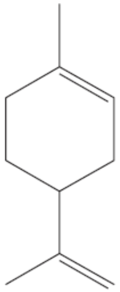
- The **smallest** possible carbocyclic ring has **three carbon atoms**.
- **Five- and six-membered rings** are most common, but smaller and larger rings are also found.
- Many compounds with more than one carbocyclic ring are known.



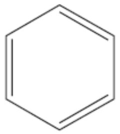
testosterone
(testes)
mp 155°C



muscone
(musk deer)
bp 327–330°C



limonene
(citrus fruit oils)
bp 178°C

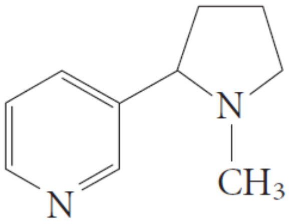


benzene
(petroleum)
mp 5.5°C, bp 80.1°C

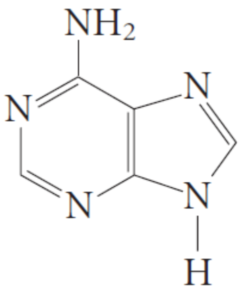
CLASSIFICATION ACCORDING TO MOLECULAR FRAMEWORK

c) Heterocyclic Compounds

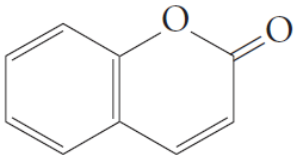
- Heterocyclic compounds make up the third and largest class of molecular frameworks for organic compounds.
- In heterocyclic compounds, at least one atom in the ring must be a heteroatom, an atom that is not carbon.
- The most common heteroatoms are oxygen, nitrogen, and sulfur, but heterocyclics with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



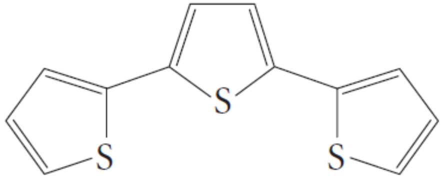
nicotine
bp 246°C



adenine
mp 360–365°C
(decomposes)



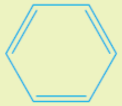
coumarin
mp 71°C



α-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
A. Functional groups that are a part of the molecular framework	—C—C—	alkane	$CH_3—CH_3$	ethane, a component of natural gas
	>C=C<	alkene	$CH_2{=}CH_2$	ethylene, used to make polyethylene
	—C≡C—	alkyne	HC≡CH	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
B. Functional groups containing oxygen				
1. With carbon–oxygen single bonds	—C—OH	alcohol	CH_3CH_2OH	ethyl alcohol, found in beer, wines, and liquors
	—C—O—C—	ether	$CH_3CH_2OCH_2CH_3$	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**	$-\overset{O}{\overset{\|}{C}}-H$	aldehyde	$CH_2{=}O$	formaldehyde, used to preserve biological specimens
	$-\overset{\|}{\underset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{\|}{\underset{\|}{C}}-$	ketone	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	acetone, a solvent for varnish and rubber cement
3. With single and double carbon–oxygen bonds	$-\overset{O}{\overset{\|}{C}}-OH$	carboxylic acid	$CH_3\overset{O}{\overset{\|}{C}}-OH$	acetic acid, a component of vinegar
	$-\overset{O}{\overset{\|}{C}}-O-\overset{\|}{\underset{\|}{C}}-$	ester	$CH_3\overset{O}{\overset{\|}{C}}-OCH_2CH_3$	ethyl acetate, a solvent for nail polish and model airplane glue
*C. Functional groups containing nitrogen***	$-\overset{\|}{\underset{\|}{C}}-NH_2$	primary amine	$CH_3CH_2NH_2$	ethylamine, smells like ammonia
	$-C{\equiv}N$	nitrile	$CH_2{=}CH-C{\equiv}N$	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	—C(=O)—NH_2	primary amide	H—C(=O)—NH_2	formamide, a softener for paper
E. Functional group with halogen	—X	alkyl or aryl halide	CH_3Cl	methyl chloride, refrigerant and local anesthetic
F. Functional groups containing sulfur†	—C—SH (with bonds above and below C)	thiol (also called mercaptan)	CH_3SH	methanethiol, has the odor of rotten cabbage
	—C—S—C— (with bonds above and below each C)	thioether (also called sulfide)	$(CH_2{=}CHCH_2)_2S$	diallyl sulfide, has the odor of garlic

*The >C=O group, present in several functional groups, is called a **carbonyl group**. The —C(=O)—OH group of acids is called a **carboxyl group** (a contraction of *carb*onyl and hydr*oxyl*).

The —NH_2 group is called an **amino group.

†Thiols and thioethers are the sulfur analogs of alcohols and ethers.