

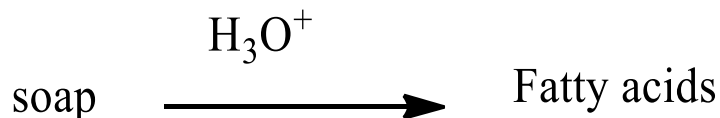
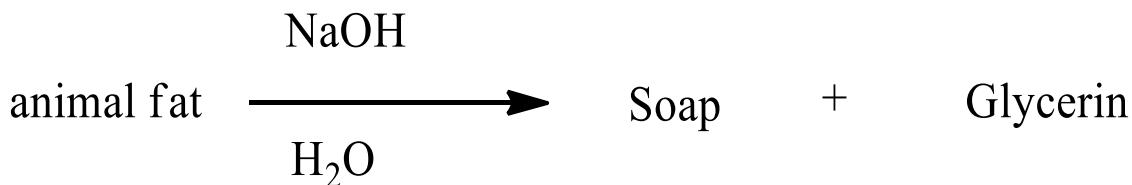


HAWASSA UNIVERSITY
Department of Chemistry
Organic Chemistry-I
(Chem 2042)

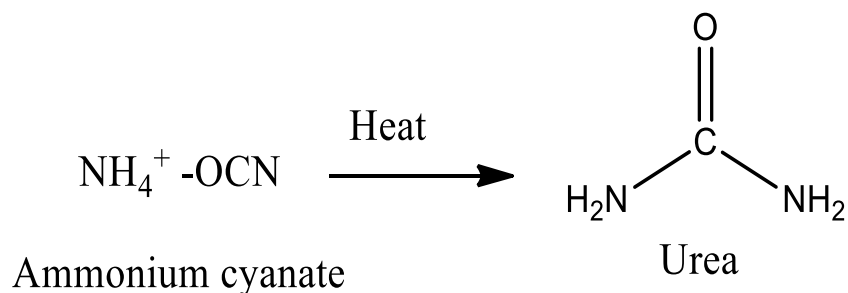
Historical Background of Organic Chemistry

- The foundation of organic chemistry date from the **mid 1700s**, when chemistry was evolving from an alchemist's art in to modern science. At that time, unexplainable differences were noted between substances obtained from living sources and those obtained from minerals.
- Compounds obtained from plants and animals were difficult to isolate and purify. Even when pure . they were often difficult to work with, and they tended to decompose more easily than compounds obtained from minerals.
- The swedish chemist torbern Bergman in 1770 was the first to express this difference between organic and inorganic substances , and the term organic chemistry soon came to mean the chemistry of compounds found in living organisms.

- To many chemistry of the time , the only explanation for the differences in behavior between organic and inorganic compounds was that organic compounds must contain a peculiar “vital force” as a result of their origin in living sources.
- One consequence of this vital force , chemists believed, was that organic compounds could not be prepared and manipulated in the laboratory as could inorganic compounds.
- As early as 1816 , however, this vitalistic theory received a heavy blow when michel chevereul found that soap , prepared by the reaction of alkali with animal fat , could be separated in to several pure organic compounds, which he termed fatty acids.
- For the first time , one organic substance (fat) was converted in to others (fatty acids plus glycerin) without intervention of an outside vital force.



- Little more than a decade later, the vitalistic theory suffered still further when Friedrich Wöhler discovered in 1828 that it was possible to convert the “**inorganic**” salt **ammonium cyanate** into the “**organic**” substance **Urea**, which had previously been found in human urine.



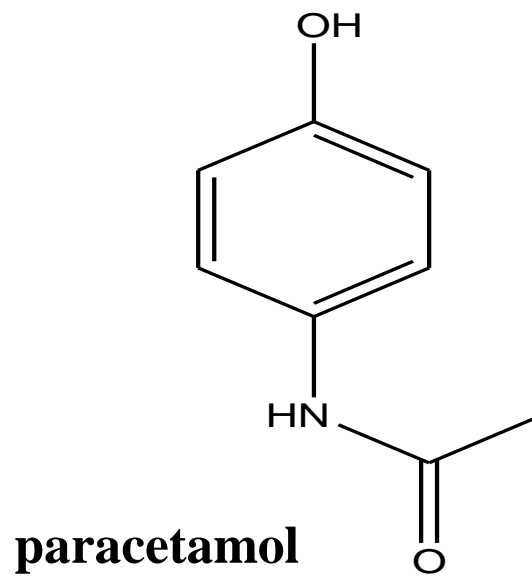
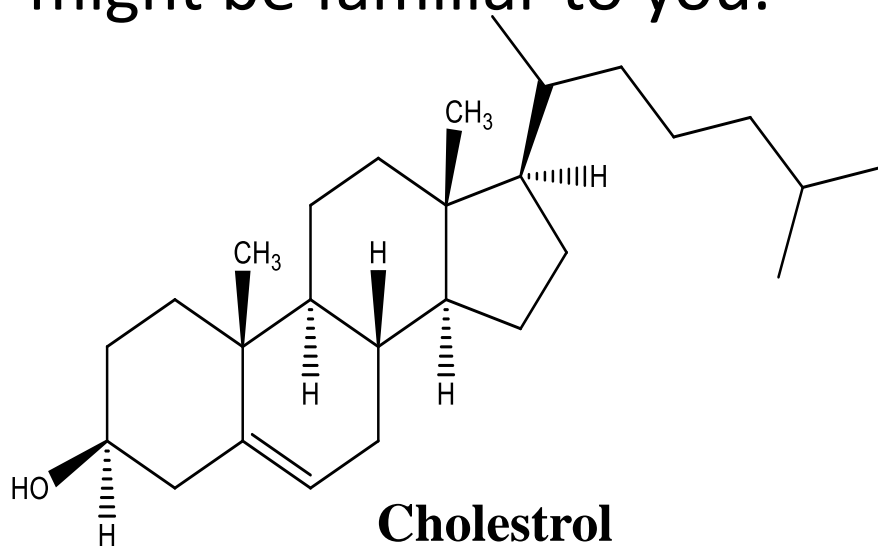
What is organic chemistry?

- Organic chemistry is the scientific study of the structure, properties, composition, reactions, and synthesis of organic compounds that by definition contain carbon. ...
- Many organic compounds contain nitrogen, oxygen, halogens, and more rarely phosphorus or sulphur.
- Some exceptions: for example
 - ☞ carbonates,
 - ☞ carbon dioxide, etc... are not studied by organic chemistry.

Why should you study it?

- To answer this question is all around you. Every living organism is made of organic chemicals.
 - ☞ Organic chemistry plays an important part in our daily life because food, clothes, paper, ink, rubber, soap, perfumes, medicines etc. are indispensable to us for proper living.
 - ☞ Organic compounds are important constituents of many products e.g., paint, food, plastic, explosive, medicine, petrochemical, pesticide etc.

- Anyone with the curiosity about life and living things, and anyone who wants to be part of the many exciting developments now happening in medicine and the biological science , must first understand organic chemistry.
- Look at the following drawing for instance, which show chemical structure of some molecules whose names might be familiar to you.



Special nature of carbon

1. CATENATION

- **Catenation** is the ability to form bonds between atoms of the same element.
- Carbon forms chains and rings, with single, double and triple covalent bonds, because it is able to form strong covalent bonds with other carbon atoms
- Carbon forms a vast number of carbon compounds because of the strength of the C-C covalent bond. Other Group IV elements can do it but their chemistry is limited due to the weaker bond strength.

Bond	Atomic Radius	Bond Enthalpy
C-C	0.077 nm	+348 kJmol ⁻¹
Si-Si	0.117 nm	+176 kJmol ⁻¹

- The **larger the atoms**, the **weaker the bond**. **Shielding** due to filled inner orbitals and **greater distance from the nucleus** means that the shared **electron pair is held less strongly**.
- $\text{C} - \text{C} > \text{Si} - \text{Si} > \text{Ge} - \text{Ge} > \text{Sn} - \text{Sn}$ in catenation because
 - **Bond strength decreases as bond length increases**
- $\text{C} - \text{C} > \text{N} - \text{N} > \text{O} - \text{O}$ in catenation because
 - **Bond strength decreases as the number of lone pairs increases**

2. carbon can form chains and rings

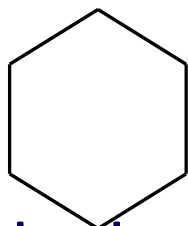
❖ carbon atoms can be arranged in

✓ straight chains

✓ branched chains and

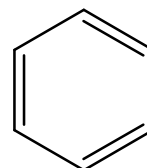
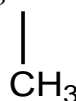
✓ Rings

eg.



eg. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

eg. $\text{CH}_3\text{CHCH}_2\text{CH}_3$



3. atoms/groups can be placed in different positions on a carbon skeleton

➤ the c=c double bond is in a different position

eg. $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$

but-1-ene

$\text{CH}_3\text{CH}=\text{CHCH}_3$

but-2-ene

➤ the chlorine atom is in a different position

eg. $\text{CH}_3\text{CHCH}_2\text{CH}_3$



2-chlorobutane

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$



1-chlorobutane

Energy Levels and Atomic Orbitals

Atomic structure

- What is an Atom?
- Atom is the smallest piece of matter that still retains the properties of that matter.
- What are they composed of?
- atom consists protons, neutrons and electrons
- What makes one element different from another element?
- Ans = Number of protons.

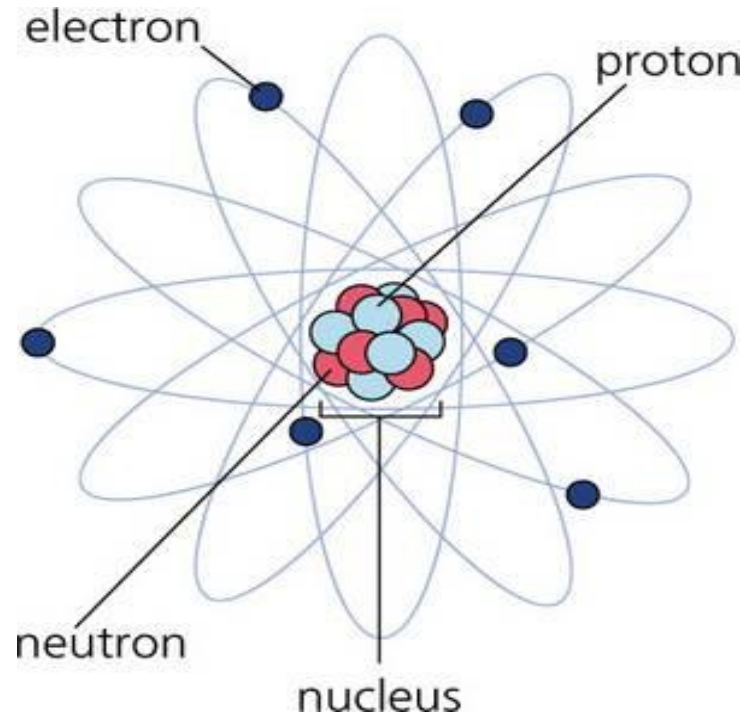
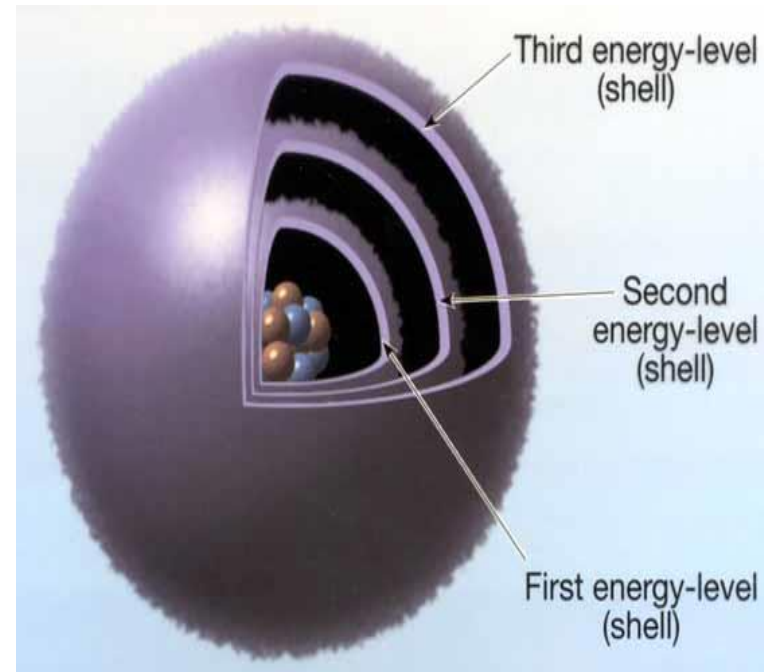
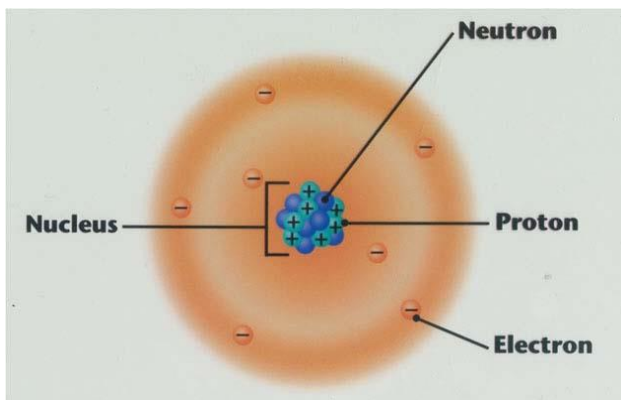


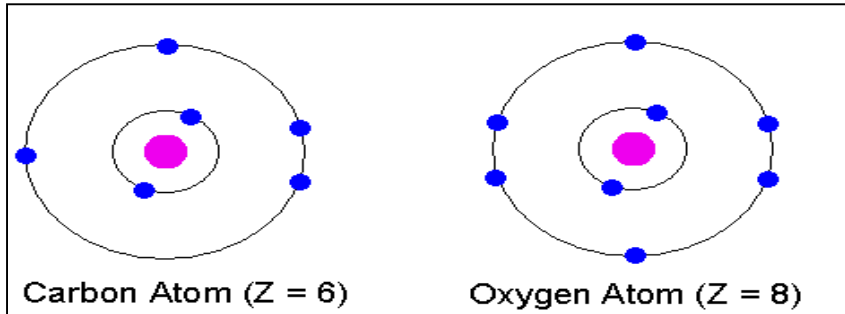
Table 1.1**Properties of Subatomic Particles**

Particle	Symbol	Relative charge	Relative mass (mass of proton = 1)	Actual mass (g)
Electron	e^{-}	1 $-$	1/1840	9.11×10^{-28}
Proton	p^{+}	1 $+$	1	1.67×10^{-24}
Neutron	n^0	0	1	1.67×10^{-24}

- Electrons are found in different levels around the nucleus.
- These are called Energy Levels or shells.
- Each energy level also has “sublevels” or



- Each energy level can hold a certain number of electrons.



- first level holds only 2 electrons
- 2nd level holds 8 electrons etc...

Valence electrons

- Electrons in the outermost energy levels are called valence electron.
- Valence electrons determines how an atom will act in a chemical reaction.
- Atoms with equal numbers of valence electrons have similar properties.
- Carbon has 4 valence electrons

- Based on *quantum theory*, which says matter also has properties associated with waves.
- According to quantum theory, it's impossible to know the exact position and momentum of an electron at the same time. This is known as the ***Uncertainty Principle***.
- This model of the atom uses complex shapes of **orbitals** (sometimes called *electron clouds*)
- Orbitals: volumes of space in which there is *likely* to be an electron.

So, this model is based on probability rather than certainty.

- According to quantum mechanics, each electron is described by **four** quantum numbers:
 1. Principal quantum number (n)
 2. Angular momentum quantum number (l)
 3. Magnetic quantum number (m_l)
 4. Spin quantum number (m_s)
- The first three define the wave function for a particular electron. The fourth quantum number refers to the magnetic property of electrons.

I. Principal Quantum Number (n)

- This quantum number is the one on which the energy of an electron in an atom primarily depends. The smaller the value of n , the lower the energy and the smaller the orbital.
- The principal quantum number can have any positive value: 1, 2, 3, . . .
- Orbitals with the same value for n are said to be in the same shell.
- Generally it defines about Which energy level the e^- is in.
- $n= 1-7$ (there are only 7 energy levels)
- the larger the value of n , the farther away from the nucleus and the higher the energy of the electron.
- $n=1$ (first shell, K) $n= 2$ second shell(L), so forth... or

II. Angular momentum quantum number = l

- Specifies sub energy levels within the main energy levels(subshells) and related to shape of the electron subshell
- Each shape “sublevel” can only have 2 electrons(Max electrons in each sublevel).

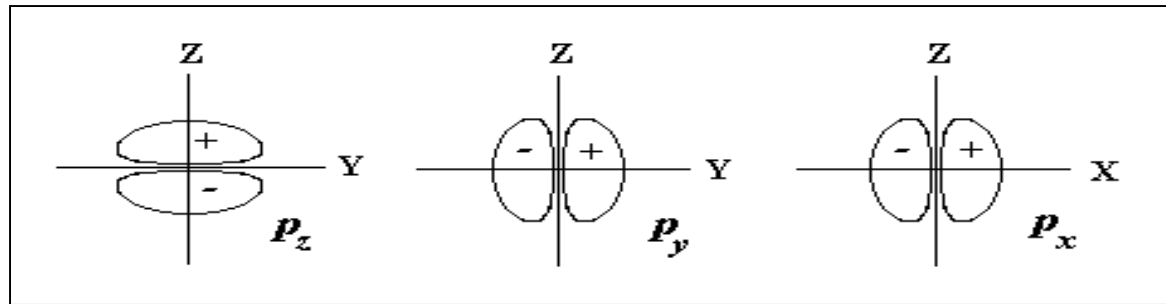
$$l = 0 \dots n-1$$

Number designation of l	0	1	2	3	4	5
Letter designation of l	s	p	d	f	g	h

Table 1.2 : principal quantum number , shell designation and subshells		
Principle quantum number (n)	Shell Designation	Subshells
1	K	s
2	L	s,p
3	M	s,p,d
4	N	s,p,d,f

III. Magnetic quantum number= m_l

- Describes orientation in space x, y, z (Number of orbitals or energy states for each subshell)
- Example p-orbitals oriented in the space x , y and z seems like the following

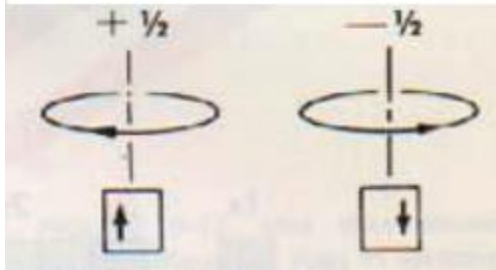


$$m_l = 2l + 1$$

- Example: For a given l , m_l can range from $+l$ to $-l$
 - $l=0$ (s subshell) $\Rightarrow m_l = 1$ energy state (0)
 - $l=1$ (p subshell) $\Rightarrow m_l = 3$ energy states (+1, 0, -1)
 - $l=2$ (d subshell) $\Rightarrow m_l = 5$ energy states (+2, +1, 0, -1, -2)

IV. spin quantum number= m_s

- Describes the spin of the electron in the orbital (either Clock or counter-clock wise).



- See the following to have summarized concepts on the 4 quantum numbers.

- For $n = 1$, $l = 0$ and $m_l = 0$
 - There is only one subshell and that subshell has a single orbital
 - (m_l has a single value ---> 1 orbital)
 - This subshell is labeled s ("ess") and we call this orbital 1s
 - Each shell has 1 orbital labeled s.
 - It is SPHERICAL in shape.

- For $n = 2$, $l = 0$ and 1
- There are 2 types of orbitals — 2 subshells
 - For $l = 0$ $m_l = 0$
 - this is a s subshell
 - For $l = 1$ $m_l = -1, 0, +1$
 - this is a p subshell with 3 orbitals

Table 1.3**Summary of Principal Energy Levels, Sublevels, and Orbitals**

Principal energy level	Number of sublevels	Type of sublevel
$n = 1$	1	1s (1 orbital)
$n = 2$	2	2s (1 orbital), 2p (3 orbitals)
$n = 3$	3	3s (1 orbital), 3p (3 orbitals), 3d (5 orbitals)
$n = 4$	4	4s (1 orbital), 4p (3 orbitals), 4d (5 orbitals), 4f (7 orbitals)

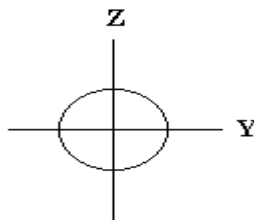
Orbitals

- An orbital is a region of space where the probability of finding an electron is large (the space where an electron spends 90% to 95% of its time).

What do orbitals look like?

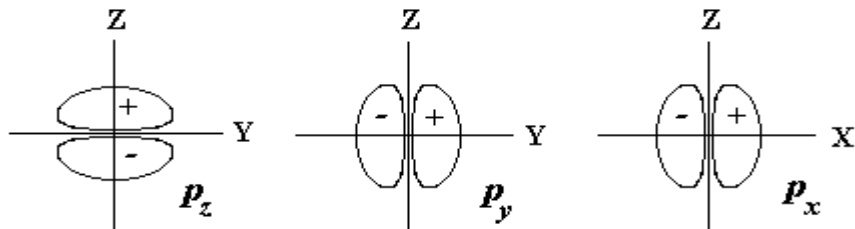
- There are four different kinds of orbitals, denoted ***s***, ***p***, ***d***, and ***f***, each with a different shape

- An s orbital is **spherical**, with the nucleus at its center;



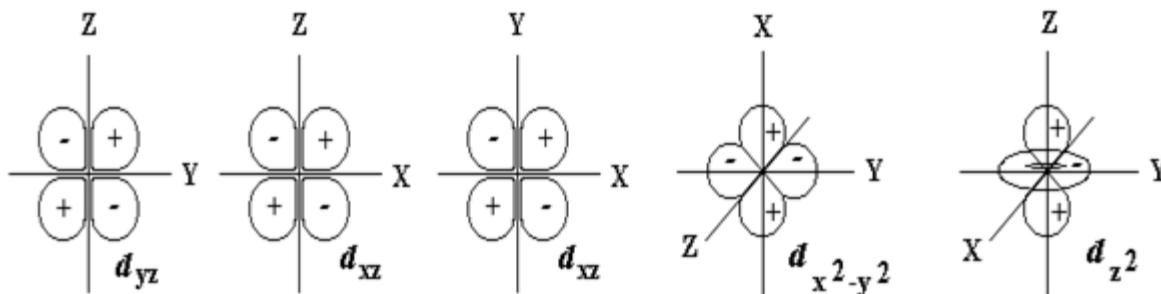
s-orbital

- A p -orbital is **dumbbell-shaped**;



p-orbital

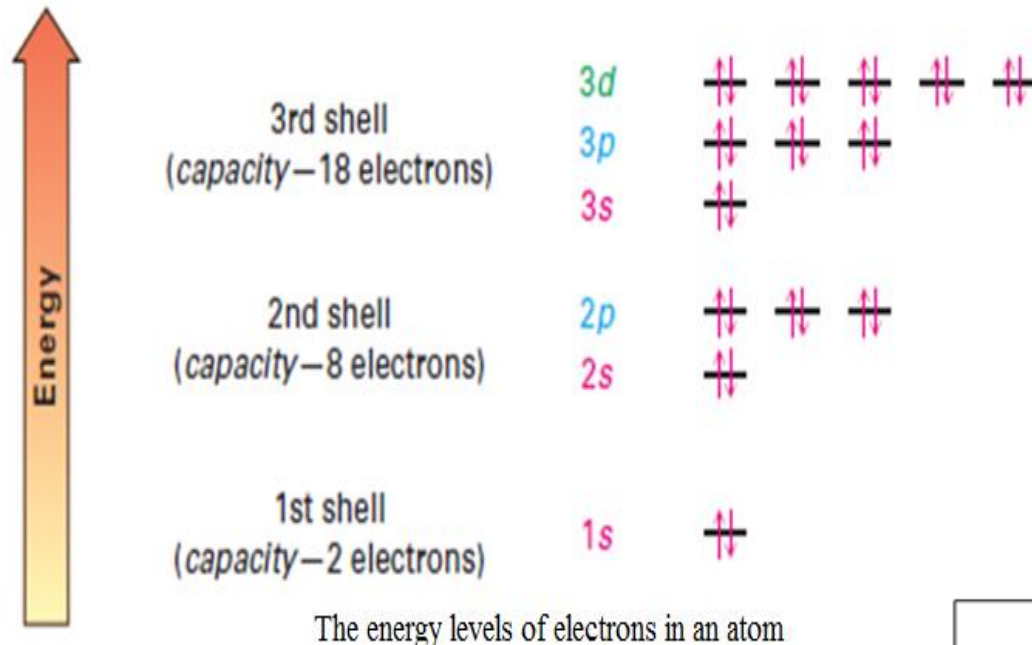
- And four of the five d orbitals are **cloverleaf shaped**, the fifth d orbital is shaped like an **elongated dumbbell with a doughnut around its middle**.



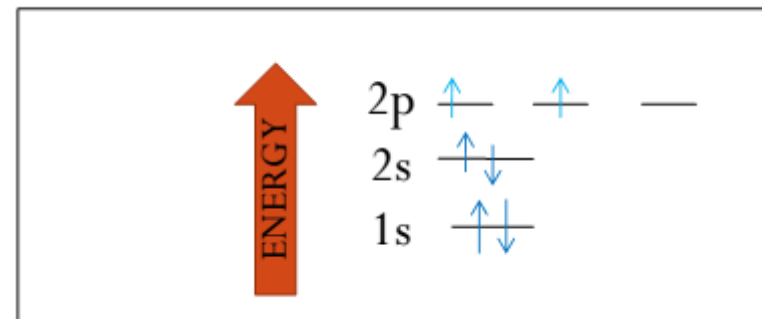
d-orbital

Energy Level	Types of Orbitals	Maximum Electrons
1	1 (S)	2
2	2 (S & P)	8
3	3 (S, P, D)	18
4	4 (S, P, D & F)	32

- The orbitals in an atom are organized into different electron shells, centered around the nucleus and having successively larger size and energy.
- Different shells contain different numbers and kinds of orbitals, and each orbital within a shell can be occupied by two electrons.



- atomic number of carbon=6
- electron configuration - $1s^2 2s^2 2p^2$



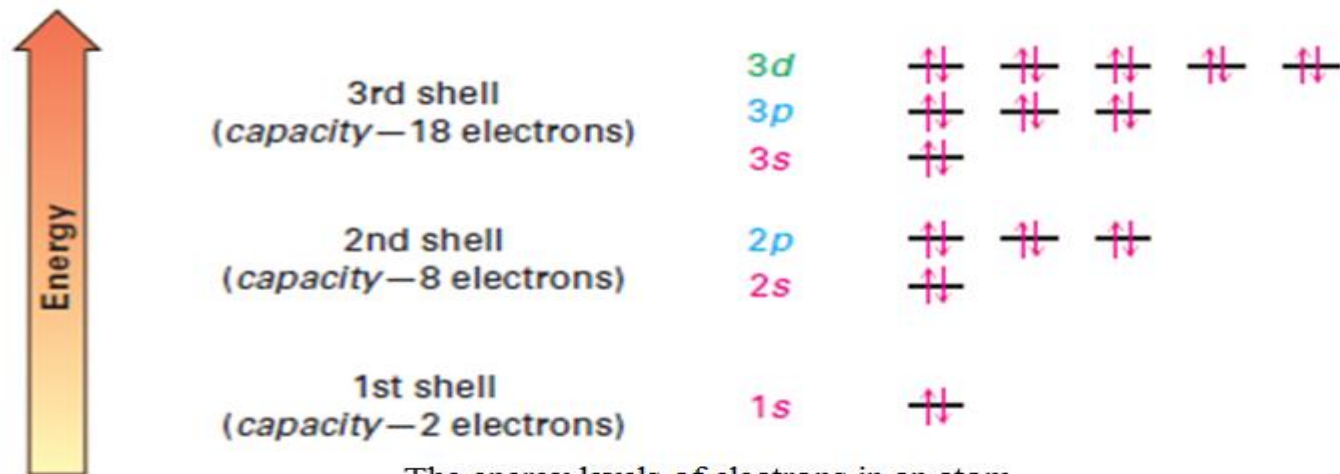
Electron configuration

How electrons fill the orbitals

- Each atom has an infinite number of possible electronic configurations.
- We are here only concerned with the ground-state electronic configuration, which has the lowest energy.
- The ground-state electronic configuration of an atom can be determined by the following three principles.

i. Pauli Exclusion Principle

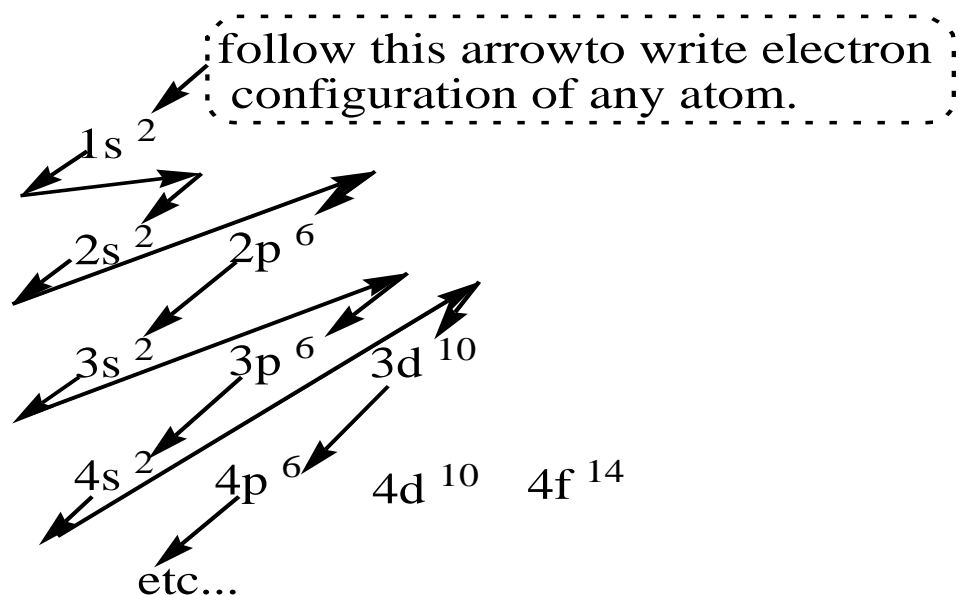
- It states that no more than two electrons can occupy each orbital, and if two electrons are present, their spins must be paired



The energy levels of electrons in an atom

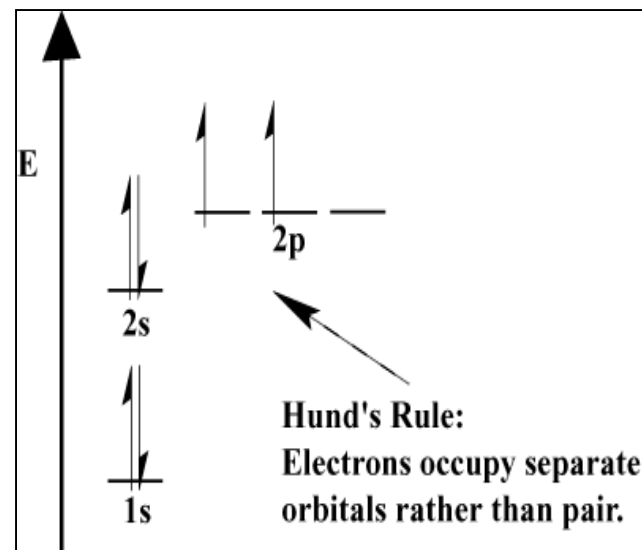
II. *Aufbau principle* (Building up principle)

- It states that the orbitals fill in **order of increasing energy**, from lowest to highest.
- Because a 1s orbital is closer to the nucleus it is lower in energy than a 2s orbital, which is lower in energy than a 3s orbital.
- Then the electron configuration of any element could be written in the form of $1s^2, 2s^2, 2p^6$ etc



III. Hund's rule

- It explains that when **degenerate orbitals** (orbitals that have same energy) are present but not enough electrons are available to fill all the shell completely, then a single electron will occupy an empty orbital first before it will pair up with another electron.
- This is understandable, as it takes energy to pair up electrons.
- Therefore, the six electrons in the carbon atom are filled as follows: the first four electrons will go to the 1s and 2s orbitals, a fifth electron goes to the $2p_x$, the sixth electron to the $2p_y$ orbital and the $2p_z$ orbital will remain empty



○ Bonding In Carbon Compounds

 **Valence Bond Concept**

 **Lewis structure**

 **Orbital Hybridizations**

 **Molecular Orbital Concept**

✍ Before we are discussing the bonding condition in carbon containing compound, let us have a clear understanding on the nature of chemical bonding.

Nature of Chemical Bond :

✍ Chemical bond

✍ The forces that hold atoms together to make compounds or molecules or

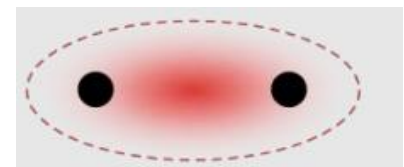
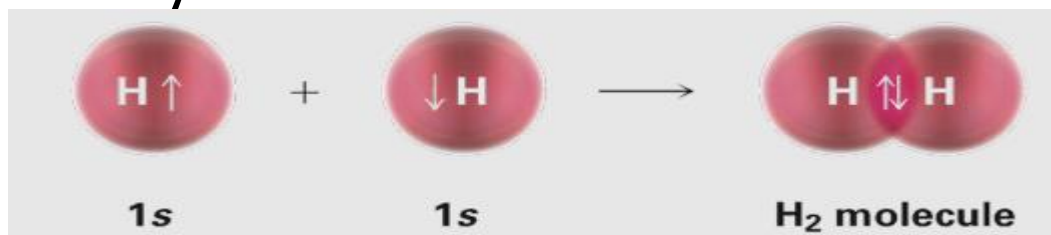
✍ When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance.

Types of Chemical Bonding

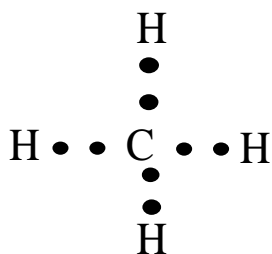
✍ There are three types of chemical bonds

1. ***Ionic bonding*** involves the ***transfer*** of electrons and is usually observed when a ***metal*** bonds to a ***nonmetal***.
2. ***Metallic bonding*** involves ***electron pooling*** and occurs when a ***metal*** bonds to another ***metal***.
3. ***Covalent bonding*** involves the ***sharing*** of electrons and is usually observed when a ***nonmetal*** bonds to a ***non-metal***

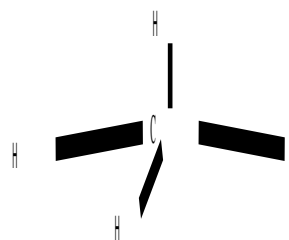
Eg



- Chemical bonds in organic compounds are bonds between two carbon atoms or between a carbon atom and another atom of any other element.
- Bonds in organic compounds are always **covalent bonds**, that is, atoms bonded together share a pair of electrons, one given by each atom.
- Example :- Methane (CH_4)



Electron dot structure of methane



line-bond structure of methane

Lewis structures

✍ A simple way of indicating the **covalent bonds** in molecules is to use what are called ***Lewis structures***, or **electron-dot structures**

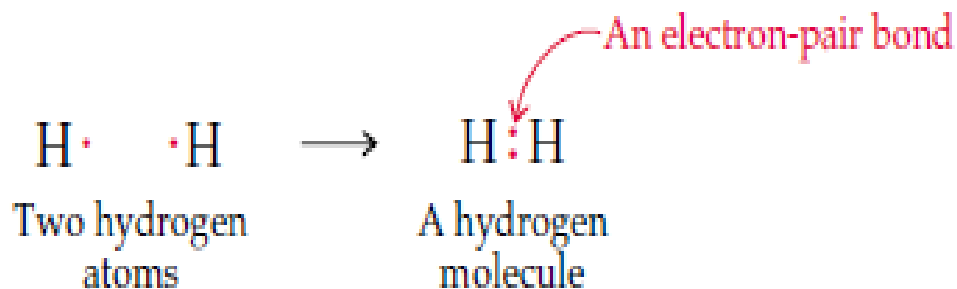
✍ An electron-dot structure represents an atom's valence electrons by dots and indicates by the placement of the dots how the valence electrons are distributed in a molecule.

○

✍ A simple way of indicating the **covalent bonds** in molecules is to use what are called ***Lewis structures***, or **electron-dot structures**


✍ An electron-dot structure represents an atom's valence electrons by dots and indicates by the placement of the dots how the valence electrons are distributed in a molecule.


✍ For example: Hydrogen molecule




- Atoms other than hydrogen also form covalent bonds by sharing valence electron pairs.
- Octet rule** is an important guiding principle that makes it possible to predict the formulas and electron-dot structures of a great many molecules.
- As a general rule, an atom shares as many of its valence-shell electrons as possible, either until it has no more to share or until it reaches an octet configuration.

- A general method of drawing electron-dot structures that works for any compound is to use the following steps:


 **Step-1:**-Find the total number of valence electrons for all atoms in the molecule. Add one additional electron for each negative charge in an anion and subtract one electron for each positive charge in a cation.

 **Step 2.** Decide what the connections are between atoms, and draw a line to represent each covalent bond.

 The **central atom** is the **least electronegative** one (except H).


 **Step 3:** Subtract the number of valence electrons used in bonding from the total number calculated in step 1 to find the number that remain. Assign as many of these remaining electrons as necessary to the terminal atoms (other than hydrogen) so that each has an octet.

 **Step 3 :-** If unassigned electrons remain after step 3, place them on the central atom.

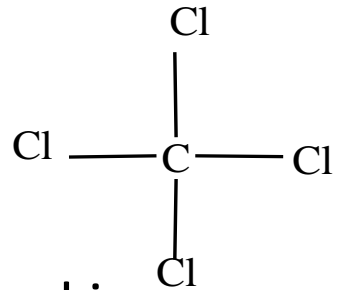
 **Step 5.** If no unassigned electrons remain after step 3 but the central atom does not yet have an octet, use one or more lone pairs of electrons from a neighboring atom to form a multiple bond (either double or triple). Oxygen, carbon, nitrogen, and sulfur often form multiple bonds.


 **Exercise :-** draw the electron dot structure of carbon tetrachloride (CCl₄)

 **Solution**

 **Step 1:-** Total valence electron= valence electrons of C + valence electrons of Cl-----= 4 + 4(7)= 32

 **step-2:-** draw a line to represent each covalent bond

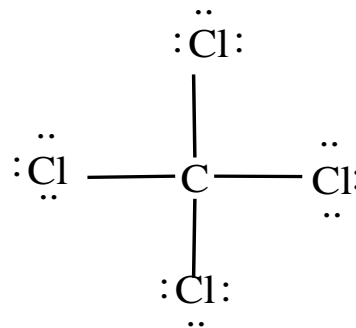


 **Step -3:-** Subtract the number of valence electrons used in bonding from the total number calculated in step 1

 In **step two** we used 8 electron to connect carbon and chlorine

 Remained electrons = 32-8 = 24

- ✍ Then the 24 electrons are assigned to the four terminal chlorine atoms to reach an octet configuration for each:



- ✍ Check the compound whether it obeys octet rule
- ✍ Since all electrons are assigned and the compound fulfils an octet rule we can not go further for step four and five
- ✍ **Exercise 1:-** Draw an electron-dot structure for each of the following molecules:

a. CH_4 b. CH_4O c. $\text{C}_2\text{H}_4\text{O}_2$

- ✍ **Exercise 2:-** Draw both electron-dot and line-bond structures for chloromethane, CH_3Cl .

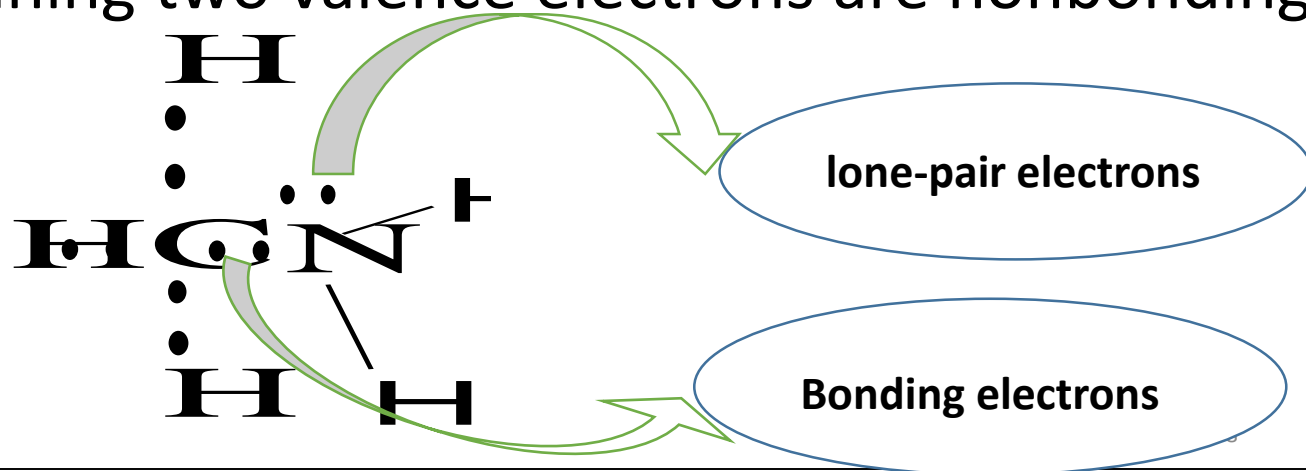
- Valence electrons used in bonding are called **bonding electrons**

- Valence electrons not used in bonding are called **nonbonding electrons, or lone-pair electrons**

- Nitrogen atom in ammonia (NH₃)

- ✓ Shares six valence electrons in three covalent bonds and remaining two valence electrons are nonbonding

lone pair



Electron Distribution in a Covalent Bond

- Are electrons shared equally in a covalent bond?
- If not, why not?
- Because of the difference in electronegativity between the connected atoms, it is difficult to say they share electrons equally.
- **Electronegativity** – attraction of one atom in a bond for the electrons in that bond
- Due to the electronegativity difference of atoms covalent bonds are classified as
 - **Polar covalent bond**
 - **Non polar covalent bond**


- **Polar covalent bond:-** Covalent bonding between unlike atoms results in unequal sharing of the electrons
- electronegativity difference of the atoms is 0.5 to 0.9.
 - ✓ Example – the bond between CCl_4
- **Non polar covalent bond:-** Covalent bonding between the same atoms results in equal sharing of the electrons
- electronegativity difference of the atoms is less than
 - ✓ Example – the bond between CH_4
- ✍ Classify each bond as nonpolar covalent, polar covalent, or

ionic:

- (a) O-H
- (b) N-H
- (c) Na-F
- (d) C-Mg

Hint

Electronegativity value of C,H,N,Na,F
& Mg = 2.5 ,2.1 ,3,0.9 ,4 & 1.2
respectively

 **As we have seen earlier Covalent bonds are formed**
when two atoms approach each other closely so that a
singly occupied orbital on one atom *overlaps* a singly
occupied orbital on the other atom

○ Two models have been developed to describe covalent
bonding

☞ *The valence bond theory and*

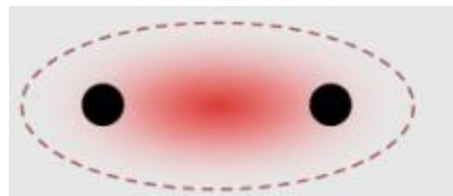
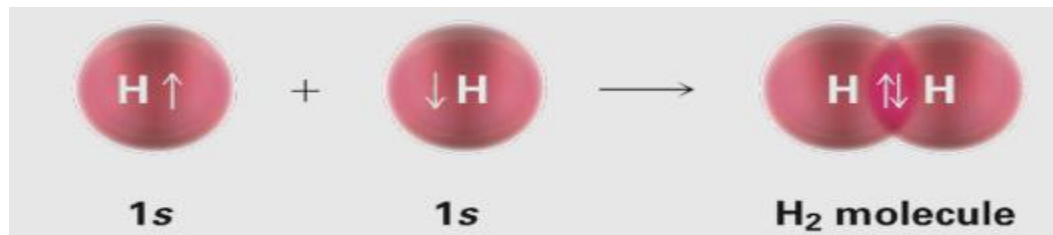
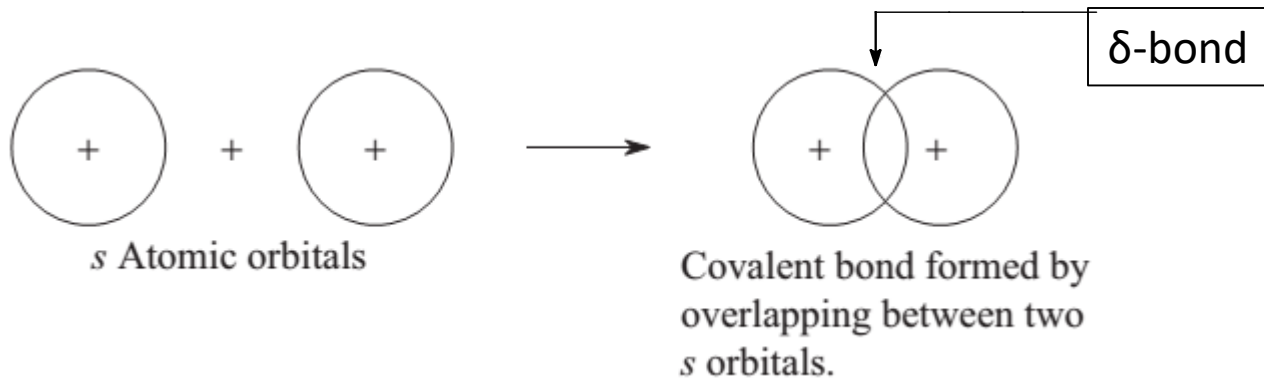
☞ *The molecular orbital theory*

valence bond theory

- ✍️ Valence bond theory was the first structural theory applied to the empirical information about organic chemistry.
- ✍️ During the second half of the nineteenth century, correct structural formulas were deduced for a wide variety of organic compounds.
- ✍️ The concept of “valence” was recognized. That is, carbon almost always formed four bonds, nitrogen three, oxygen two, and the halogens one.

- According to valence bond theory ,
 - ↳ a covalent bond forms when two atoms approach each other closely and a singly occupied orbital on one atom overlaps a singly occupied orbital on the other atom.
- The electrons then paired in the overlapping orbitals and are attached to the nuclei of both atoms, thus bonding the atoms together.

- In the H_2 molecule, for example, H–H bond results from the overlap of two singly occupied hydrogen 1s orbitals
- H–H bond is *cylindrically symmetrical*, **sigma (σ) bond**



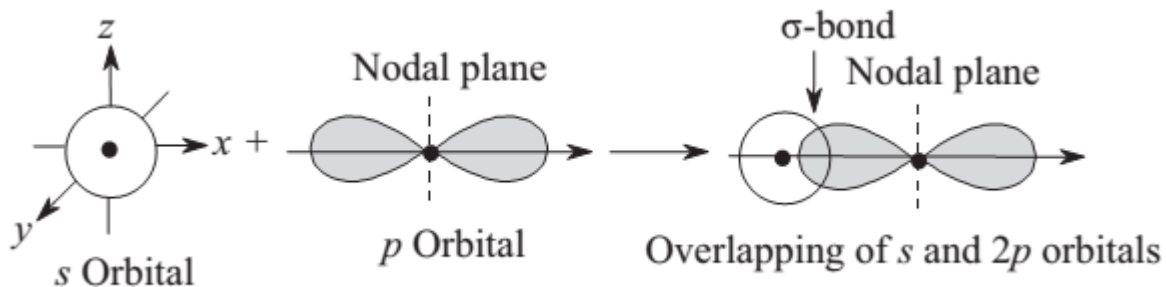
cylindrically symmetrical

Sigma (s) and Pi (p) Bonds

- Sigma and pi bonds, as observed according to valence bond theory, may be explained as follows.

Sigma (δ) Bond

- When two atomic orbitals overlap to form a covalent bond in such a way that the electron cloud density is symmetrical about the internuclear axis, then the bond is known as sigma bond (δ -bond).
- Covalent bond between two s atomic orbitals is always a sigma bond. Covalent bond between an s orbital and a p orbital can also be a sigma bond. Two p orbitals can also form a sigma bond.

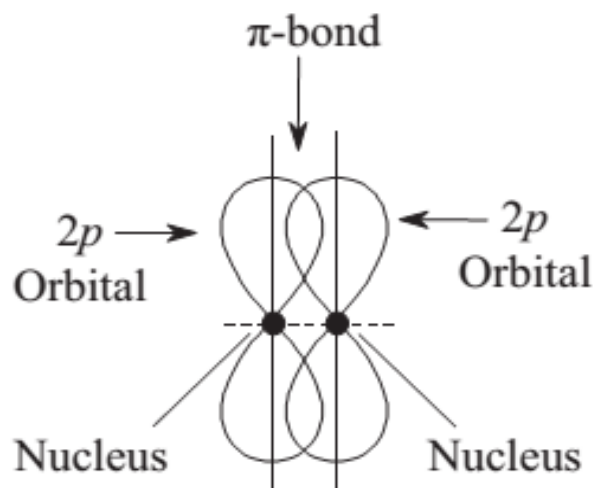


Overlapping between an s and a p orbital

Pi (Π) Bond

- When the p atomic orbitals overlap laterally to form a covalent bond in such a way that electron clouds of the orbitals remain concentrated above and below the plane occupied by the two bonded atoms, it is known as a *pi bond*.
- This bond is not symmetrical about the axis through the two atoms but rather has a nodal plane containing this axis.

- When two atoms are joined by more than one bond, say a double bond, then one bond is always a pi bond and the other is a sigma bond. In case of a triple bond between two atoms, two are pi bonds and one is a sigma bond.
- There is always release of energy during the formation of a covalent bond between two atoms.



Formation of Π -bond between two p orbitals

Sigma (δ) and Pi (Π) Bond

Sigma (σ)bond

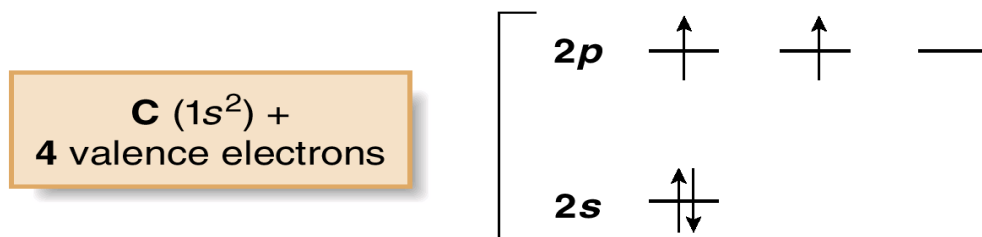
- It is formed by the end to end overlap of orbitals
- The orbitals involved in the overlapping are s-s , s-p or p-p
- It is strong bond
- The electron cloud is symmetrical about the line joining the two nuclei
- It consists of one electron cloud , which is symmetrical about the internuclear axis
- Free rotation about σ -bond

π -bond

- It is formed by the lateral overlap of orbitals
- These bonds are formed by the overlap of p - p orbitals only
- It is weak bond
- The electron cloud is not symmetrical
- There are two electron clouds lying above and below the plane of the atomic nuclei
- Rotation is restricted in case of π -bond

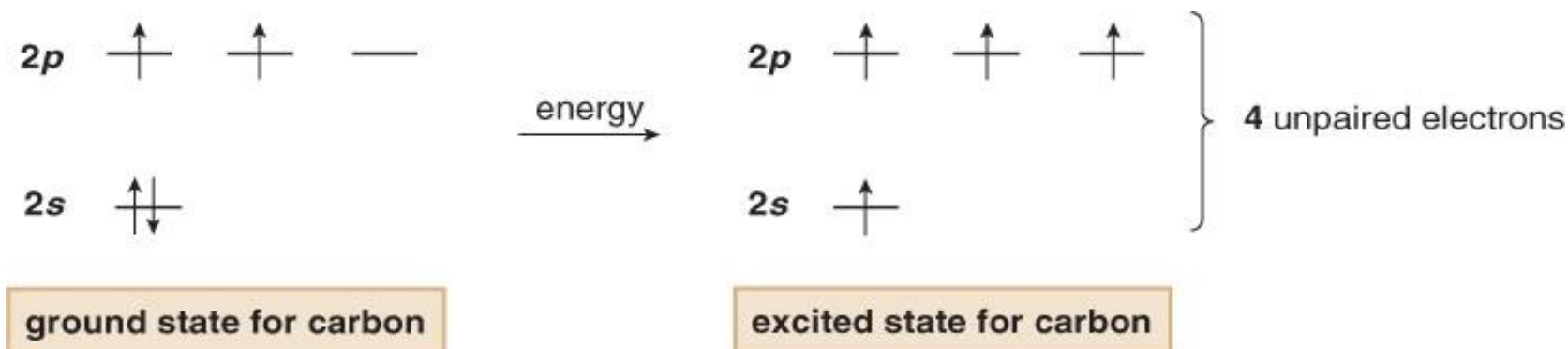
Hybridization

- Carbon has two core electrons, plus four valence electrons.
- To fill atomic orbitals in the most stable arrangement, electrons are placed in the orbitals of lowest energy.
- For carbon, this places two in the $2s$ orbital and one each in $2p$ orbitals.



- Note: The lowest energy arrangement of electrons for an atom is called its ground state.
- In this description, carbon should form only two bonds because it has only two unpaired valence electrons, and CH_2 should be a stable molecule.
- However, CH_2 is a very unstable species that cannot be isolated under typical laboratory conditions. Note that in CH_2 , carbon would not have an octet of electrons.

- There is a second possibility. Promotion of an electron from a 2s to a vacant 2p orbital would form four unpaired electrons for bonding.
- This process requires energy because it moves an electron to a higher energy orbital. This higher energy electron configuration is called an **electronically excited state**.



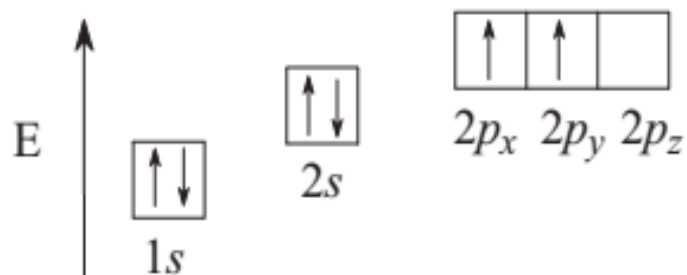
- But this description is still not adequate. Carbon would form two different types of bonds: three with $2p$ orbitals and one with a $2s$ orbital. However, experimental evidence points to carbon forming four identical bonds in methane.
- To solve this dilemma, chemists have proposed that atoms like carbon do not use pure s and pure p orbitals in forming bonds. Instead, atoms use a set of new orbitals called hybrid orbitals.
- **Hybridization** is the combination of two or more atomic orbitals to form the same number of hybrid orbitals, each having the same shape and energy.

sp³ Hybridization

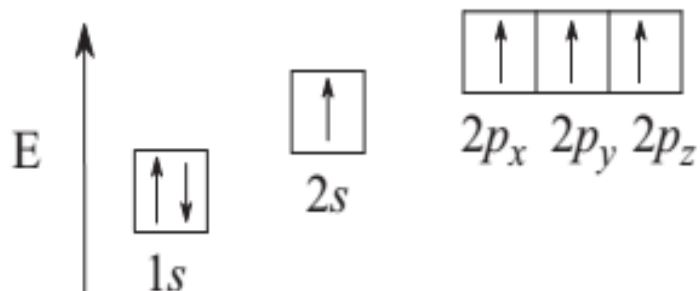
- From earlier discussions it is understood that in saturated organic compounds carbon exhibits tetravalency and all the bonds in such compounds (CH₄, CCl₄) are identical.
- In the excited state, carbon contains four unpaired electrons, one in 2s orbital and three in 2p orbitals, creating four hybridized sp³ orbitals.
- Each of these has 25% s and 75% p character; electron repulsion favors a tetrahedral shape, so the orbitals are 109.5° apart from each other.
- These four atomic orbitals (the s orbital and all three p orbitals) apparently hybridize into four equivalent molecular orbitals referred to as the sp³ hybrids.
- These four orbitals arrange themselves in a **tetrahedral geometry** in order to minimize repulsion effects.

sp³ Hybridization

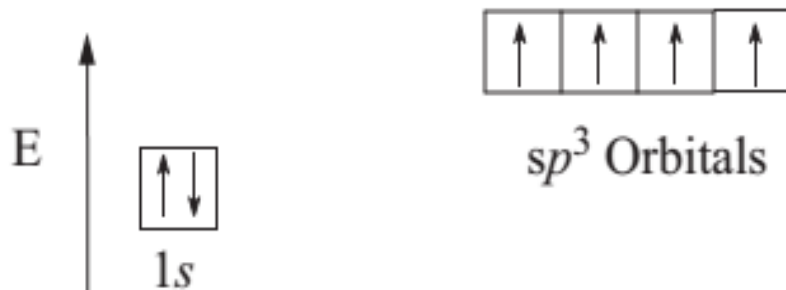
Ground state electronic configuration of carbon:



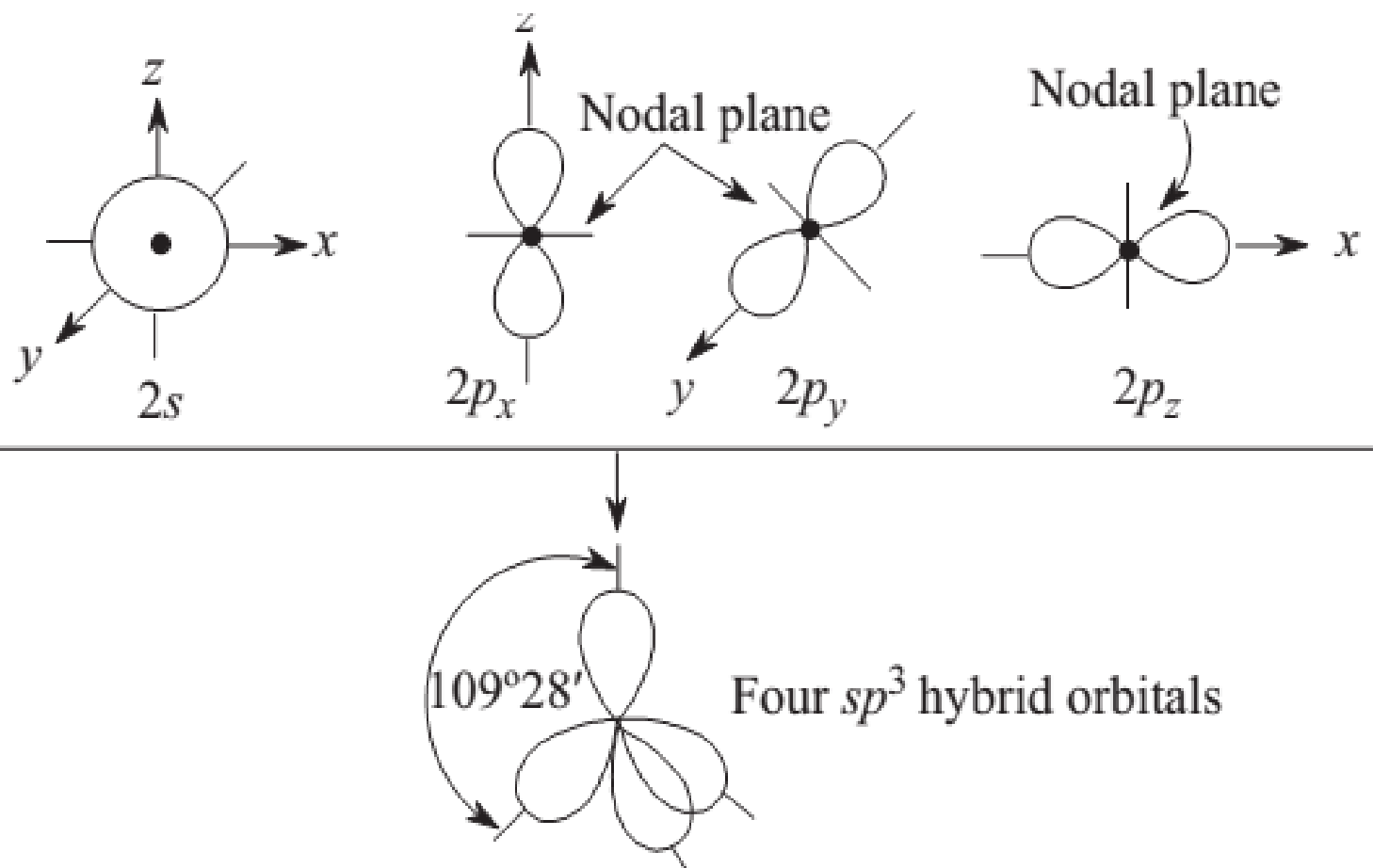
Excited state electronic configuration of carbon:



Electronic configuration after sp³ hybridization:

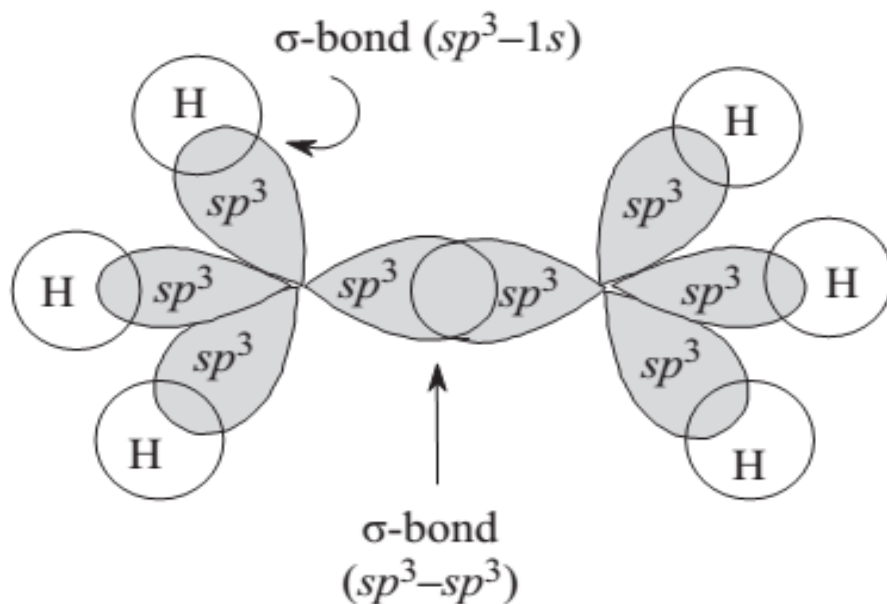


sp³ Hybridization



structure of ethane

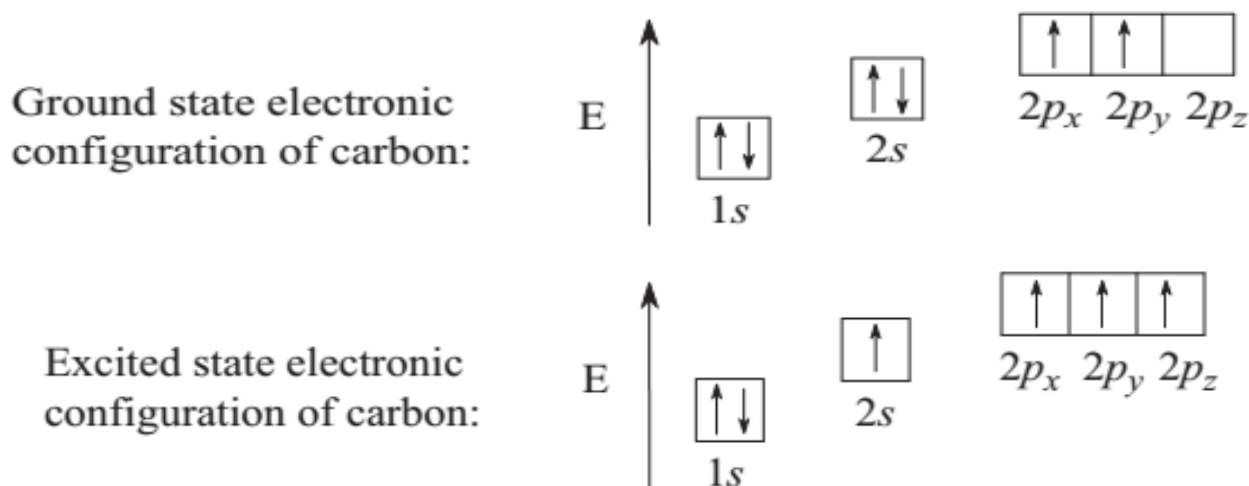
- Both the carbon atoms in ethane are sp^3 hybridized. Two carbon atoms are joined by a sp^3-sp^3 sigma (σ) bond.
- The other three sp^3 orbitals of each carbon atom are joined to three hydrogen atoms through sp^3-1s sigma bond.
- The structure of ethane may be represented as shown below.



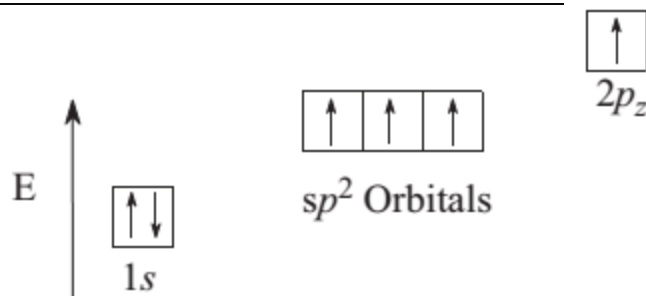
Tetrahedral structure of ethane

sp² Hybridization

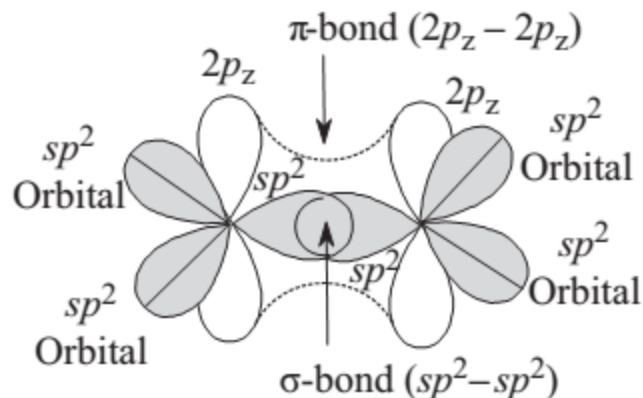
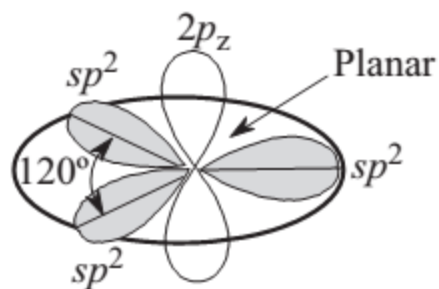
- The small amount of energy needed to promote an electron from the 2s to one of the 2p levels is compensated by bond formation.
- The three filled atomic orbitals mix to form three sp² orbitals—each is of 33% s character and 67% p character.
- The last p orbital stays the same. The front lobes (and their corresponding back lobes) face in opposite directions (at 120° from each other). Electron repulsion therefore creates a trigonal planar geometry.



Electronic configuration
after hybridization:

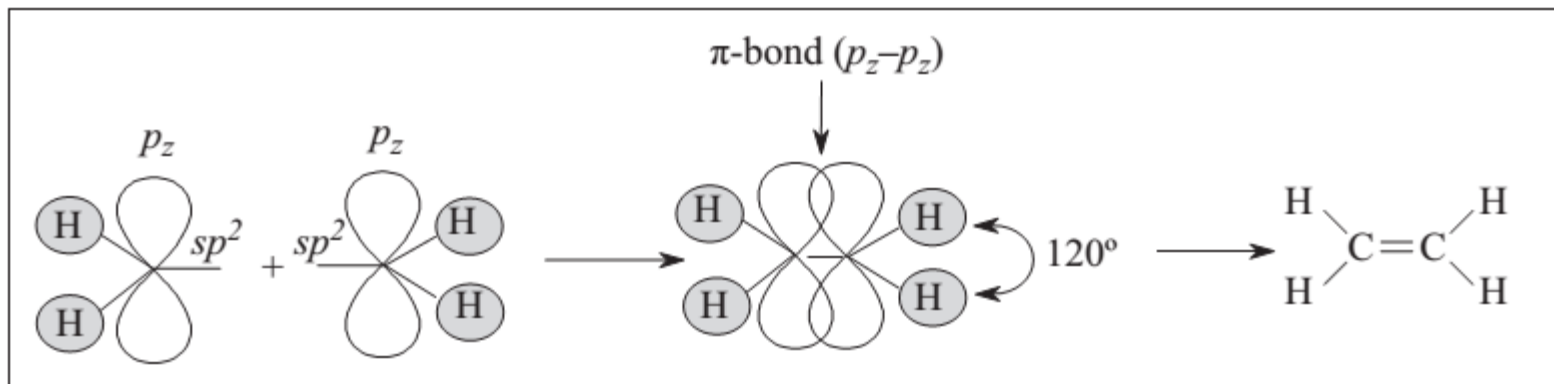


- Geometric shape of an sp^2 hybrid carbon atom is trigonal planar in which the angle between the two sp^2 hybrid orbitals is 120° (Fig. 3.21). Each of the two carbon atoms has one remaining p orbital containing a single electron.
- Maximum separation of this p orbital from the sp^2 orbital is achieved when it is perpendicular to the plane containing the three sp^2 orbitals.
- These perpendicular dumbbell shaped p orbitals form the pi bond through lateral overlapping, with lobes above and below the plane occupied by sp^2 hybrid orbitals.



Structure of ethylene

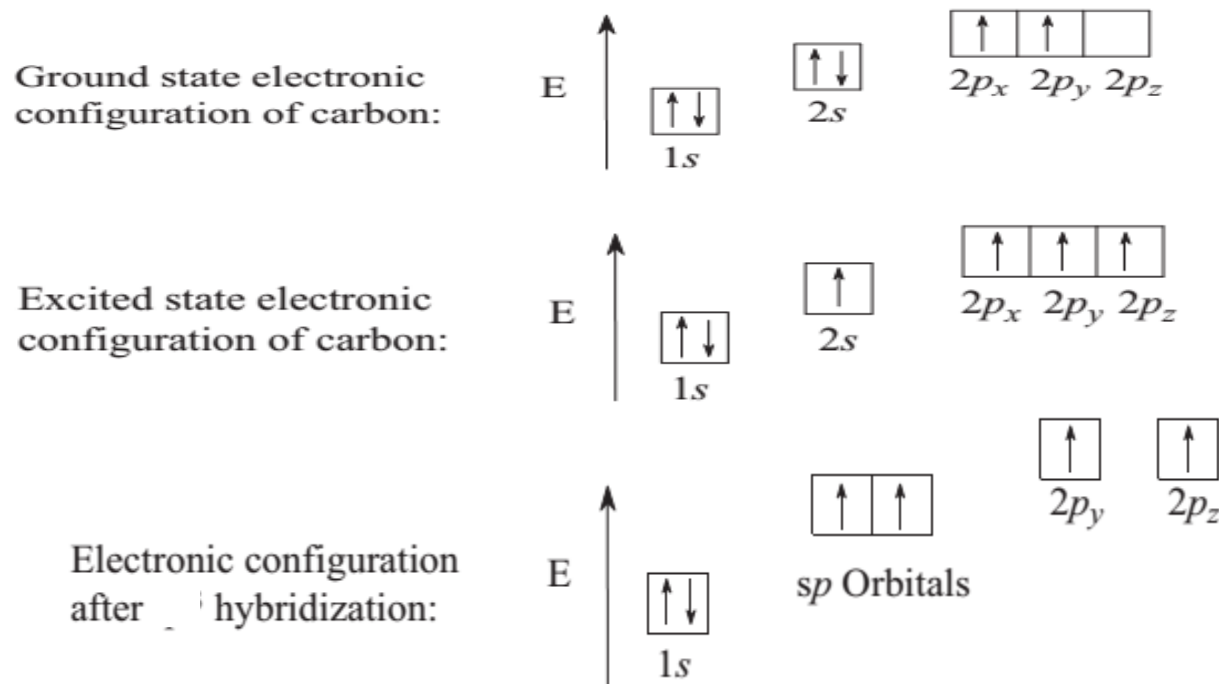
- Both the carbon atoms in ethylene are sp^2 hybridized and each of them contains a pure $2p_z$ orbital. There is a (sp^2-sp^2) sigma bond between the two carbon atoms.
- The other two sp^2 hybrid orbitals on each carbon atom are linked to two hydrogen atoms through sp^2-1s sigma bond.
- $2p_z$ Orbitals, each having one electron, combine laterally to form a pi (Π) bond. Altogether, there are five sigma bonds and one p-bond in ethylene. The geometric shape of ethylene is shown below.



Structure of ethylene

sp Hybridization

- sp hybrids share characteristics evenly between s and p orbitals. The other unhybridized p orbitals remain the same. The front lobes of the sp orbitals point in opposite directions (at 180°). The back lobes also point in opposite directions. A linear structure is created.
- In general: The overlap of the lobes of atoms creates bonds; large front lobes overlap more completely, resulting in a relatively stronger bond.

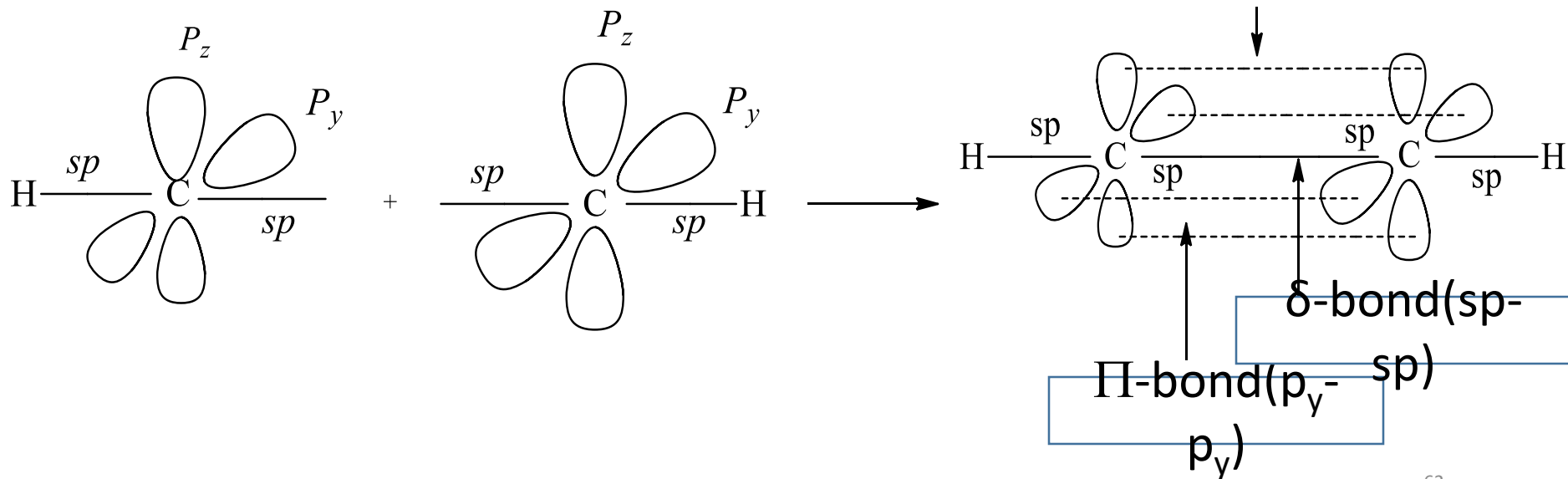


sp hybrids: Linear Structures

- Geometric shape of an *sp* hybridized carbon atom is planar and linear. The angle between two hybrid orbital is 180° .
- Each *sp* hybrid orbital contains two pure *2p* orbitals. Geometric shape of two *sp* orbitals is shown below. They are linear and planar.
- When an *sp* hybridized carbon forms covalent bonds with two monovalent atoms to form a molecule of the type $\text{X-C}\equiv\text{C-X}$, then the shape of the molecule is also linear and planar.

Structure of *Acetylene or Ethyne* (C_2H_2)

- Both the carbon atoms in acetylene are sp hybridized and each of them contains two unhybridized pure $2p$ orbitals ($2p_y$, $2p_z$).
- Two atoms are joined by a strong sigma bond formed between $sp-sp$ orbitals. There are two pi bonds between the carbon atoms ($2p_y-2p_y$ and $2p_z-2p_z$).
- The second sp hybrid orbital on each carbon atom is linked to a hydrogen atom by $sp-1s$ sigma bond. Acetylene is normally shown as $H-C\equiv C-H$; orbital representation of acetylene is shown below.



Molecular Orbital Theory

- Molecular orbital (MO) theory uses a Linear combination of atomic orbital's (LCAO) to represent molecular orbital's resulting from bonds between atoms. These are often divided into three types, bonding , antibonding and non bonding.
- A bonding orbital concentrates electron density in the region *between* a given pair of atoms, so that its electron density will tend to attract each of the two nuclei toward the other and hold the two atoms together.

- An anti-bonding orbital concentrates electron density "behind" each nucleus (i.e. on the side of each atom which is farthest from the other atom), and so tends to pull each of the two nuclei away from the other and actually weaken the bond between the two nuclei.
- Electrons in non-bonding orbital's tend to be associated with atomic orbital's that do not interact positively or negatively with one another, and electrons in these orbital's neither contribute to nor detract from bond strength.

- There are two for orbital combination to occur

- I. Additive combination (in-phase)
- II. Subtractive combination (out phase)

I. Additive combination

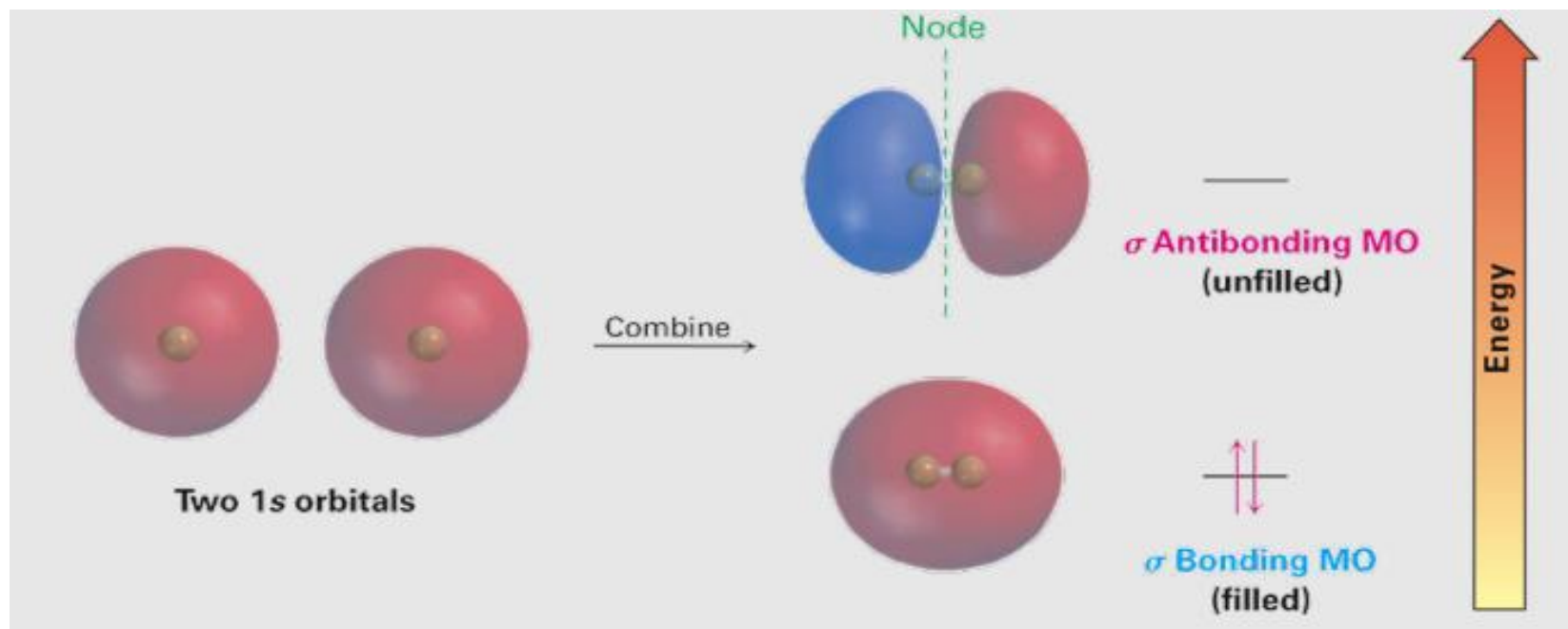
- Leads to the formation of molecular orbital that is lower in energy and roughly egg shaped
- Note that the additive combination is a single egg shaped molecular orbital; it is not the same as the two overlapping 1s atomic orbital of the valence bond description

II. Subtractive combination

- Leads to the formation of molecular orbital that is higher in energy and has a node between a nuclei
- Is a single molecular orbital with the shape of an elongated dumbbell

- The additive combination is lower in energy than the two atomic orbitals and is called a bonding molecular orbital. Because in this MO spend their time in the region between the two nuclei, thereby bonding the two atoms together
- The subtractive combination is higher in energy than the two atomic orbital's and is called an antibonding molecular orbital because any electrons it contains can't occupy the central region between the nuclei , where there is node and can't contribute to bonding. The two nuclei therefore repel each other

- The π bonding MO is from combining p orbital lobes with the same algebraic sign
- The π antibonding MO is from combining lobes with opposite signs
- Only bonding MO is occupied for H_2



Difference between bonding MO and anti-bonding MO

Bonding MO

- Gets formed by the addition overlap of atomic orbitals
- It is having lower energy than the Atomic orbitals from which it is formed
- The electron charge density in between the nuclei is high and hence the repulsion between the nuclei is very low . This causes stablization of the bonding MO. In other words , the electrons in the bonding MO tends to favour stable bond formation

Anti-bonding MO

- Gets formed by the subtraction overlap of atomic orbitals
- It is having higher energy than the Atomic orbitals from which it is formed
- The electron charge density in between the nuclei is very low and hence the repulsion between the nuclei is high. This causes de-stablization of the anti-bonding MO. In other words , the electrons in the anti-bonding MO tends to oppose bond formation

Valence bond theory and molecular orbital theory

Valence bond theory

- Bonds are formed by overlap of atomic orbitals
- Before atoms bond, their atomic orbitals can hybridize to prepare for bonding
- Molecular geometry arises from hybridization of atomic orbitals
- σ -and π -bonding orbitals
- electrons are Localized
- Convenient for presentation

molecular orbital theory

- Energy level diagrams for simple diatomic molecules
- Bonding vs. antibonding orbitals
- bond order is easily calculated
- Other predictive features: excited states, paramagnetism
- Electrons are delocalized
- More difficult to conceive and present
- “Hydrogen-like Atomic Orbitals” are used to form Molecular Orbitals

Formal charge

- **Formal charge** is the charge calculated for an atom in a Lewis structure on the basis of an equal sharing of bonded electron pairs.

$$\text{Formal charge} = \left(\begin{array}{c} \text{Number of} \\ \text{valence} \\ \text{electrons in} \\ \text{free atom} \end{array} \right) - \left(\begin{array}{c} \text{Number of} \\ \text{nonbonding} \\ \text{electrons} \end{array} \right) - \frac{1}{2} \left(\begin{array}{c} \text{Number of} \\ \text{bonding} \\ \text{electrons} \end{array} \right)$$

- Formal charge can be used to determine **the most plausible Lewis structure** when more than one possibility exists for a compound.

Four criteria for choosing the more important resonance structure:

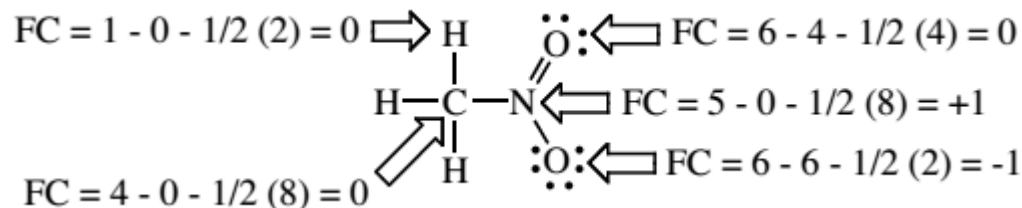
CRITERIA 1: Smaller formal charges (either positive or negative) are preferable to larger charges;

CRITERIA 2:-A more negative formal charge should exist on an atom with a larger electronegative (EN) value.

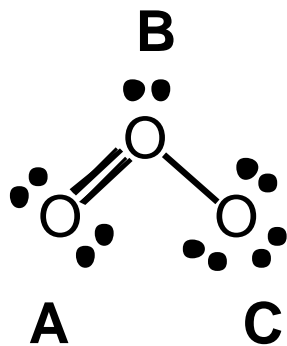
CRITERIA 3 :-Get unlike charges as close together as possible

CRITERIA 4:- Avoid like charges (+ + or - -) on adjacent atoms

- **Example** :- Calculate the formal charge of each atoms in nitromethane ?



- The three hydrogen atoms are equivalent and thus have the same neutral charge.
- The oxygen atoms do not have the same bond order with the nitrogen, so these oxygen atoms are not equivalent. The sum of the atomic charges = 3×0 (for the hydrogens) + 0 (for the carbon) + $(+1$ for the nitrogen) + $(0$ for the double bonded oxygen) + $(-1$ for the single bonded oxygen) = 0 = molecular charge.
- Although the molecule is neutral, the nitrogen and one of the oxygens carry charge.



Q. Calculate the formal charge of each oxygen atoms in ozone?

For O_B

valence $e^- = 6$

nonbonding $e^- = 2$

bonding $e^- = 6 \times 1/2 = 3$

Formal charge = +1

For O_C

valence $e^- = 6$

nonbonding $e^- = 6$

bonding $e^- = 2 \times 1/2 = 1$

Formal charge = -1

For O_A

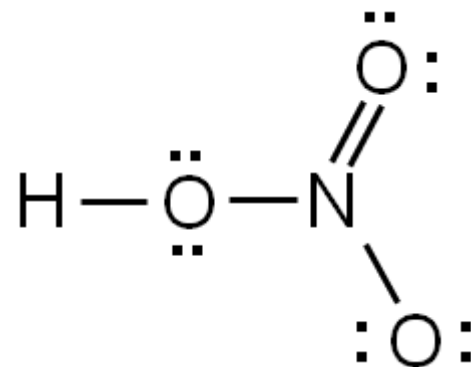
valence $e^- = 6$

nonbonding $e^- = 4$

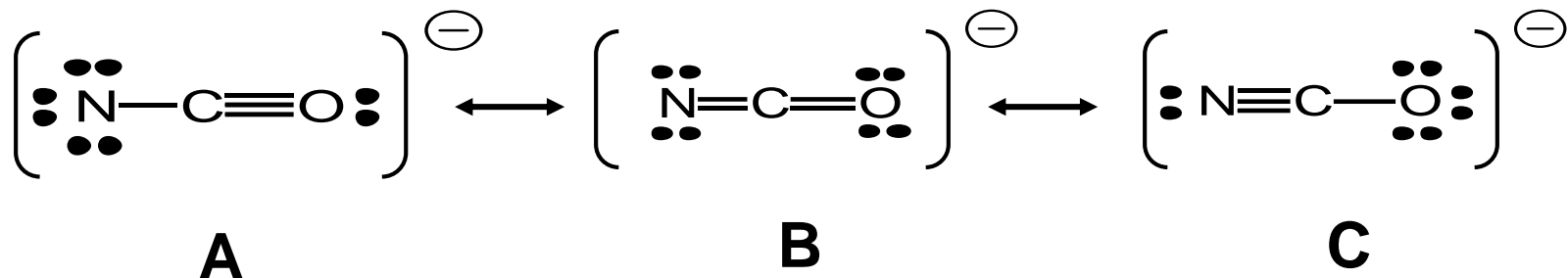
bonding $e^- = 4 \times 1/2 = 2$

Formal charge = 0

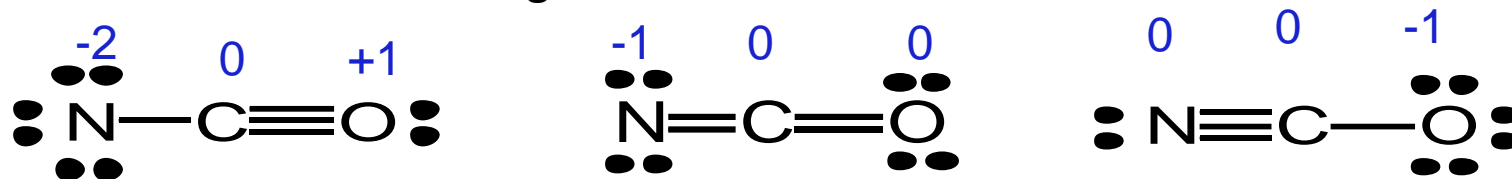
Q. Calculate the formal charge of each atoms on nitric acid?



- EXAMPLE: NCO^- has 3 possible resonance forms and determine which resonance structure is most plausible Lewis structure ?



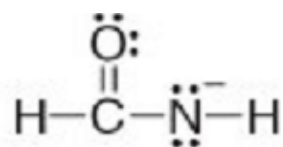
- Now Determine Formal Charges



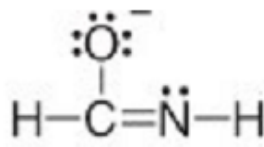
- Forms B and C have smaller formal charges; this makes them more important than form A. (CRITERIA 1)
- Form C has a negative charge on O which is the more electronegative element, therefore C contributes the most to the resonance hybrid. (CRITERIA 2)

Introduction to resonance

- ☞ **Resonance** is the process whereby (generally) **pi-electrons** can be **delocalized** by exchanging **double bonds** and **single bonds**.
- ☞ **Resonance** can be used to delocalize both **lone pairs** of electrons and **cationic charges** which are adjacent to double bonds.
- ☞ **Delocalization** of **positive** and **negative** charges lead to relatively stable **cations** and **anions**, respectively.
- ☞ Some molecules cannot be adequately represented by a single Lewis structure.
- ☞ **For example**, two valid Lewis structures can be drawn for the **anion** $(\text{HCONH})^-$.



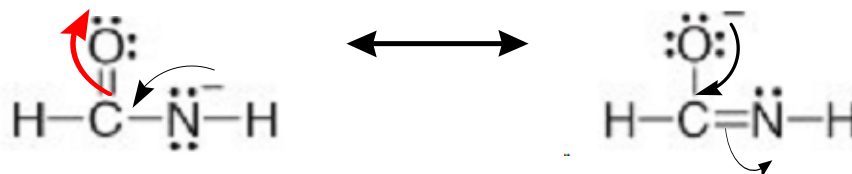
X



Y

☞ **Resonance structures** are two Lewis structures having the same placement of atoms but different arrangement of electrons.

☞ The delocalization of electrons is indicated by double curved arrow



☞ These structures (X & Y) are called resonance structures or resonance forms. A double headed arrow is used to separate the two resonance structures.

☞ Resonance allows certain electron pairs to be delocalized over two or more atoms, and this delocalization adds stability.

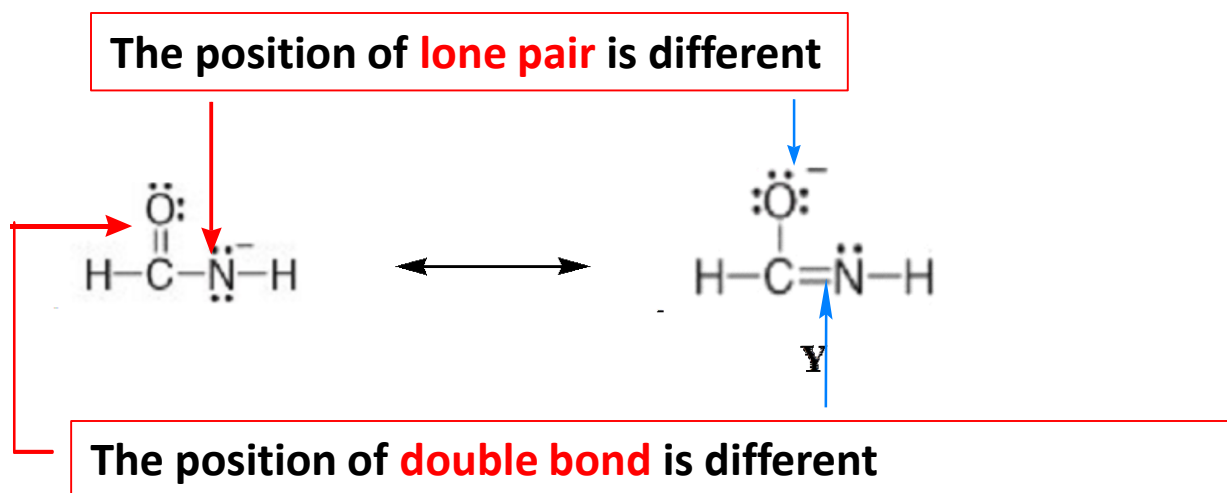
☞ A molecule with two or more resonance forms is said to be resonance stabilized.

The following basic principles of resonance theory should be kept in mind:

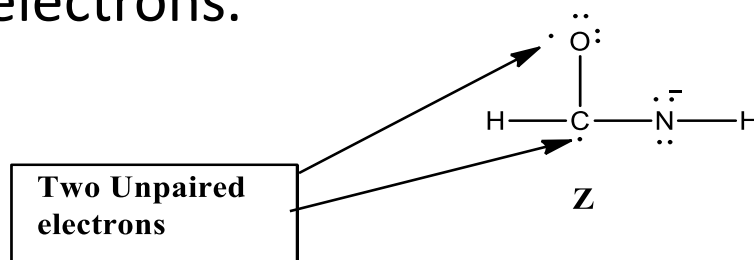
- ☞ **Resonance structures are not real.** An individual resonance structure does not accurately represent the structure of a molecule or ion. Only the hybrid does.
 - ↪ The true structure is a composite of both resonance forms and is called a **resonance hybrid**.
 - ↪ The hybrid shows characteristics of both structures.
- ☞ **Resonance structures are not in equilibrium** with each other. There is no movement of electrons from one form to another.
- ☞ **Resonance structures are not isomers.** **Two isomers** differ in the **arrangement** of **both atoms** and **electrons**, whereas **resonance structures** differ only in the **arrangement** of **electrons**.

Drawing Resonance Structures

☞ **Rule [1]:** Two resonance structures **differ** in the **position** of **multiple bonds** and **non bonded electrons**. The placement of atoms and **single bonds** always stays the same.

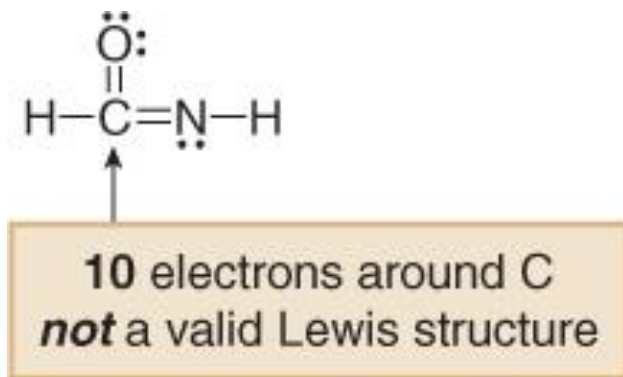


☞ **Rule [2]:** Two resonance structures must have the same number of unpaired electrons.



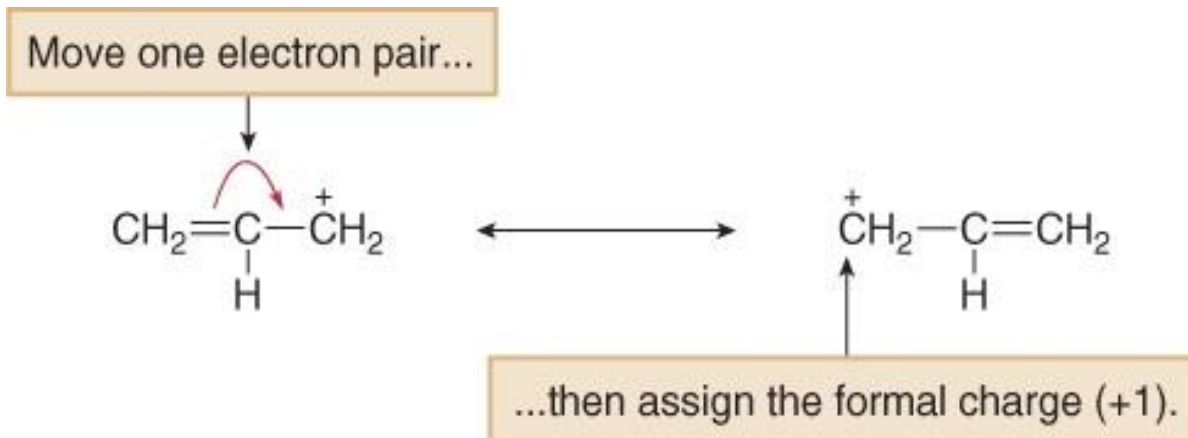
- **X** and **Y** have no unpaired electrons
- **Z** is not resonance structure of **X** and **Y**

- ☞ **Rule [3]:** Resonance structures must be **valid Lewis structures**. Hydrogen must have two electrons and no second-row element can have more than eight.



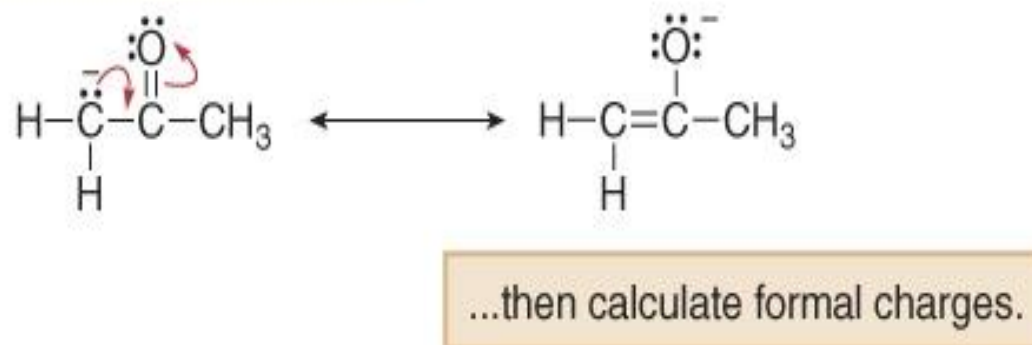
- ☞ **Curved arrow notation** is a convention that is used to show how electron position differs between the two resonance forms.
- ☞ **Curved arrow notation shows the movement of an electron pair.** The tail of the arrow always begins at the electron pair, either in a bond or lone pair. The head points to where the electron pair “moves.”

Example 1:

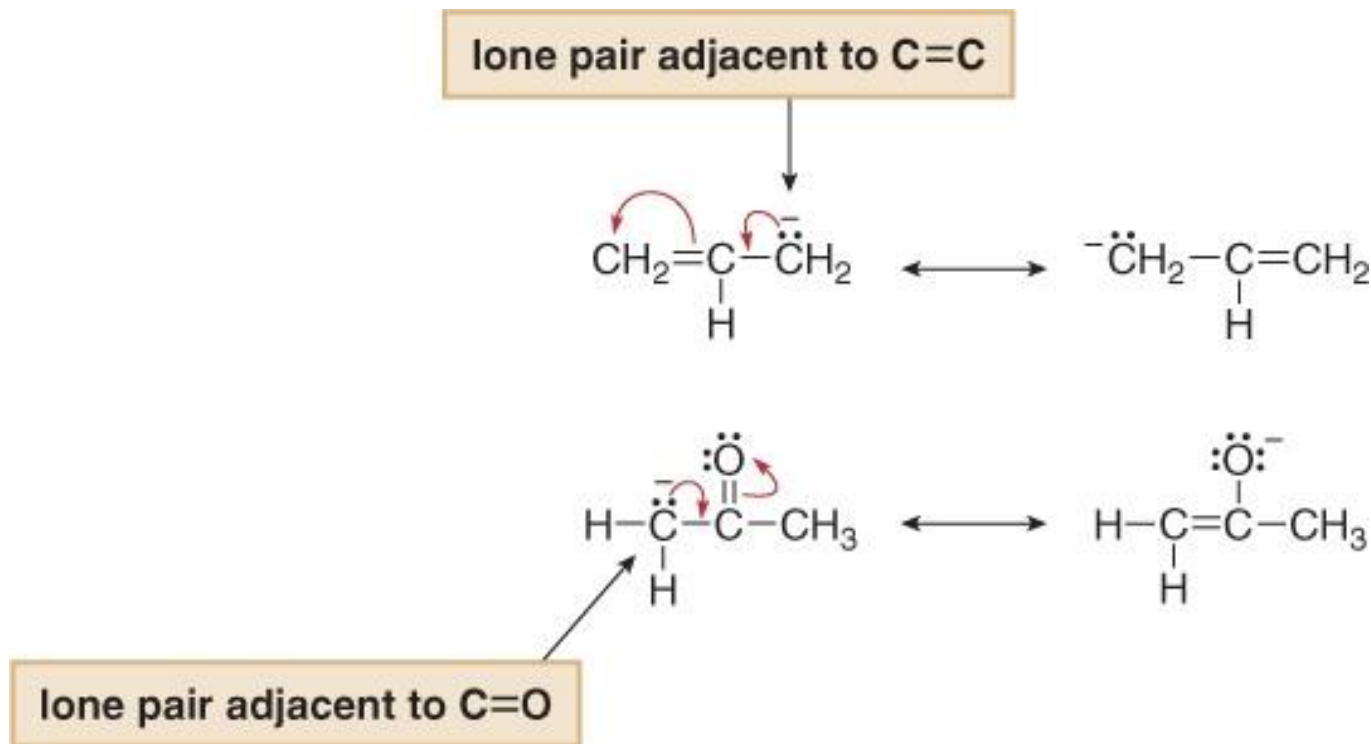


Move two electron pairs...

Example 2:

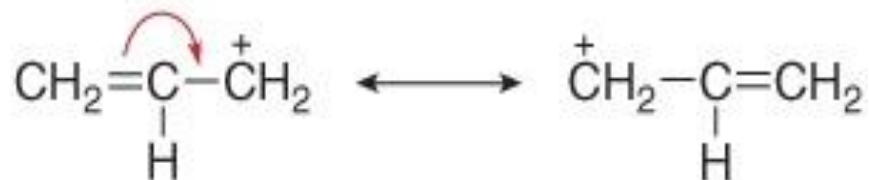


○ Resonance Structure Examples



- In the two examples above, a lone pair is located on an atom directly bonded to a double bond:

(+) charge adjacent to a double bond



(+) charge adjacent to an atom with a lone pair

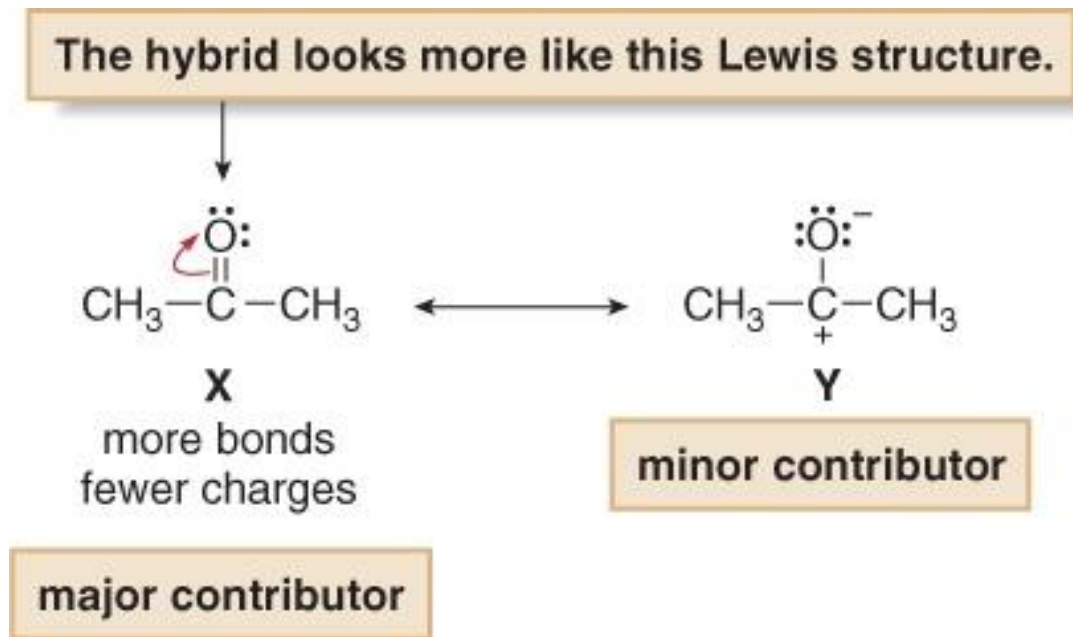


- In the above examples, an atom bearing a (+) charge is bonded either to a double bond or an atom with a lone pair:

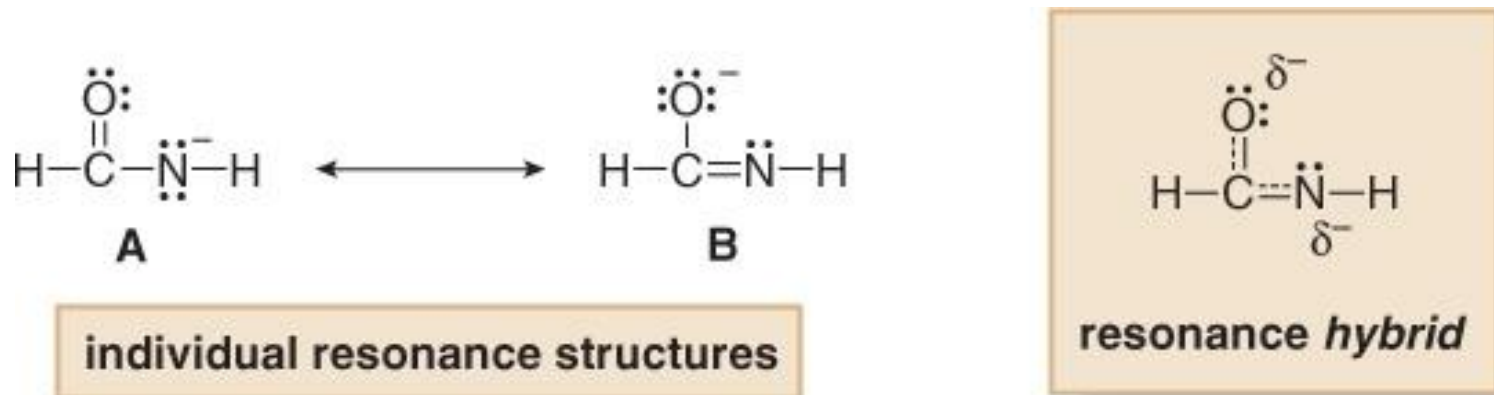
Resonance Hybrids

- A resonance hybrid is a composite of all possible resonance structures. In the resonance hybrid, the electron pairs drawn in different locations in individual resonance forms are delocalized.
- When two resonance structures are different, the hybrid looks more like the “better” resonance structure. The “better” resonance structure is called the **major contributor** to the hybrid, and all others are **minor contributors**.
- The hybrid is a weighted average of the contributing resonance structures.

- A “better” resonance structure is one that has more bonds and fewer charges.



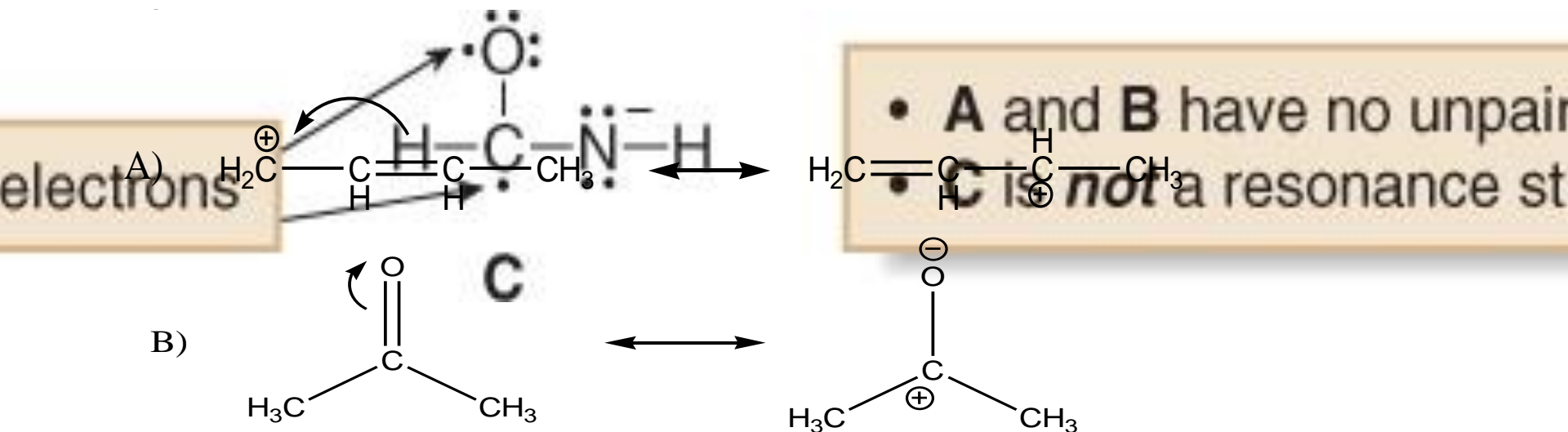
Drawing Resonance Hybrids



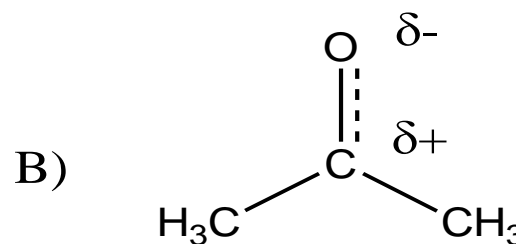
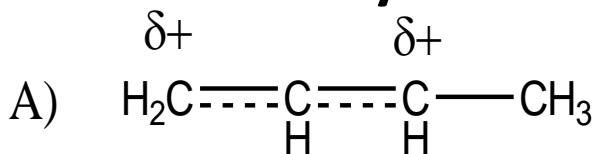
Two Unpaired electrons

❖ Question :- Draw the other resonance structure and resonance hybrids of the following compounds.

❖ Answer



II. The resonance hybrids are



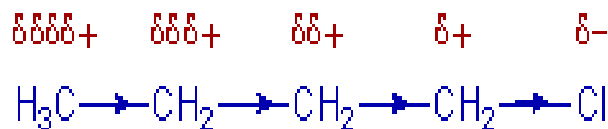
Factors influencing electron availability and reactivity of organic compounds

1. Inductive effect

- The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect.

Salient features of inductive effect

- It arises due to electronegativity difference between two atoms forming a sigma bond.
- It is transmitted through the **sigma bonds**.
- The magnitude of inductive effect decreases while moving away from the groups causing it.



- It is a **permanent** effect.
- It influences the chemical and physical properties of compounds.

TYPES OF INDUCTIVE EFFECT

- The inductive effect is divided into two types depending on their strength of electron withdrawing or electron releasing nature with respect to hydrogen.

i. Negative inductive effect (-I):

- The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by -I.

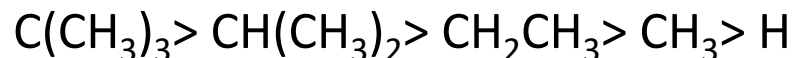
- Decreasing order of -I effect:



ii. Positive inductive effect (+I):

- It refers to the electron releasing nature of the groups or atoms and is denoted by +I.

- Decreasing order of +I effect:



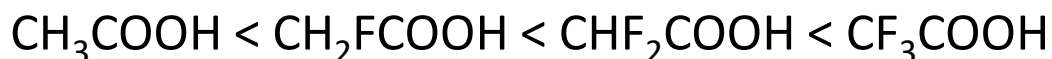
Importance of Inductive Effect

○i. Acidic strength of carboxylic acids and phenols:

- The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion and thus stabilizing it.
- Hence the **acidic strength increases** when **-I groups are present**.
- However the **+I groups decrease the acidic strength**.

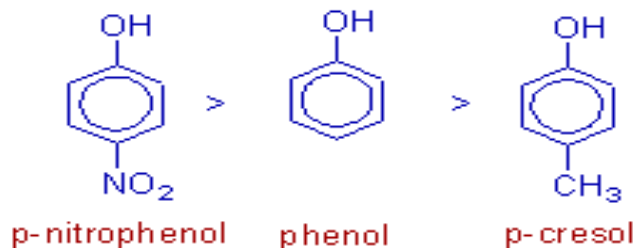
Example:

- i. The acidic strength increases with increase in the number of electron withdrawing Fluorine atoms as shown below.



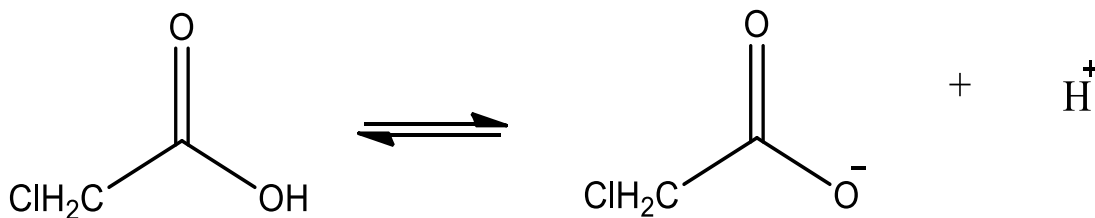
- ii. Formic acid is stronger acid than acetic acid since the $-\text{CH}_3$ group destabilizes the carboxylate ion.

- iii. the acidic strength of phenols increases when -I groups are present on the ring.

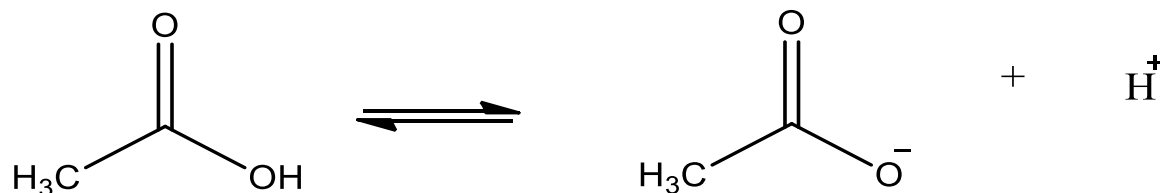


Features of Inductive Effect

- **Chloroacetic acid is a stronger acid than acetic acid**

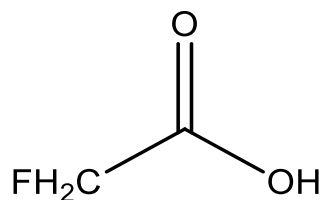


$$K_a = 1.4 \times 10^{-3}$$

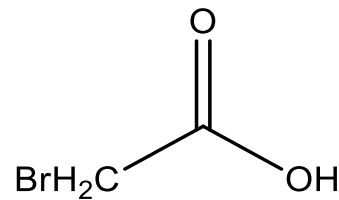


$$K_a = 1.75 \times 10^{-5}$$

- **The larger is the electron-withdrawing effect of a group, the greater is the –I (inductive) effect.**



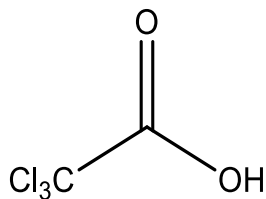
$$K_a = 2.5 \times 10^{-3}$$



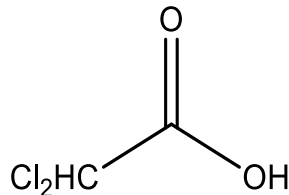
$$K_a = 1.3 \times 10^{-3}$$

Features of Inductive Effect

3. Inductive effect is additive

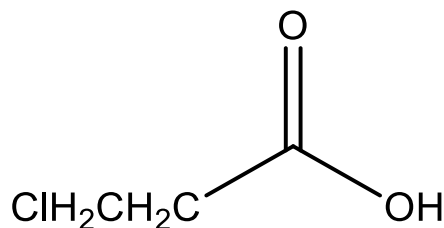


$$K_a = 2.3 \times 10^{-1}$$

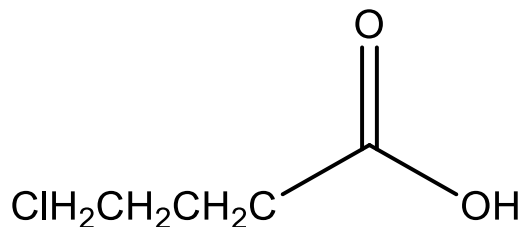


$$K_a = 5.4 \times 10^{-2}$$

4. Since this effect is transmitted through a chain it becomes less effective with distance



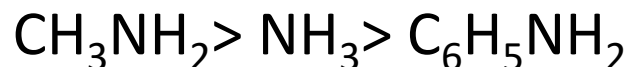
$$K_a = 8.32 \times 10^{-4}$$



$$K_a = 3.02 \times 10^{-5}$$

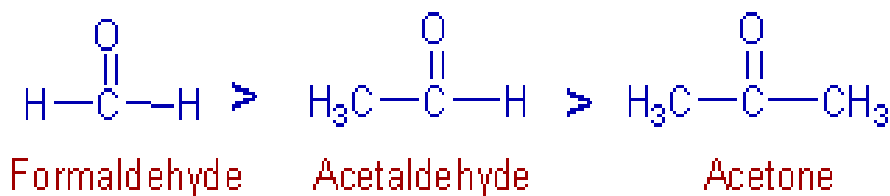
ii. Basic strength of amines:

- ❑ The electron donating groups like alkyl groups increase the basic strength of amines.
- ❑ Whereas the electron withdrawing groups like aryl groups decrease the basic nature.



iii. Reactivity of carbonyl compounds:

- ❑ The +I groups increase the electron density at carbonyl carbon. Hence their reactivity towards nucleophiles decreases.

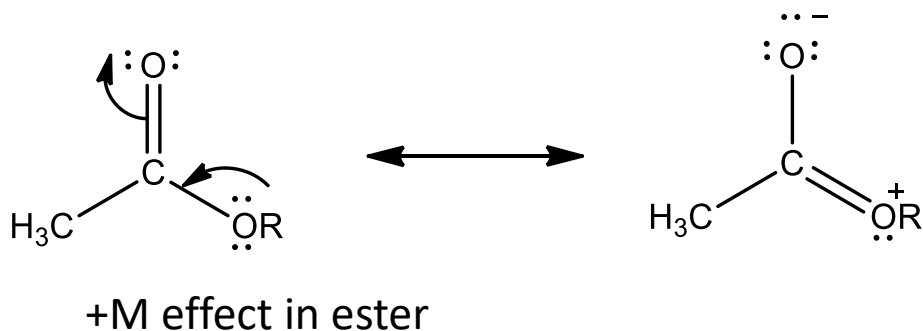


Resonance Effect or Mesomeric Effect

- Resonance is basically a case of displacement of valence electrons in a permanent way and that may cause polarity in the resonance hybrid. Displacements of electrons are most significant in a conjugated system.
-
- The conjugative mechanism of electron displacement in the normal state of a molecule or ion is usually referred to as *resonance effect* or *mesomeric effect* (mesomerism).
- Just like inductive effects (I effects), mesomeric effects, symbolized as M, are permanent effects and cause permanent polarity in the system (molecule or ion).
- Mesomeric effects are of two types,
 - positive mesomeric effect(+M or +R) and
 - negative mesomeric effect (−M or −R).

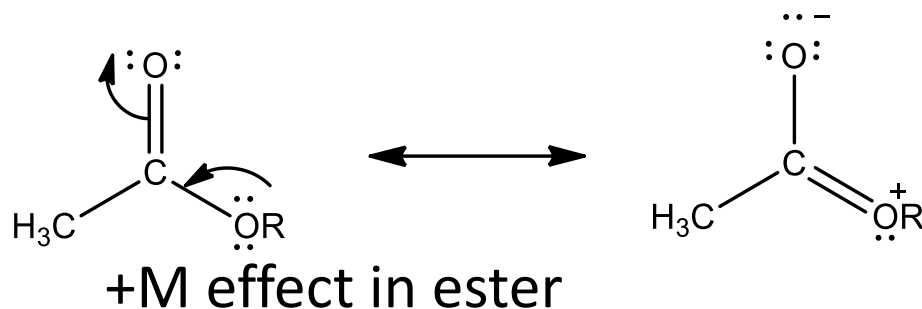
Resonance Effect or Mesomeric Effect

- **+M Effect**
- According to Ingold, if in a conjugated system like $X-C=C$, electron displacement occurs in such a way as to increase the electron density of unsaturated residue and decrease that of X, then the group or atom X is behaving electropositively and the resulting mesomeric effect is labelled as +M effect.
- +M effect in vinyl fluoride and in an ester may be shown as below:



- **+M Effect**

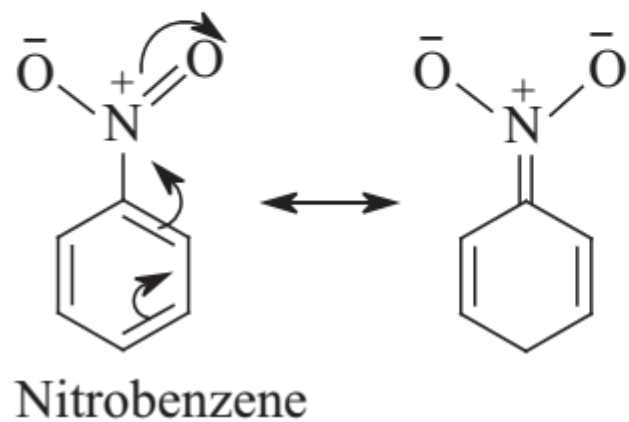
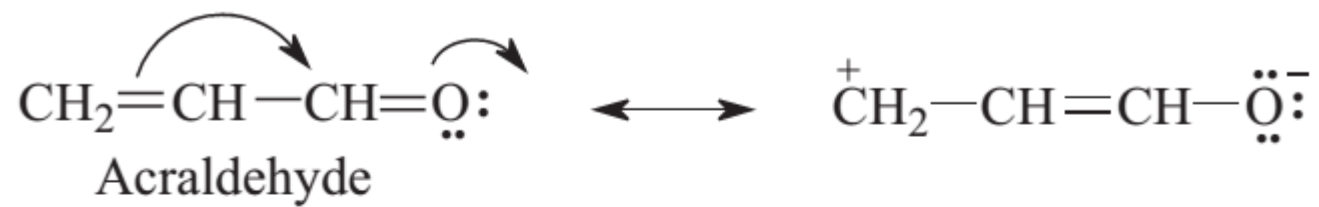
- According to Ingold, if in a conjugated system like $X-C=C$, electron displacement occurs in such a way as to increase the electron density of unsaturated residue and decrease that of X, then the group or atom X is behaving electropositively and the resulting mesomeric effect is labelled as +M effect.
- +M effect in an ester may be shown as below:



- **- M Effect**

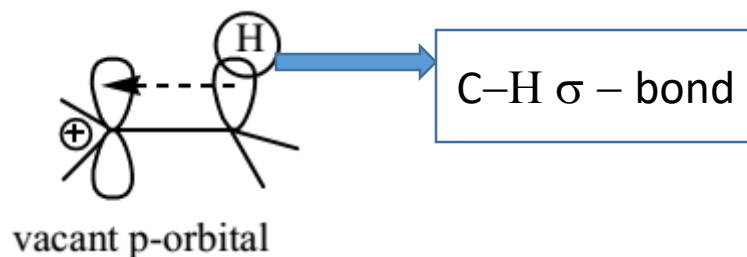
- If in a conjugated system like $Y=C-C=C$, the group 'Y' withdraws electrons from the system, then the resulting mesomeric effect is labelled as -M effect.
- For example, acraldehyde exhibits -M effect as shown below. Another example of -M effect is observed in nitrobenzene.

- *M Effect*



Hyperconjugation

- A σ – bond can stabilise a neighbouring carbocation (or positively charged carbon) by donating electrons to the vacant p-orbital. The positive charge is delocalised or ‘spread out’, and this stabilising effect is known as “*no-bond resonance*”.



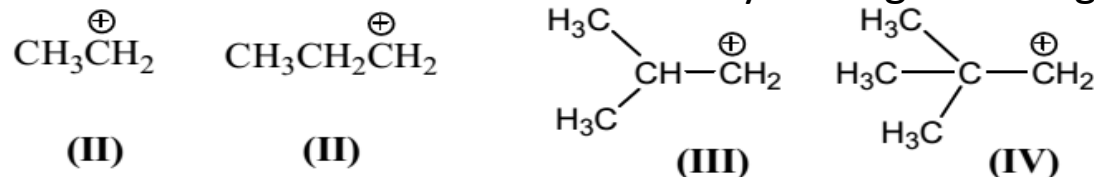
- The electrons in the σ –bond spend time in the vacant p-orbital

□ Points to Remember :

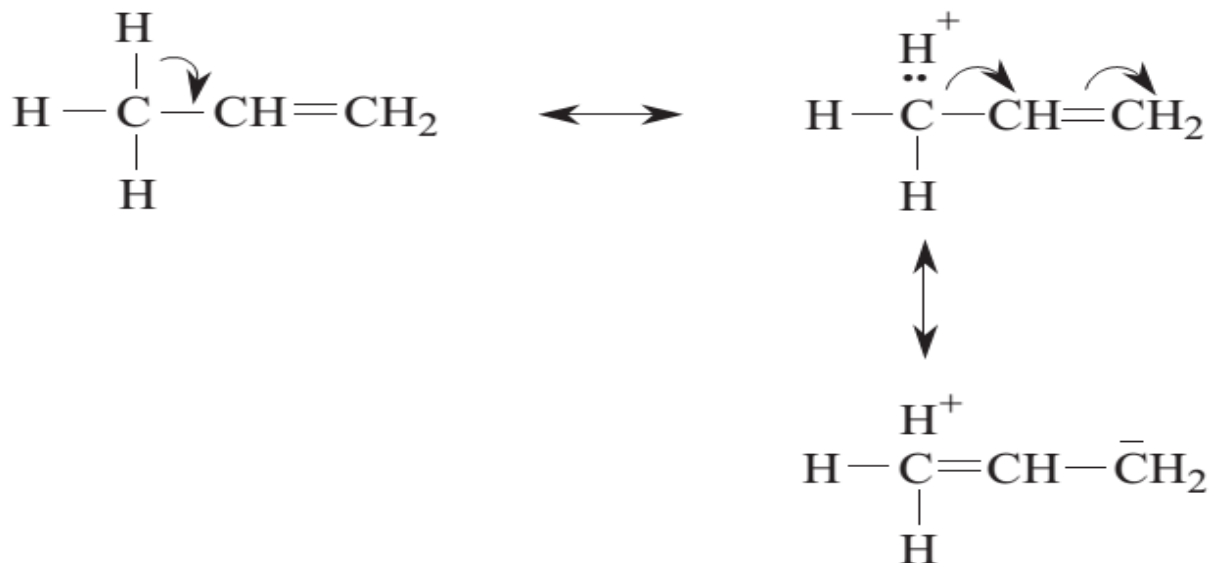
Number of α hydrogen \propto number of hyperconjugating structure \propto stability

$$\propto \frac{1}{\text{Heat of hydrogenation}} \propto \text{Polarity} \propto \text{dipole moment} \propto \frac{1}{\text{bond length}}$$

- **Problem :** The correct order for the stability among following compound is



Propene



- In the above resonating structure, one of the $\text{H}-\text{C}$ bonds is considered to be cleaved. From this point of view, hyperconjugation is often called *no bond resonance*.
- Although, $\text{H}-\text{C}$ bond is shown to be broken, H^+ is never free from the system or changes its position in the molecule.
- Again each of the three H atoms of CH_3 group can take part in exhibiting hyperconjugation in an identical manner leading to the same type of result.

- ❑ The greater the number of hyperconjugative structures the more stable will be the system. Hyperconjugation is also known as Baker–Nathan effect.
- ❑ Due to hyperconjugative effect, electron density of the unsaturated part of the molecule increases and hence the multiple bonds in these systems are found to be more reactive than what is expected from +I effect only.

Steric effects

- ❑ Steric effects are nonbonding interactions that influence the shape (conformation) and reactivity of ions and molecules.
- ❑ Steric effects complement electronic effects, which usually dictate shape and reactivity.
- ❑ Steric effects result from repulsive forces between overlapping electron clouds.

- ❑ *Steric hindrance* is a consequence of steric effects. Steric hindrance is the slowing of chemical reactions due to steric bulk.
- ❑ It is usually manifested in *intermolecular reactions*, whereas discussion of steric effects often focus on *intramolecular interactions*. Steric hindrance is often exploited to control selectivity, such as slowing unwanted side-reactions.

❑ A substitution reaction on a halide by a hydroxide does not work in this case because of steric hindrance.

