Unit - I

CHEMICAL BONDING

MOLECULAR ORBITAL THEORY

Covalent Bond :

Covalent bond is a type of linkage in which two atoms combine with one another by sharing a pair of electrons in their outer shells so that the combining atoms to attain the nearest noble gas configuration in their valency shells. The electrons thus shared, contribute towards the stability of both the atoms.

To explain the concept of covalent bond we need theories to answer questions like why covalent bonds are formed, how the electrons are arranged in space in a molecule, how the sharing of electrons could takes place etc. One such theory is Molecular Orbital theory.

Basic concepts of Molecular Orbital Theory :

According to molecular orbital theory,

1. All the atomic orbitals of the atom, participating in molecule formation, get disturbed when the nuclei approach each other.
2. The atomic orbitals get mixed up to give equivalent number of new orbitals called **molecular orbitals**.
3. Just as each electron in a single atom can be represented a certain wave-function ψ, every electron in a molecule can be denoted by a similar wave function characteristic of a particular molecular orbital.
4. Like atomic orbital, a molecular orbital cannot accomodate more than a maximum of two electrons.
5. The two electrons should have opposite spins.
6. However there is a clear cut difference between atomic and molecular orbitals. An electron in the atomic orbital is influence by only one positive nucleus while an electron in the molecular orbital is under the combined influence of two or more nuclei.

Bonding and Anti Bonding Orbitals :

We have seen molecular orbitals are formed by combining the atomic orbitals of the bonded atoms. For this purpose we apply the principle of **Linear Combination of the Atomic Orbitals** (LCAO). In a diatomic molecule the wave function for an electron in the field of two nuclei A and B will be given by two modes of combinations, symmetric and antisymmetric. So we have

$$\psi_s = \psi_A + \psi_B \qquad (1)$$

$$\psi_a = \psi_A - \psi_B \qquad (2).$$

The probability of finding an electron in the molecular orbital by LCAO according to equation (1) is greater than that in either of ψ_A or ψ_B. In other words the molecular orbital represented by ψ_s has a lower energy than ψ_A or ψ_B. This orbital therefore leads to the formation of a stable chemical bond. So this orbital is called **bonding orbital**.

The probability of finding an electron in the molecular orbital by LCAO according to equation (2) is less than that in either ψ_A or ψ_B. In other words the molecular orbital represented by ψ_a has higher energy than ψ_A and ψ_B. This orbital therefore cannot lead to the formation of a stable chemical bond. So this orbital is called **antibonding orbital.**

The formation of bonding molecular orbitals ψ_S and antibonding molecular orbitals ψ_a from two atomic orbitals ψ_A and ψ_B is given in the following figure 1.

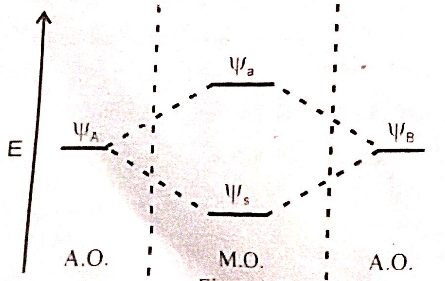


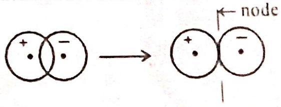
Figure - 1

Thus we find two atomic orbitals combine to give two molecular orbitals one of which is bonding and the other antibonding.

When the two atomic orbitals overlap in a linear fashion we get two MOs. They are termed as σ (bonding) and σ* (antibonding). The overlapping atomic orbitals may be pure or hybridised. Thus we can have s-s, p-p, sp³-s, sp²-s, sp-s etc. overlaps. Each such overlap would give one σ and one σ* orbital.

When the two atomic orbitals overlap in a side wise fashion we get two MOs. They are termed as π (bonding) and π* (antibonding). We can have π–π overlap (lateral). This gives π and π* orbitals.

Differences between bonding and anti bonding orbitals.

Bonding molecular orbital	**Anti-bonding molecular orbital**
1. Formed by the combination electron wave of same sign i.e., by addition overlap of atomic orbitals 	Formed by the combination of electron waves of opposite sings i.e., by the subtraction overlap of atomic orbitals 
2. Possess lower energy than the atomic orbitals from which it is formed	Possess higher energy than the atomic orbitals from which it is formed.
3. The electron density in between the nuclei is high. So the attraction between the nuclei is high. This explains the formation of a bond between the atoms	The electron density in between the the nuclei is low. So the repulsion between the nuclei is high. This explains the non formation of a bond between the atoms.

Bond order :

Bond order = $(N_b - N_a)$

N_b = Number of electrons in bonding molecular orbitals.

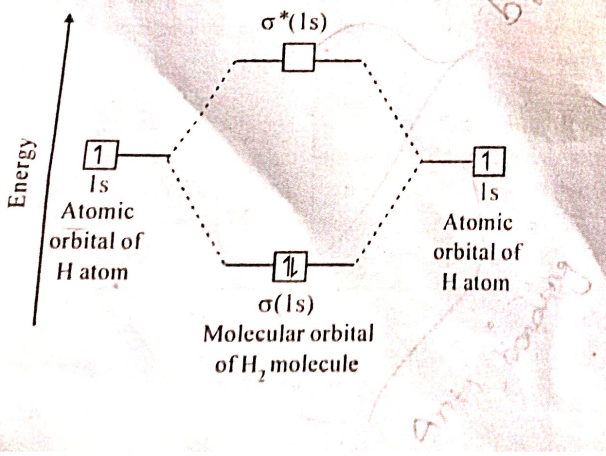
N_a = Number of electrons in anti - bonding molecular orbitals.

Bond order gives the number of bonds in a molecule. When the bond order increase stability i.e., strength of the molecule also increase. Similarly when the bond order increases bond length decreases.

Application of Molecular Orbital Theory

H_2 - Molecule

Let us consider the formation of hydrogen molecule according to molecular orbital theory. Two atomic orbitals, (1s), one from each hydrogen atom approach to form a molecule. The number of molecular orbitals formed from atomic orbitals is equal to the number of atomic orbitals. The molecular orbital which lowers the energy, brings about stability in the system and is responsible for bonding between the atoms. This type of molecular orbitals are therefore called **bonding molecular orbitals.** The bonding molecular orbitals of the type which is formed from 1s atomic orbitals are denoted as σ (1s). The electron density in a bonding molecular. orbital is more in the inter nuclear region than at the ends. The other type of molecular orbitals correspond to higher energy status. The electron density of such molecular orbitals is maximum at the ends. The electron density is almost zero in internuclear region. This is called the **antibonding molecular orbital** (denoted with an asterisk* mark).



The hydrogen molecule is formed from $1s^1$ atomic orbitals of two atoms. They give rise to two molecular orbital σ(1s) and σ* (1s). The two electrons are filled according to aufbau principle. Thus both these electrons go to the lower energy bonding molecular orbital and antibonding molecular orbital remains vacant.

Thus in hydrogen the bond order = $\frac{1}{2}$ (number of electrons in bonding orbitals − number of electrons in antibonding orbitals)

$$= \frac{1}{2}(2-0) = \frac{1}{2} \times 2 = 1. \quad : \frac{1}{2}(N_b - N_a)$$

That is, H_2 molecule is bonded by one bond as H–H

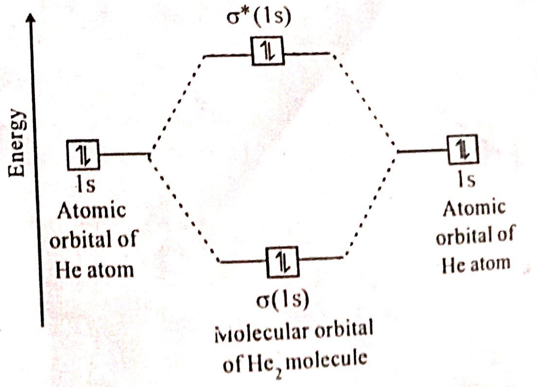
Its molecular orbital configurations is $\sigma(1s)^2\,\sigma^*(1s)^0$.

The molecular orbital diagram of hydrogen molecule is given in figure-2.

He_2 - Molecule

Let us consider the possibility of combination of two helium atoms to form He_2 molecule. Each helium atom has two 1s electrons. Thus there are four electrons to be accommodated. The (σ1s) molecular orbital will accommodate 2 electrons and (σ*1s) will accommodate 2 electrons as shown in the following.

The MO configuration is $(\sigma 1s)^2, (\sigma^* 1s)^2$.



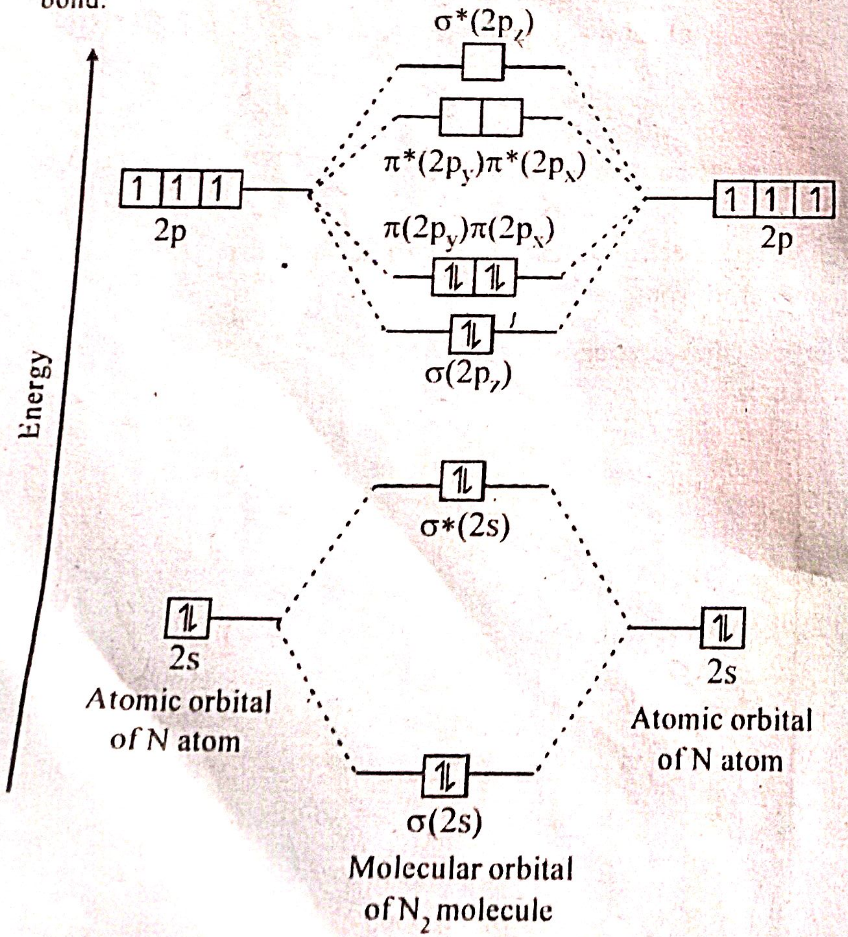
There are two electrons in each of the bonding and antibonding orbitals.

The number of bonds ½ (2 – 2)=0. That is, the **bond order** is zero. In other words, there can be no bond between two He atoms, i.e., **He_2 - molecule** cannot exist.

#: 10M

N_2 - Molecule

The electronic configuration of N is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Each atom contributes 5 valence electrons (2+1+1+1). The molecule would have eight molecular orbitals as shown in figure 4. Ten electrons are to be accommodated in them. Eight electrons go to the bonding molecular orbitals and two electrons go to antibonding molecular orbital. This gives the number of bonds as = ½ (8 – 2) =3. Thus N_2 molecule has a triple bond.



From the M.O. picture of N_2 the following become evident.

1. Bond order = ½ (number of electrons in bonding orbitals – number of electrons in the antibonding orbitals). = ½ (8 – 2)=3.
2. There are two electrons each in σ 2s and σ* 2s orbitals. So these become nonbonding electrons. There are two electrons in (σ 2p) M.O. and four electrons in (π 2p) MOs. So there is one σ bond and two π bonds in nitrogen.
3. Since there are no unpaired electrons in the M.O. structures the molecule will be **diamagnetic**.

Thus the MO structure of nitrogen explains its properties.

HYDRIDES

Hydrides are binary compounds of hydrogen with other elements whose electro negativity is lower than that of hydrogen.

According to this definition the term hydride is not used to compounds like H_2O, H_2S, NH_3, PH_3, HF, HCl, HBr etc. This term is not used for the binary compounds of hydrogen with non-metals.

Classification :

The hydrogen are classified according to the electronegativity of the elements, which form the hydrides, Paneth classified the hydrides as follows.

1. Salt -like hydrides or ionic hydrides
2. Volatile or covalent hydrides
3. Metallic hydrides and
4. Polymeric hydrides.

1. Salt like or Saline hydrides or ionic hydrides :

They are also called electrovalent hydrides. Only elements with very low electronegativity values can transfer electrons to the hydrogen atom and form salt-like hydrides. The elements of IA, IIA and IIIA form hydrides of this type having the composition MH_x where x is the group valency of the metal.

Example : LiH, NaH, CaH_2

2. Volatile or Covalent hydrides:

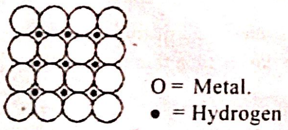
These hydrides are formed by the highly electronegative elements by sharing of electrons with hydrogen. They have the general formula $XH_{(8-n)}$ where n is the group number of the element. The metals belonging to IIB, IVB, VB, VIB and VII B groups form this type of hydrides.

Example : HF, CH_4, NH_3

3. Metallic hydrides or interstitial hydrides:

(d-block)

The transition elements and rare-earth metals combine with hydrogen to produce hydrides, which are metallic in appearance. They do not possess definite composition. In these hydrides the hydrogen atoms seem to occupy the interstities of the metals. Hence they are called as interstitial hydrides.



4. Polymeric hydrides (or) complex hydrides or polynuclear hydrides:

In polymeric hydrides two or more metal atoms are linked by hydrogen bridges.

Lithium

Examples : $LiAlH_4$, $LiBH_4$.

Lithium Boron hydride

Preparation of Hydrides:

1. Preparation of salt-like or ionic hydrides:

a) Hydrides of alkali metals :

They are easily obtained by direct reaction between the pure metals and hydrogen at suitable temperatures (150°C – 800°C)

$$2Li + H_2 \xrightarrow{700°C - 800°C} 2LiH$$

$$2Na + H_2 \xrightarrow{400°C} 2NaH$$

b) Hydrides of alkaline earth metals:

They are also prepared in the same manner as alkali hydrides are prepared

$$Ca + H_2 \xrightarrow{150°C - 300°C} CaH_2$$

$$Sr + H_2 \xrightarrow{800°C} SrH_2$$

$$Ba + H_2 \xrightarrow{150°C} BaH_2$$

c) Hydrides of III A groups:

Aluminium hydride is prepared by treating an etherial solution of aluminium chloride with lithium hydride or lithium aluminium hydride.

$$AlCl_3 + 3LiH \xrightarrow{Ether} AlH_3 + 3LiCl$$

$$AlCl_3 + 3LiAlH_4 \xrightarrow{Ether} 4AlH_3 + 3LiCl$$

2. Preparation of covalent hydrides:

i. By the direct combination of the element with hydrogen.

$$F_2 + H_2 \longrightarrow 2HF$$

ii. By the action of water on borides, carbides, nitrides, and silicides of metals.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

iii. By the action of dilute acids on borides, carbides, nitrides of silicides of metals.

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$$

$$Mg_2Si + 4HCl \longrightarrow 2\,MgCl_2 + SiH_4$$

iv. By the action of hydrogen on a metal or its compound.

$$AsCl_3 + 6H \longrightarrow AsH_3 + 3HCl$$

$$SbCl_4 + 6H \longrightarrow SbH_3 + 3HCl$$

$$GeCl_4 + 8H \longrightarrow GeH_4 + 4HCl$$

v. By the reduction of suitable halide with lithium aluminium hydride.

$$SnCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + SnH_4$$

$$GeCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + GeH_4$$

3. Preparation of metallic hydrides:

i. The metallic hydrides are obtained by occlusion or adsorption of hydrogen at moderate or high temperatures. For example palladium adsorbs 900 volumes of hydrogen. Similarly other metals adsorb hydrogen forming metallic hydrides.

ii Metallic hydrides are also obtained by absorption of hydrogen on a metal, which is made cathode during electrolysis.

4. Preparation of polymeric hydrides:

When lithium hydride is treated with aluminium chloride in ether lithium aluminum hydride is obtained.

$$4LiH + AlCl_3 \xrightarrow{Ether} LiAlH_4 + 3LiCl$$

When sodium hydride react with dibrome inpresence of either sodium boro hydride is formed.

$$2NaH + B_2H_6 \xrightarrow{Ether} 2NaBH_4$$

When Born fluoride is treated with sodium hydride, sodium boro hydride is formed.

$$BF_3 + 4\,NaH \longrightarrow NaBH_4 + 3NaF$$

Sodium aluminium hydride can be prepared by the direct combination of Li, Al and H_2 under high pressure in the presence of ether.

$$Na + Al + 2H_2 \xrightarrow[150^\circ C,\ 136\ atm.]{Ether} NaAlH_4$$

[illegible]

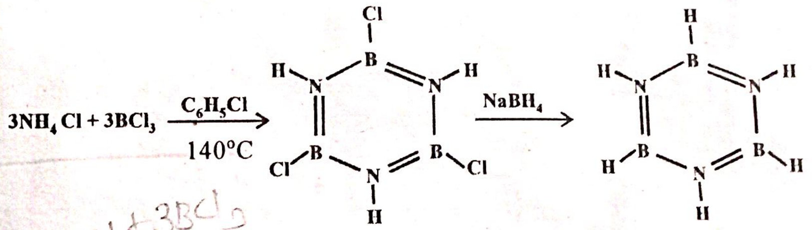
1. Borazole or Borazine : $B_3N_3H_6$

5m / 10M

*

Preparation :

1. Borazole can be prepared by heating ammonium chloride and boron trichloride in the presence of chlorobenze. The product obtained namely B - tri chloroborazine is reduced by sodium borohydride in polyether to give borozine.



+ $NaCl_2$

$3NH_4Cl + 3BCl_3$

B, B, B - tri chloroborazine

Borazole

2. Borazole can be prepared by heating a mixture of $LiBH_4$ and NH_4Cl in vaccum at 230°C , This method gives 30% borazine.

$$3NH_4Cl + 3LiBH_4 \xrightarrow{230^\circ C} B_3H_3H_6 + 3LiCl + 9H_2$$

3. It is prepared by heating ammnonia with diborane.

$$2B_2H_6 + 6NH_3 \longrightarrow \underset{\text{adduct}}{3[B_2H_6.2NH_3]} \longrightarrow 2B_3N_3H_6 + 12H_2$$

Properties :

i. Borazole is a colourless mobile volatile liquid.

ii. Borazole decomposes slowly on standing giving H_2 and diborane.

iii. Hydrolysis : Borazole undergoes hydrolysis at high temperature to give boric acid.

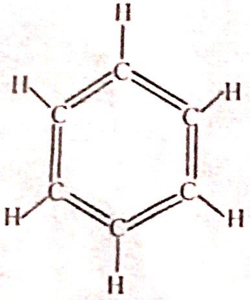
$$B_3N_3H_6 + 9H_2O \longrightarrow 3H_3BO_3 + 3NH_3 + 3H_2\uparrow$$

Inorganic benzene :

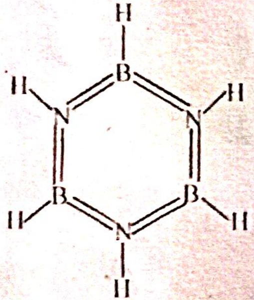
i. Borazine is a six membered cyclic compound like benzene where the ring positions are occupied by boran and nitrogen in alternative positions like benzene. There is a system of conjugated single and double bonds.

ii. Borazine undergoes addition and substitution reaction with HCl and Br_2 etc. like in the case of benzene.

iii. The ring structure of borazine is related to layer structure of BN, like the structure of benzene is related to layer structure of graphite. But borazine does not posses aromatic character.



Benzene



Borazole

Uses :

i. It is used as a solvent.

ii. It is used to prepare boric acid.

iii. It is usd to prepare diborane.

iv. It is used to produce inorganic polymers.

2. Sodium Borohydride : $NaBH_4$

Preparation :

1. Methyl borate disolved in Tetrahydro furan reacts with sodium hydroxide to form sodium borohydride.

$$4NaOH + B(OCH_3)_3 \longrightarrow 3CH_3ONa + NaBH_4$$ +20

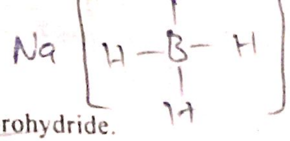
2. Sodium hydride reacts with diborane to form sodium borohydride

$$2NaH + B_2H_6 \longrightarrow 2NaBH_4$$

Uses :

1. It is used to prepared Diborane

$$3NaBH_4 + 4BF_3 \longrightarrow \underset{\text{Diborane}}{2B_2H_6} + 3NaBF_4$$

Na 

2. It is used to prepare within lithium borohydride.

$$NaBH_4 + LiCl \longrightarrow LiBH_4 + NaCl$$

3. It is used as a reducing agent in organic chemitry.

$$\underset{\text{2 - Butanone}}{CH_3 - CH_2 - CO - CH_3} \longrightarrow \underset{\text{2 - Butanol}}{CH_3 - CH_2 - CHOH - CH_3}$$

3. Lithium aluminium hydride : $LiAlH_4$

Preparation

1. By the direct synthesis from elements.

$$Li + Al + 2H_2 \longrightarrow Li[AlH_4].$$

2. By the direct combination of Lithium hydride and aluminium chloride in ether solution.

$$4\,LiH + AlCl_3 \xrightarrow{\text{ether}} Li[AlH_4] + 3LiCl$$

3. By double decomposition. LiCl and sodium aluminium hydride react to give lithium aluminium hydride.

$$LiCl + Na[AlH_4] \longrightarrow NaCl + Li[AlH_4]$$

Applications :

1. Reduction properties. It is strong reducing agent and reduces certain halides of groups III, IV and V to convalent of the elements concerned.

$$4BF_3 + 3Li[AlH_4] \xrightarrow{LiAlH_4} \underset{\text{Diborane}}{2B_2H_4} + 3LiF + 3AlF_3$$

$$AlCl_3 + 3Li[AlH_4] \longrightarrow 4AlH_3 + 3LiCl$$

$$SiCl_4 + Li[AlH_4] \longrightarrow SiH_4 + LiCl + AlCl_3$$

2. Reduction of organic compounds. It is an ideal reducing agent for aldehydes, ketones and carboxylic acids.

R - CH2 , C6H5 . H - [illegible]

-RCHO $\xrightarrow{LiAlH_4}$ RCH$_2$OH
Aldehyde Alcohol

CH3 - RCOR CH3 $\xrightarrow{LiAlH_4}$ RCHOHR
Acid Sec. alcohol

CH3 - RCOOH $\xrightarrow{LiAlH_4}$ RCH$_3$ + 2H$_2$O
Alkane

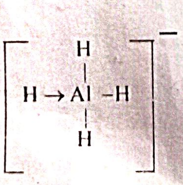
3. Hydrolysis. It is hydrolysed by water evolving hydrogen.

$Li[AlH_4] + 2H_2O \longrightarrow LiAlO_2 + 4H_2$

4. It is used as powerful reducing agent for both organic and inorganic substances.

Structure :

The structure of $[AlH_4]^-$ ion is **tetrahedral** Li as shown below.



$$\left[\begin{array}{c} H \\ | \\ H \rightarrow Al - H \\ | \\ H \end{array}\right]^-$$

University Questions

1. What are the basic concepts of M.O. theory?
2. What are bonding and antibonding orbitals explain with example.
3. What are the differecences between bonding and antibonding orbitals?
4. What are non - bonding orbital explain with an example?
5. Explain the structure of hydrogen molecule based on molecule orbital theory?
6. Draw the molecular orbital configuration of N$_2$ molecule and explain its magnetic properties.

7. Draw the molecular orbital configuration of F$_2$ molecule and explain its magnetic properties.
8. Define bond order.
9. Calculate the bond order of oxygen and nitrogen molecules.
10. What are hydrides?
11. How hydrides are classified?
12. What are ionic hydrides. Give examples?
13. What are covalent hydrides. Give examples?
14. What are metallic hydrides?
15. What are polymeric hydrides give on examples?
16. How sodium borohydride is prepared?
17. What are the uses of sodium borohydries.
18. How is borazole is prepared?
19. What are the uses of borazole?
20. Why borazole is called an inorganic benzene?