



# RAJASTHAN PUBLIC SERVICE COMMISSION

Volume - 2

**Concerned Subject Part – 1** 



# RAJASTHAN FOOD SAFETY OFFICER

S.No.	Chapter	Page					
		No.					
	UNIT - 1						
1.	Chemical Bond	1					
2.	рН	12					
3.	Thermodynamics	14					
4.	Equilibrium State	23					
5.	Chemical Kinetics	32					
6.	Hydrocarbons	36					
7.	Methods of Preparation & Chemical Properties	39					
8.	Metallurgy	43					
9.	Qualitative & Quantitative Analysis	44					
10.	Solution	45					
11.	Suspension	51					
12.	Surface Tension	52					
13.	Surface Chemistry	54					
14.	Catalysis	58					
	UNIT - 2						
1.	Foodborne Microbes	59					
2.	Factors Affecting Microbes	64					
3.	Sources of Micro-Organisms in Food	69					
4.	Food Spoilage Microorganisms	71					
5.	Fermentation- Principles, Types and Limitations	73					
6.	Dairy Fermentation, Fermented Foods	77					
7.	Traditional Indian Foods	79					
UNIT - 3							
1.	Bio Molecules	87					
2.	Carbohydrates	91					
3.	Protein Metabolism	94					
4.	Lipids	99					
5.	Enzymes	100					
6.	Human Diet – Nutrition	104					
7.	Plant Alkaloids	106					
8.	Plant and Toxins	109					

UNIT - 4					
1.	Animal Kingdom	113			
2.	Prokaryotic/ Eukaryotic Cell	122			
3.	Animal Tissue	123			
4.	Plants and Animal Products used as Food by Human	124			
5.	Human Anatomy and Physiology	127			
6.	Digestive System	130			
7.	The Respiratory System	136			
8.	Circulatory System	139			
9.	Heart	140			
10.	Excretory System	144			
11.	Nervous System	146			
12.	Endocrine System	153			
13.	Muscular System- Types of Muscles and Muscle Contraction	157			
14.	Reproductive System	159			
15.	Immune System	161			
16.	Human Disease	164			
17.	National Health Program	166			

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# **Chemical Bond**

- A bond is an attractive force that binds two atoms together.
- Energy decreases in bond formation.
- Bond strength  $\propto$  1/energy

**Octave Rule** - If 8m becomes in the outer shell of an element, then it attains stability.

#### Na = 2, 8, 1

Example –

Na = 2, 8

Cl = 2, 8, 7

Cl<sup>-</sup> = 2, 8, 8

#### Exception

- H, He becomes stable when it is 2e.
- II and III class halides.

$BeCl_2 - 4e$	VI
BeCl <sub>3</sub> –	$SF_6 - 12e$
BF <sub>3</sub>	VII
6e	IF <sub>7</sub> –14e
	VIII
V	$O_{_5}F_{_8} - 16e$
PCI. – 10e <sup>–</sup>	

**Principle of Sugan** - No element can expand its octave. The more e<sup>-</sup> in it, the more unit bonds it can form.

Unit Bonds

#### Sidgwick's Theory

 According to this, any element can expand its octet, because it uses its orbitals.

	Bond	Electron
Periodic I	2	4
Periodic II Li Be, B, C, N, O, f	4	8
Periodic III, IV	6	12
Periodic V, VI	8	16

(Covalancy) Maximum bonding strength

#### Q. What is the co-valency of H in $N_2O_5?$

Ans.



For example -  $H_2O$ ,  $H_3O^+$ ,  $H_4O^{+2}$  Formation of all three is possible, because maximum bond forming capacity of H is 4.

# **E.g.** $CCl_4 + H_2O \rightarrow X$

 $SF_6 + H_2O \rightarrow X$ 

These are two inert molecules.

For example – IF<sub>7</sub>, CIF<sub>7</sub> formation is not possible in CIF<sub>7</sub>, as cannot form more bonds than Cl<sub>6</sub>.

#### Types of Bonds

There are 6 types of bonds.

- 1. Ionic bond
- 2. Covalent bond
- 3. Sub-covalent bond
- 4. Hydrogen bond
- 5. Vander Waal bond
- 6. Metallic bond

#### Ionic bond

- It is also called "electrovalent bond".
- This bond is formed by the exchange of e<sup>-</sup> between the metal and the non-metal.
- Metals give electrons, while nonmetals take e<sup>-</sup>.
  - Metal  $\xrightarrow{e}$  Non-metal

#### Note –

The ionization energy/potential of the metal should be less.

- The e<sup>-</sup> affinity of the non-metal should be high.
- The lattice energy of the compound should be high.



#### Lattice Energy

The amount of energy required to break one mole of an ionic substance into its constituent elements is called lattice energy.

$$\begin{array}{c} \mathsf{NaCl} \longrightarrow \mathsf{Na^{+}} & \mathsf{Cl^{-}} \\ \mathsf{(s)} \longrightarrow \mathsf{(g)} & \mathsf{(g)} \end{array} \Delta \mathsf{H} = +788 \end{array}$$

Lattice energy × Charge

 $Mg^{+2}O^{-2} > Na^{-1}F^{-1}$ 

Because the charge of Mg<sup>+2</sup> is greater than that of Na<sup>+1</sup>.

Decreasing order of lattice energy

$$\frac{11+6}{MgO} > \frac{11+7}{MgCl_2} > \frac{1+6}{Na_2O} > \frac{1+7}{NaCl}$$

#### Properties

- Ionic compounds are solid because there is a strong force of attraction between them.
- The melting and boiling points of ionic compounds are high because there is a strong force of attraction between them.



- lonic compounds do not conduct electricity in solid state, but do conduct electricity in molten or aqueous state because free ions are present.
- Ionic compounds dissolve in water because the heat of hydration is greater than the lattice energy.
- Water is the best solvent because of its high dielectric constant.

(The dielectric constant is the force that drives two ions apart.)

NaCl 
$$\xrightarrow{H_2O}$$
  $\xrightarrow{\bigtriangledown}$   $\overset{\bigtriangledown}{\boxtimes}$   $\overset{\lor}{\boxtimes}$   $\overset{(+)}{\boxtimes}$   $\overset{(+)}{\boxtimes}$ 

Dielectric constant –  $H_2O = 82$ ,  $D_2O = 78$ 

#### **Fayans Law**

The covalent character of ionic compounds is determined by Fiennes's law.

Covalent character × polarization

#### For more polarization.....

The cation should be small. 1 The smaller the cation, the more polarizable. Decreasing order of covalent character.

LiCl > NaCl > KCl > RbCl

2. The size of the anion should be large. The size of  $A_gF < A_gCI < A_gBr < A_gI - I$  is large so the polarization will be more and covalent properties will also be more.

NaF < NaCl < NaBr < NaI

- 3. The charge on the cation and anion should be more.  $Na^{+}Cl > Mg^{+2}Cl_{2} < Al^{+3}Cl_{3} < Si^{+4}Cl_{4}$ 
  - In this, the size of Si is small and the cation charge is the largest, hence the covalency will be more.

 $NaCl^{-1} < Na_2SO_4^{-2} < (Na_3PO_4^{-3})$ 

- Na<sub>3</sub>PO<sub>4</sub>C are more covalent because the charge is more.
- 4. d group compounds are more covalent than s group compounds.
  - Or

Cations with pseudo-reactive configuration are more covalent.

$$\begin{array}{ccc} CaCl &> NaCl\\ d \mbox{ group } S \mbox{ group }\\ & \downarrow & \downarrow\\ AgCl &> NaCl\\ & \downarrow & \downarrow\\ d \mbox{ group } S \mbox{ group }\\ Cu_2Cl_2 &> NaCl \end{array}$$

#### Note -

 $S_nCl_4 > S_nCl_{2(s)}$ 

It contains SnCl<sub>2</sub> in solid state so it is ionic.

Hydrolysis of more covalent is easily done. Solid Form

 $BeCl_2 > MgCl_2 > CaCl_2 > BaCl_2$ 

Covalent properties and the course of hydrolysis Question - The increasing order of hydrolysis of AlCl<sub>3</sub>, CCl<sub>4</sub>, SiCl<sub>4</sub>, PCl<sub>5</sub>? Answer -

 $CCl_4 < AlCl_3 < SiCl_4 < PCl_5$ 

Note - CCl<sub>4</sub> does not undergo hydrolysis.

 $\text{CCI}_4 + \text{H}_2\text{O} \rightarrow \text{X}$  $SF_6 + H_2O \rightarrow X$ 

#### **Covalent Bond**

A covalent bond is formed by the sharing of electrons between two non-metal atoms.

Unit Bond	Double Bond
Cl <u>×</u> Cl	O = O
Triple Bond	Double Bond
$N \equiv N$	C = C
$\downarrow$	$\downarrow$
Maximum Binding Energy	Both are $\pi$ bonds

#### Characteristics of Covalent Compounds

(1) All covalent compounds are found in liquid or gaseous state.

Exceptions - Diamond, graphite, fullerene corundum Al<sub>2</sub>O<sub>3</sub>, silicon carbide SiC

These are macromolecules and are solid due to 3D geometry.

(2) Their melting and boiling points are very low. Because the van der Waals force is weak in them.

$$\bigcirc = C = \bigcirc + \bigcirc = C = \bigcirc$$
  
Will break

(3) Covalent comp er, but form water bonds. They dissolve in water.

(E) None of these Ans. (E)

Note -

Only that compound dissolves in water in which H combines with FON and forms H bond. Hence none of them forms H bond.

(4) Covalent bond is directional i.e., definite shape and structure of molecules are found while ionization is non-directional.

CaCl<sub>2</sub> - × Ionic Compound

BeCl<sub>2</sub> – Linear (Covalent)

Note -

Both ionic and covalent character are found in KCl -KCN, NaOH.

#### Sub-covalent Bond

- ppersnotes Unleash the topper in you
- This is a special type of bond.
- In this bond both the shared isomers give the same atom.
- This is indicated by the arrow  $(\rightarrow)$ .

$$A \rightarrow B$$

- Donor Recipient
- In a sub-covalent bond, the hybridization of the acceptor atom increases by one.

 $SP^2 \rightarrow SP^3$ 

#### Example -

$$H = \begin{bmatrix} F & H & F \\ \sigma & \sigma & \sigma \\ \sigma & \sigma & \sigma \\ \sigma & \sigma & \sigma \\ H & F & H \\ (6e) & sp^2 & sp^3 \end{bmatrix} \xrightarrow{F} F$$

The hybridisation of the acceptor atom increases by one, so here in BF<sub>3</sub> SP<sup>2</sup> to SP<sup>3</sup> hybridised.

#### Example -



#### Example -

$$\begin{bmatrix} H \\ I \\ H - N \rightarrow H \\ I \\ H \end{bmatrix}^{+} CI^{-} \rightarrow$$

Ionic, covalent and sub-covalent bonds are present in it.

Nausadar (NH<sub>4</sub>Cl) - purified by sublimation method.

#### Example -

CuSO<sub>4</sub> 5H<sub>2</sub>O (Blue stone)

$$CuSO_4 + 5H_2O \rightarrow CuSO_4 5H_2O \xrightarrow{\Delta} CuSO_4H_2O + 4H_2O$$

(It is also called the test of sensitive water)



- The coordination number of Cu is 4, because 4, H<sub>2</sub>O and molecules are directly attached to Cu.
- It is a toxic substance, so it is used to make medicine to kill rats.

#### Example -





$$O_a = 6 - [1 + 6] =$$

$$O_b = 6 - [2 + 4] = 0$$

Example 
$$-O_3$$
  
 $O = 6 - [3 + 2] = +1$   
 $O_a = 6 - [2 + 4] = 0$   
 $O_b = 6 - [1 + 6] = -1$   
Example -  
 $N = 5 - [4 + 0] = +1$   
 $C = -1$   
 $N_2O$   
 $N \equiv N \rightarrow 0$   
 $5 - [4 - 0] = +1$ 

 $R \stackrel{\times}{-} N \stackrel{\times}{\underline{\times}} C$ 

#### H-Bond

When H<sub>2</sub> is directly bonded to (F, O, N) then H<sub>2</sub> gets +ve charge and other atom gets -ve charge. Hence the atoms are joined together by the force of attraction which is called H-bond.

[FON – H]

#### Example -

- $CH_3 O CH_3 \rightarrow H Do not make bond$
- $H F \rightarrow H Make bond$
- $NH_3 \rightarrow H Make bond$

 $H_2S \rightarrow H - Do not make bond$ 

$$CH_{3} - C \rightarrow H - Make bond$$

$$H_{3} - C \rightarrow H - Make bond$$

$$H_{3} - C \rightarrow H - Make bond$$

- The energy of the H bond is 40.80 kJ/mole.
- Order of strength of H bond

F > O > N

Note -

$$H-F...H>H-O...H>H-N...H$$

Here H-F-H is stronger because electron affinity of F is more so now the bond will also be stronger.



Eg.

$$\frac{\mathsf{H}_2\mathsf{O}}{(l)} > \frac{\mathsf{HF}}{(l)} > \frac{\mathsf{NH}_3}{(g)}$$

- Here H<sub>2</sub>O forms stronger H bond than HF, because H<sub>2</sub>O molecule forms four bonds, while HF single bond, hence H<sub>2</sub>O is stronger bond.
- There are two types of H-bonds.
- (1) Intermolecular H-bond This bond is found in only one molecule.

#### Example –

O-Nitrophenol is volatile in steam, so it is purified by steam distillation method.



(2) Intramolecular H-bond - It is found between two or more same or different molecules.



**Note** - The intermolecular H bond is stronger than the intramolecular H bond.

#### Uses of H- bond

(i) H-bonding brings about a change in the state of matter.

 $HF - HCI H_2O H_2S$ 

- Liquid Gas Liquid Gas
- (ii) H-bonding increases the melting point and boiling point.

$$(H_2O)$$
  $H_2S < H_2Se < H_2T_e < H_2PO < H_2O$ 

(Hydrides of Due to H-bond 12<sup>th</sup> Group)

ond High Melting and boiling point (个)

 $(\overline{NH_3})$  PH<sub>3</sub> < AsH<sub>3</sub> <  $(\overline{NH_3})$  < SbH<sub>3</sub> < BH<sub>3</sub>

- There is an increasing order of boiling point.
- There is an increasing order of external enthalpy.
- (iii) H-bonding increases the stability.

 PH<sub>3</sub> (phosphine) is a flammable gas, while NH<sub>3</sub> is a stable gas.

Bond -  $NH_3$  and urea ( $NH_2CONH_2$ ) are highly soluble in water.

- Due to H bonding in ice, a cage-like structure is formed, due to which the volume of ice increases and the density decreases.
- At 4<sup>o</sup>C temperature, all the H bonds of H<sub>2</sub>O break and water molecules become close to each other, due to which the density becomes maximum.



(iv) The two strands of DNA are joined together by H bonds.

A = T (Two H- bond)

 $G \equiv C$  (Three H- bond)

(v) Alcohol fires are extinguished by water, while petrol fires are not, because alcohol forms H-bonds with water, due to which the ignition temperature increases.

**Flash point** - The minimum temperature at which a substance spontaneously catches fire is called flash point.

White phosphorus & 30°

Petrol (India) – 125<sup>0</sup>

(vi) Adding sodium (Na) to water causes fire because H<sub>2</sub> gas catches fire.

Na + H<sub>2</sub>O  $\rightarrow$  NaOH + H<sub>2</sub>  $\uparrow$  (Flammable gas)

 $Na \xrightarrow{Air} Na_2O \xrightarrow{H_2O} NaOH \xrightarrow{CO_2} Na_2CO_310H_2O \xrightarrow{\Delta} Na_2CO_3$ 

#### **Metallic Bond**

- This bond is found in metals.
- This bond is understood from the electron gaseous theory.

$$M \rightarrow M^{+n} + ne^{-}$$
  
Karnel Free  $e^{-}$ 

- In this way, the force between the kernel and the valence electrons located in the lattice sites or lattice points is called metallic bond.
  - (i) Metals are good conductors of electricity because free metals are present in them.
  - (ii) When one end of the metal is heated, the other end becomes hot.
  - (iii) Metals can be cast in the form of sheets and wires.



(iv) The conductivity of a metal decreases with increase in temperature because the resistance increases.

**Note** - This theory does not explain the high conductivity of silver.

- This theory could not explain why the conductivity of the semiconductor increases on increasing the temperature.
- These defects can be understood on the basis of band theory.
- Band theory Two types of bands are found in metals.
   Condition driving

 $\Delta E = energy gap (Forbidden area)$ 

#### Connector

Note - The more the difference in the value of  $\Delta E$ , the more the resistance will increase due to which the conductivity will decrease.

 The difference of ΔE is minimum in silver, hence it is more conductive.

Ag > Au > Cu Conductivity order

Conductor

 $\downarrow$  $\Delta E$ 

↑

Valency

Semiconductor

- The conductivity of semiconductors increases when the temperature is increased or by adding impurities.
   Note - At 0<sup>o</sup>K temperature, semiconductors turn into insulators and conductors turn into superconductors.
- Hg (mercury) shows the property of superconductivity at 4°k.

#### Vander Waal bond

- This is the weakest force of attraction.
- Vander Waal bond is of the following types -
  - (i) Instantaneous dipole (London force) -
    - It is found in nonpolar molecules.

#### Example -

Inert gases  $CO_2$  I<sub>g</sub>  $C_6H_6$   $CCI_4$  etc. are all associated (s) (s)

with instantaneous dipoles.

#### Hybridization

(ii) Dipole-dipole force -

 $\circ~$  This force is present in polar molecules.  $H^{\delta +} - C I^{\delta -}~~ H^{\delta +} - ~C I^{\delta -}$ 

- (iii) Dipole induced dipole -
  - It is found between polar and nonpolar molecules

 $I_2 + H^{\delta +} Cl^{\delta -}$ 

(iv) Ion-dipole force - It is found between ions and polar molecules.

 $\circ$   $\quad$  An ion dipole force is found in hydration.

Triangular - Triangular

$$Na^+ + H_2O$$
  $Na =$ 

(v) Ion-induced force -

$$CH_2 = CH_2 \xrightarrow{H^+} CH_2^+ - CH_2^+$$

Electromeric effect

 Water is a polar substance, which makes it a good solvent.

#### Vesper Theory

- Vesper theory has been given by Nyholm and Gillespie.
- Hybridization in a compound is determined by the number of σ and L.P.

NH<sub>3</sub>

4

Example -CH<sub>4</sub>

4 + 0

Δ

Bond Number L.P. Number

3 + 1

4 – SP<sup>3</sup> hybridization

 $H_2O$ 

2 + 2

• Atoms in a molecule are found at maximum distance from each other due to which repulsion is minimum.

$$\begin{array}{c} 180^{\circ} \\ CI \\ \hline Be \\ \hline CI \\ \hline$$

 When lone electron pairs (L.P.) are present in a molecule, its shape gets distorted due to repulsive forces.

$$\begin{array}{ccc} \mathsf{CH}_4 & \mathsf{NH}_3 & \mathsf{H}_2\mathsf{O} \\ \mathsf{B.P.}-\mathsf{B.P.} & < \mathsf{L.P.}-\mathsf{B.P.} & < \mathsf{L.P.}-\mathsf{L.P.} \\ \mathsf{Tetrahedral} & \mathsf{Pyramidal} & \mathsf{V}\text{-shaped} \\ \mathsf{109^\circ28'} & \mathsf{107^\circ} & \mathsf{104^\circ} \end{array}$$

Total Number of Number of Molecule/Ion Hybridization Example **Bond Pairs** L.P. Electrons in Shape the Valence Shell 2 2 0 Linear HgCl<sub>2</sub>, BeF<sub>2</sub>, [Ag (CN)<sub>2</sub>] sp 3 3 0 Planar triangular BCl<sub>3</sub>, SO<sub>3</sub> sp<sup>2</sup> 2 T-shaped figure SnCl<sub>2</sub> 1 sp<sup>2</sup>



4	4	0	Tetrahedral	sp³	CH <sub>4</sub>
	3	1	Triangle	sp³	NH <sub>3</sub>
	2	2	Pyramidal	sp³	H <sub>2</sub> O, OF <sub>2</sub>
5	5	0	T shape	sp <sup>3</sup> d or dsp <sup>3</sup>	PCl₅, XeO₃F₂
	4	1	Trigonal	sp <sup>3</sup> or dsp <sup>3</sup>	SF <sub>4</sub> , TeCl <sub>4</sub> , XeO <sub>2</sub> F <sub>2</sub>
			Bipyramidal		
	3	2	Irregular	sp <sup>3</sup> or dsp <sup>3</sup>	ClF <sub>3</sub> , BrF <sub>3</sub> , XeOF <sub>2</sub>
			tetrahedron		
6	8	6	Geometric shape	d <sup>2</sup> sp <sup>3</sup> /sp <sup>3</sup> d <sup>2</sup>	

• Number of orbitals attached to the e<sup>-</sup>atom of the valence e<sup>-</sup>bond with the central atom

BeCl <sub>2</sub>	$\frac{2+2}{2}=2$	s + l.p. 2 + 0	sp	Linear
BCl <sub>3</sub>	$\frac{3+3}{2}=3$	3 + 0	sp <sup>2</sup>	Triangular
SnCl <sub>2</sub>	$\frac{4+2}{2}=3$	2 + 1	sp <sup>2</sup>	V shape
NH3	$\frac{5+2}{2}=4$	3 + 1	sp <sup>3</sup>	Pyramidal
NH4 <sup>+</sup>	$\frac{5+4-1}{2}=4$	4 + 0	sp <sup>3</sup>	Tetrahedral
H <sub>2</sub> O	$\frac{6+2}{2}=4$	2 + 2	sp <sup>3</sup>	V shape
PCIs	$\frac{5+5}{2}=5$	5 + 0	sp <sup>3</sup> d	Trigonal Bipyramidal
SF4	$\frac{6+4}{2}=5$	4 + 1	sp <sup>3</sup> d	Rocker/Irregular tetrahedral
CIF3	$\frac{7+3}{2}=5$	3 + 2	sp <sup>3</sup> d	T shape
XeF <sub>2</sub>	$\frac{8+2}{2}=5$	2+3	16 sp <sup>3</sup> d	Linear you
XeF <sub>4</sub>	$\frac{8+4}{2}=6$	4 + 2	sp <sup>3</sup> d <sup>2</sup>	Square planar
XeF <sub>6</sub>	$\frac{8+6}{2}=7$	6 + 1	sp <sup>3</sup> d <sup>3</sup>	Deformed Octahedron

 $\ensuremath{\text{Note}}$  - If there are  $O_2$  molecules (oxygen molecules), they are not taken in number.

• -ve add charge.

• +ve subtracts the charge.

XeOF <sub>4</sub>	-	$\frac{8+0+4}{2}=6$	(σ + l.p.) (5 + 1)	hybridization sp <sup>3</sup> d <sup>2</sup>	Shape Square pyramidal
XeO₃	-	$\frac{8+0}{2}=4$	(3 + 1)	sp <sup>3</sup>	Pyramidal
SO <sub>4</sub> <sup>-2</sup>	-	$\frac{6+0+2}{2}=4$	(4 + 0)	sp³	Tetrahedral
$PO_4^{-3}$	=	$\frac{5+0+3}{2}=4$	(4 + 0)	sp <sup>3</sup>	Tetrahedral
BrF₃	_	$\frac{7+3}{2} = 5$	(3 + 2)	sp³d	T shaped



ICl <sub>2</sub> <sup>-2</sup>	_	$\frac{7+2+1}{2}=5$	(2 + 3)	sp³d	Linear
ICl <sub>2</sub>	-	$\frac{7+2}{2} = 4.5 \approx 5$	(2 + 3)	sp³d	Linear
NO <sub>2</sub>	_	$\frac{5+0}{2}=2.5\approx3$	(2 + 1)	sp²	Triangular
l <sub>3</sub> -	_	$\frac{7+2+1}{2}=5$	(2 + 3)	sp³d	Linear

 $[| - | - |]^{-}$ 

• Hybridization of carbon in organic matter

Hybridization	σ + l.p.	Angle	Shape
sp	2 + 0	180°	Linear
sp <sup>2</sup>	3 + 0	120°	Triangular
	2 + 1	Х	V shape
sp <sup>3</sup>	4 + 0	109°28'	Tetrahedral
	3 + 1	Х	Pyramidal
	2 + 2	Х	V shape
sp <sup>3</sup> d	5 + 0	90°, 120°	Trigonal bipyramidal
	4 + 1	$\Lambda$ $\Lambda$ $\lambda$	Like a swing
	3 + 2		T shape
	2 + 3	pach that	Linear
sp <sup>3</sup> d <sup>2</sup>	6 + 0	90°	Octahedral
	5 + 1		Square pyramidal
	4 + 2		Square planar
sp <sup>3</sup> d <sup>3</sup>	7 + 0	72°, 90°	Pentagonal
	6 + 1		Bipyramidal
			Distorted octahedron

# Molecular Orbital Theory (MOT)

- Developed by Hund and Mullican.
- Oxygen molecule shows paramagnetic properties due to having two unpaired electrons in the restriction orbital.

8 I	9 	10 	11 	12 	13 	14 	15 	16 	17 	18 I	19 	20 	e <sup>-</sup> Numbers
0	0.5	1	1.5	2	2.5	3	2.5	2	1.5	1	0.5	Ó	Bond Orders
0   0	1   0.5	2   1	3   0.5	4   0	5   0.5	6   1	7   0.5						

- All odd numbered electrons are paramagnetic.
- Exceptions 10, 16 electrons show para-magnetism.

• In which electrons are in even number, they are diamagnetic.

#### Example –

-	
O <sub>2</sub> = 16 bond order = 2	(Paramagnetic)
$O_2^- = 16 + 1 = 17e^-$ bond order = 1.5	(Paramagnetic)
$O_2^{-2} = 16 + 2 = 18e^{-} = 1$	(Diamagnetic)
$O_2^+ = 16 - 1 = 15 = 2.5$	(Paramagnetic)
$O_2^{+2} = 16 - 2 = 14 = 3$	(Diamagnetic)
N <sub>2</sub> = 14 = 3	(Diamagnetic)
$N_2^+ = 14 - 1 = 13 = 2.5$	(Paramagnetic)
$N_2^- = 14 + 1 = 15 = 2.5$	(Paramagnetic)
CO = 6 + 8 = 14 = 3	(Diamagnetic)
CN <sup>-</sup> = 6 + 7 + 1 = 14 = 3	(Diamagnetic)



NO <sup>+</sup> = 7 + 8 - 1 = 14 = 3	(Diamagnetic)
$C_2 = 6 + 6 = 12 = 2$	(Diamagnetic)
$B_2 = 5 + 5 = 10 = 1$	(Paramagnetic)
$F_2 = 9 + 9 = 18 = 1$	(Diamagnetic)
$Ne_2 = 10 + 10 = 20 = 0$	(Diamagnetic)
$H_2 = 1 + 1 = 2 = 1$	(Diamagnetic)
$T_2 = 1 + 1 = 2 = 1$	(Diamagnetic)
((T <sub>2</sub> ) Tritium - Isotope of H)	

#### Bond order of multiple atoms -

PO<sub>4</sub> 
$$\bigcap_{O=O^{-}O^{-}}^{O}$$
  $\frac{Aggregate bond}{Between}$   $\frac{5}{4} = 1.25$   
or  
PO<sub>4</sub>  $\stackrel{-3}{=} 4$  Charge on oxygen = 3  
1 Charge on oxygen  $= \frac{3}{4} = 0.75$   
2 - 0.75 = 1.25 (Always subtract from two)  
 $O$   
 $SO_4$   $\bigcap_{O=O^{-}O^{-}}^{O} = \frac{6}{4} = 1.5$  Bond order  
or  
 $SO_4^{-2}$   
4 Charge on oxygen  $= \frac{2}{4} = 0.5$   
Bond order = 2 - 0.5 = 1.5  
 $CO_2 \rightarrow O = C = O = \frac{4}{2} = 2$  Bond order  
 $CO_3^{-2} = \frac{2}{3} = 0.66 = 2 - 0.66 = 1.33$   
 $NO_3^{-} = \frac{1}{3} = 0.33 = 2 - 0.33 = 1.66$ 

 $C_6H_6$  = lies between 1 and 2.

#### MOT – Given by Hund and Mullican.

- Molecular orbitals are formed when two molecular orbitals interact with each other.
- One orbital is called bonding orbital and the other orbital is called restricting orbital.
- The energy of the restriction orbital is high because of the repulsive force.
- Restricting orbitals are denoted by an asterisk (\*).



- While filling electrons in molecular orbitals, Aufbau Hundt obeys Pauli's law.
- Order of energy  $\rightarrow$  atomic number 7 or less  $\sigma 1S < \sigma^* 1S < \sigma 2S < \sigma^* 2S < \pi 2Px = \pi 2Py < \sigma 2Pz < \pi gPx$  $= \pi^* 2Py < \sigma^* 2Pz$
- More than seven (7) &

$$\sigma$$
1S <  $\sigma$ \*1S <  $\sigma$ 2S <  $\sigma$ \*2S <  $\sigma$ 2P<sub>2</sub> <  $\pi$ 2Px =  $\pi$ 2Py same  
Bond order =  $\frac{Nb - Na}{m}$ 

2Bond order  $\propto$  Bond energy, Stability/Bond length

Question - Find the pictorial bond order of oxygen molecule. Sol. -





$$BF_{3} = BCI_{3} = BBr_{3}$$
$$| \qquad | \qquad |$$
$$SP^{2} SP^{2} SP^{2}$$

But no lone pairs are present so look at the bond angle hybridization.

H-Cl does not have a bond angle.

Question.	Explain the difference between $\sigma$ bond and $\pi$ -bond.
C - I	





- With the stronger ligand the splitting energy is greater than the coupling energy, hence the coupling is formed.
- In octahedral complexes, the ligand approaches the metal along the axis, which increases the energy of the valence orbitals and decreases that of t<sub>2</sub>g. This is called crystal field splitting. If the ligand is strong then the splitting energy is more. Weak ligand has less splitting energy.

#### Weak ligand orbital representation?

In weak dentin the splitting energy is less than the coupling energy. Hence do not pair.

Splitting in the class planar - orbital depiction

#### Fission in tetrahedral - Orbital depiction?

Stability of complex compounds -

The stability of complex compounds depends on the following factors.

(i) Stability × Merger construction When poly ligand joins with the metal atom, a ring is

formed, which decreases the energy and increases the stability.

 $[Zn(EDTA)] > [CO(en)_3]^{+3} > [CO(NH_3)_6]^{+3}$ 

(ii) Stronger ligand forms more stable complex compounds.

 $Ni(CO)4 > [Ni(CN)_4]^{-2}$  $[Ni(NO_2)_6]^{+2} > [Ni(NH_3)]^{+2} > [Ni(H_2O)_6]^{+2}$ 

NO<sub>2</sub> absorbs the shortest wavelength, because NO<sub>2</sub> is a strong ligand, so the splitting energy will be high. Splitting will do more.

(iii) Stability × Charge on metals Metal size

 $Cu^{+2} < Zn^{+2} < Ni^{+2} < CO^{+2}$ 

Increasing order of stability

#### Uses

- Cis-platinum is used in cancer medicine.
- Mg<sup>+2</sup> Chlorophyll, CO<sup>+</sup> Vitamin B<sub>12</sub>
- $Fe^{+2}$  in blood (in 1 + b)
- Ni<sup>+2</sup> gives red pleasant color with DMG which is used in splash estimation.
- Rectification of splash is done by Mond method.

Ni + 4 CO  $\rightarrow$  Ni (C<sub>6</sub>)<sub>4</sub>  $\xrightarrow{\Delta}$  Ni + 4 (c) (g)

- Lead (Pb) is removed from the body with EDTA.
- EDTA is used to measure the hardness of water.
- Na Nitro prusside gives violet color with sulphur. \_ Na₂S -

$$Na[Fe(CN)_5 NO] \longrightarrow Na_4[Fe(CN)_5 NOS]$$

N – A deep blue color is formed in the test.  $Fe_4 [Fe(CN)_6]_3 - blue$ 

#### In Ring test [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>+2</sup>

#### **IUPAC** nomenclature of complex compounds

Class & 12 Chemistry &I Page - 258

A [metal ligands g)<sub>x</sub> (ligand Gg)<sub>y</sub>] B

 $[A + x \text{ ligand} + y \text{ ligand} + \text{metal} (Oxidation number}) + B]$ 

of alphabets

- If proclats (negative ligands) are present then they bond with the metal atom.
- The name of the negative ligand ends with "O" and the name of the positive one ends with 'lyam'. The neutral ligand does not have a specific name.

H⁻	-	Hydrydo
CN⁻	-	Cyano
OH⁻	-	Hydro oxo
$C_2O_4^{-2}$	-	Oxalato
NO <sub>2</sub> <sup>-</sup>	-	Nitrito (-N-)
0 – N = O	-	Nitrito (-O-)
$S_2O_3^{-2}$	-	Thio sulfato
S <sup>-2</sup>	-	Sulphido
SO <sub>4</sub> <sup>-2</sup>	-	Sulphato
$CO_3^{-2}$	-	Carbonato

Carbonato COO

```
NH<sub>2</sub>
CO - Carbonyl
```

```
NO – Nitrocyl
NH<sub>3</sub> - Amine
```

en – Ethelene Diamine

Py – Pyridine NO<sup>+</sup> - Nitrosonium

If organic dent is present -

2 Bis

3 Tris

4 Tetra

LiAlH<sub>4</sub>

 $K_4[Fe(CN)_6]$ 

 $[Fe(CN)_{6}]^{-3}$ 

- 5 Penta
- Potassium hexa cyano ferrate (II)
- Hexa cyano ferrate (III)
- K<sub>2</sub> [Ni<sup>+2</sup> (CN)<sub>4</sub> - Potassium tetra cyano nickelate (111)

glysoleto

- Lithium tetra hydro aluminate

Iron (III) hexa cyanoferrate (II) Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>

(Persian blue)  $[CO(Cx)_3]^{-3}$ Tri oxalate cobalt (III)

```
[CO(NH<sub>3</sub>)<sub>6</sub>]
                          - Hexa amine cobalt (II) chloride
```

```
[Ni (H_2O)_6]^{+2}

    Hexa aqua Nickel (II)
```

```
[Ni(NH<sub>3</sub>)<sub>4</sub>] [Ni(C)<sub>4</sub>] – Tetra amine nickel (II) tetra chloro
nickelate (II)
```



 $(NH_{3})_{4} CO] \qquad [CO(NH_{3})_{4}] (SO_{4})_{2} (Bridge packages)$   $NH_{2}$ 

Octa amine amide hydroxy dicobalt (III) sulfate  $[Ag(CH_3NH_2)_2]^+$  - Bis methyl amine silver (I) ion  $[Ni(CO)_4]$  – Tetracarbonyl nickel (O)  $[Ag(NH_3)_2]OH$  – Diamine Silver (I) hydroxide (Tollens reagent)





### рΗ

- The pH scale is a measurement scale used to measure the acidity or alkalinity of a solution.
- In the year 1909, a scientist named Sorenson gave the concept of pH scale.
- In pH, P refers to porwer and H refers to the concentration of hydrogen.
- The range of value of pH scale is 0 to 14.
- Solutions with a value less than 7 are acidic while solutions with a value greater than 7 are basic in nature.
- The pH scale was invented by SPL Sorensen in the year 1909.

рН	Nature of Solution
0 - 3.5	Strong acid
Between 3.5 and 7	Weak acid
7	Neutral solution
More than 7 and	Weak base
less than 10.5	
10.5 or higher	Strong base

#### pH Value of Important Solutions

Substance	pH Value
Concentrated hydrochloric acid	0
Dilute hydrochloric acid	1
Gastric juice	1.5
(This is also dilute hydrochloric	LX
acid.)	
Lemon juice	2.5
Liquor	3.5
Vinegar	4.0
Beer	4.5
Coffee	5
Cold Drinks	5.5
Milk	6.5
Distilled water	7
Saliva (before eating)	7.4
Saliva (after eating)	6
Blood	7.4
Egg	7.7
Human urine	6
Toothpaste	8
Baking soda	8.5
Washing soda	9
Concentrated sodium hydroxide	14

#### Importance of pH in Daily Life

- The pH range of biochemical activities occurring in our body ranges from 7 to 7.8 only. Even a slight change in it has a very fatal effect on our body.
- The pH value of water in acid rain is less than 5.6. As a result of this water, the pH value of the rivers also decreases, which has a harmful effect on the aquatic organisms.
- The pH value of fertile soil is also in a certain range which is neither more acidic nor more alkaline.
- Various types of spicy food increase the acidity of the stomach, due to which there is acidity and gas problem. Milk of magnesia which is alkaline in nature is used to remove it.
- Bee sting contains methanoic acid which is acidic in nature and causes burning sensation, alkaline nature baking soda is used to calm it down.
- Tooth enamel is made of calcium sulphate which is the hardest substance in our body. If the teeth are not cleaned, decaying bacteria produce acids that lower the pH of oral saliva below 5.5 and damage the enamel.

#### **Buffer Solution**

A solution that absorbs modest amounts of an acid or base without appreciable change in its effective acidity or basicity is called a buffer solution.

For example, a mixture of sodium acetate and acetic acid is an effective buffer solution.

• A solution whose pH value does not change significantly by adding a small amount of acid or base is called buffer solution or resistance solution.

#### These are mainly of two types

- 1. Acidic buffer The mixture of salts formed with weak acid and strong base is called acidic buffer.
- 2. Alkaline buffer The mixture of salts made with weak base and strong acid is called alkaline buffer.

Example - NH<sub>4</sub>OH + NH<sub>4</sub>Cl is an alkaline buffer.

#### **Applications of Buffer Solutions**

- 1. To study the rate of chemical reactions and to keep the pH value stable.
- 2. In the preparation of culture in the laboratory of biology.
- 3. In the production of alcohol by fermentation of molasses (maintaining pH 5 to 6.5).
- 4. In maintaining proper pH in leather cooking and in the manufacture of sugar, paper etc.
- 5. Various biochemical activities of physiological physiology are completed in the medium of certain pH value.



#### **Properties of Buffer Solution**

- 1. The pH value remains constant.
- 2. The pH value does not change when left open in the atmosphere.
- 3. Even after diluting the solution, there is no change in the pH value.
- 4. No change takes place even if a small amount of strong acid or strong base is added to the solution.
  - Vitamin C is also known as ascorbic acid.
  - When the soil becomes acidic, slaked lime or quick lime is mixed in it to reduce the acidity of Ca (calcium) and Mg (magnesium).
  - Phenol is also known as carbolic acid. It is a white crystalline compound which is poisonous. It is used in making plastics and medicines.

- On burning magnesium, it reacts with the oxygen present in the air to form magnesium oxide, which is called ash.
- Zeolite is a crystalline solid structure, which is made of silicon, aluminum and oxygen.
- Hydrochloric acid is also known as muriatic acid.
- Plaster of Paris is made by dehydrating gypsum salt.

2 CaSO<sub>4</sub>.  $2H_2O \rightarrow 2$  CaSO<sub>4</sub>  $H_2O + 3H_2O$ 

(Gypsum) Plaster of Paris (POP)

opporsholes Unleash the topper in you



## Thermodynamics

#### (NCERT Class – 11 Page – 315)

If two objects are kept in contact with each other, then they exchange heat, considering this fact as the basis, some laws of thermodynamics are given.

### Zeroth's Law

• If two bodies are in different thermal equilibrium with a third body, then they will be in thermal equilibrium with each other, given by R.H. Fowler in 1931.

 $T_A = T_B$  (will not exchange heat)



Thermal Equilibrium

**Note** - The value of thermodynamic reference temperature remains the same in thermal equilibrium.

#### **First Law of Thermodynamics**

- Heat change cannot be shown in the law of zero, so we need the first law.
- The heat given to a system is spent in the work done by the system and its internal energy.
   dQ = dw + dv

dQ = dw + dv ↓ ↓ ↓ Heat Work Internal Energy

Work - dw =  $pdv = p(V_2 - V_1)$ 

- Here the change of heat was shown but no determination of direction was made.
- 1. Isothermal Proces
  - dT = 0
  - du = 0
  - dQ = dw + du

dQ = dw (same temperature at all points) Here the entire heat supplied is converted into work.

(T = Constant)

#### 2. Isovolumetric Process

- The entire heat given here is spent in internal energy, that is, the temperature increases here.
- **3.** Adiabatic Process A process in which there is no exchange of heat is called adiabatic process.



- **4. Cyclic Process** When a system passes through different stages and comes to its initial state, then such a process is called a cyclic process.
  - du = 0
  - dQ = dw + dU
  - dQ = dw the initial and final temperature will be same.
- **5.** Free Diffusion If the gas circulates in the zeropressure region without heat exchange, then such process is called free diffusion.
  - dQ = o P = o dw = pdU = o  $dv \neq o$
  - dQ = dU + dw
  - dU = o
- The value of pressure remains the same for every reaction taking place in the open environment, hence the process is isobaric.
- For isobaric process the work done is maximum whereas for isovolumetric process the work done is minimum i.e., zero.

#### State Curve



# Q.1 All the processes which occur suddenly are called exothermic processes.

**For example** - Bursting of tire tube, formation of glass, compression rarefaction of gases, action in refrigerator.

- Isothermal processes take place slowly, hence a conductive vessel is necessary for it, while adiabatic processes take place rapidly, hence a non-conducting vessel is necessary for it.
- Conversion of 0°C ice into water and 100°C water into steam is an isothermal process.
- Only in free expansion the volume changes but still the work done is zero. (Due to zero pressure area).
- If a fan is switched on in a closed room, the temperature of the room increases.
- If a cup of tea having a temperature of 40°C is sealed in a tea kettle and the kettle is shaken vigorously, its temperature will exceed 40°C.



- If the fridge is left open in an open room, its temperature will remain unchanged.
- If a non-conducting object is covered with a red colored cloth, the amount of heat emitted from it decreases.
- The first law of thermodynamics does not determine the direction, that is why we need the second law.

Question - During adiabatic process, the pressure of a gas is proportional to the third power of its

absolute temperature, what will be the value

of  $C_P/C_V$  i.e.,  $\gamma$  for the gas.  $P \propto T^3 \Rightarrow PT^{-3} \propto 1$  or  $PT^{-3}$  Constant  $P^{1-\gamma}T\gamma = Constant$  $\lambda - v = 1 = \gamma = 0$ 

γ = -**3** 

In thermodynamics, the specific heat capacity of a substance can be defined by the following formula.

$$S = \frac{1}{m} \quad \frac{dQ}{dt}$$

Here m is the mass of the substance and dQ is the heat by which the temperature of the substance increases by dT. Spherical specific heat capacity of the substance -

$$C = \frac{1}{\mu} \frac{dQ}{dt} (\mu \text{ No. of moles of substance})$$

For an ideal gas, the spherical specific heat capacities at constant volume and constant pressure obey the following relation.

 $C_P - C_V = R$ 

 $R\,$  is the universal constant of the gas.

### Second law of thermodynamics

 The second law of thermodynamics does not allow certain processes which are compatible with the first law of thermodynamics. Its two statements are as follows.

**Statement of Kelvin Planck** - Such a process is also possible. Whose only result is to absorb heat from some heat reservoir and convert it completely into work?

**Statement of Clausius** - No such process is possible whose only result is the transfer of heat from a colder body to a warmer body.

That is, the second law of thermodynamics states that the efficiency ( $\eta$ ) of any heat engine cannot be 1 or the coefficient of performance ( $\infty$ ) of a refrigerator cannot be equal to infinity.

#### **Heat engine**

- A device in which a system undergoes a cyclic process that results in the conversion of heat into work.
- If the heat absorbed in the cycle is Q1, and the heat released to the inlet is Q2 and the output work is W, then the efficiency of the heat engine is

$$(\eta) = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

The coefficient of performance of the recirculator in a refrigerating or heat pump

$$(\infty) \propto = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

#### **Carnot Engine**

#### (Page - 328; Class – 11 NCERT)

- In a Carnot engine, heat flows from high temperature to low temperature.
- The work done in a Carnot engine is equal to the heat source and sink.
- Carnot engine is a reversible engine.
- The efficiency of a Carnot engine does not depend on the working substance.
- The efficiency of a Carnot engine depends on the temperatures of the source and the sink.

Efficiency = 
$$\frac{\text{Work done}}{\text{Heat Supplied}}$$

$$n = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$n = \left(1 - \frac{Q_2}{Q_1}\right)$$

$$n = 1 - \frac{T_2}{T_1} \times 100\%$$
If T<sub>2</sub> = 0 K then
$$n = \left(1 - \frac{0}{T_1}\right) \times 100\%$$

If 
$$T_2 = \infty$$
 then  

$$n = \left(1 - \frac{T_2}{100}\right) \times 100\%$$

$$n = \infty$$
If T<sub>2</sub>=T<sub>1</sub> then
$$n = \left(1 - \frac{T_1}{T_2}\right) \times 100\%$$