

# THEORIES OF COVALENT BOND AND

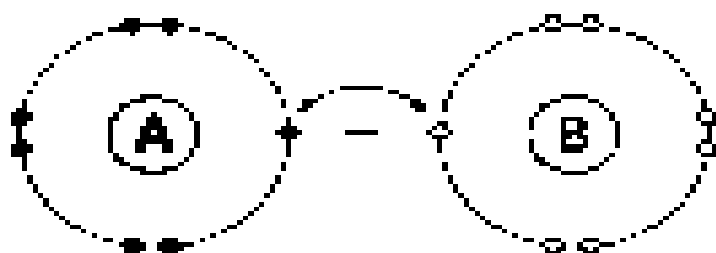
## SHAPES OF MOLECULES:

CHAPTER NO.

03

### Covalent Bond

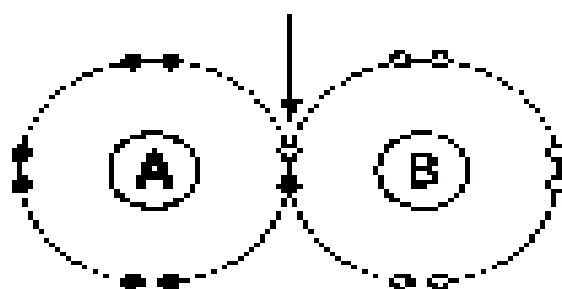
Unpaired  
valence electrons



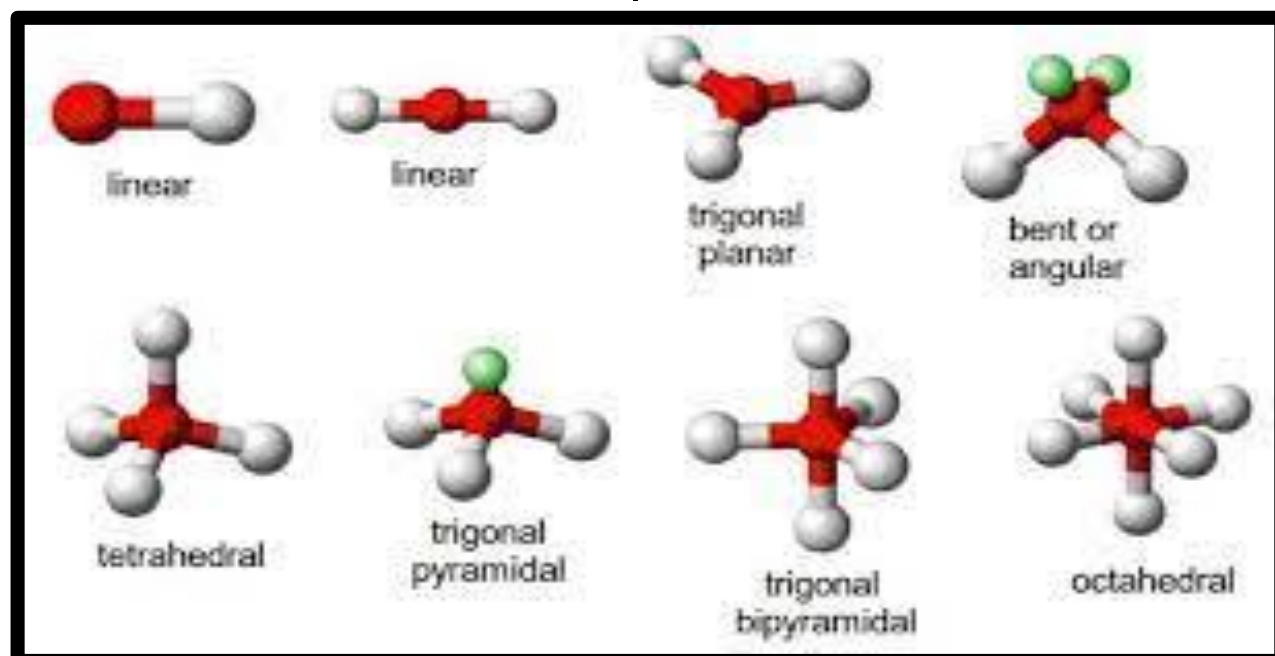
Atom 1  
(nonmetal)

Atom 2  
(nonmetal or  
metalloid)

Sharing of available  
valence electrons



Covalent molecule



**PROF: ZUBAIR AHMED SHAIKH**  
**THEORIES OF COVALENT BOND AND SHAPES OF MOLECULES:**

**MOLECULAR GEOMETRY**

**DEFINITION:** The arrangement of atoms around a central atom is called molecular geometry.

**Central Atom:** An atom that is bonded with two more than two atom is called central atom.

**Bond Angle:** The angle between the two bonds or between three bonded atoms is called bond angle.

**Bond length:** The distance between two bonded atoms is called bond length.

**OVERLAPPING**

**Definition:** the term overlapping means the sharing of common region in space between two bonded orbitals.

**TYPE OF OVERLAPPING**

There are two types of overlapping

1. Linear Overlapping
2. Parallel Overlapping.

**1. LINEAR OVERLAPPING OR  $\sigma$  BOND (SIGMA BOND):**

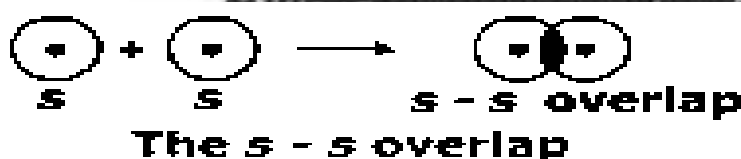
The overlapping of atomic orbitals in same straight line is called as linear overlapping. In this overlapping, two atomic orbital lose their own identities and form two new molecular orbitals. The molecular orbital with high electron density at center is called as bonding molecular orbital and it produces sigma bond ( $\sigma$ -bond) whereas the molecular orbitals having maximum density at sides is called as anti-bonding molecular orbital and produces sigma star and ( $\sigma^*$ -bond)

The example of linear overlapping is following

- i. s - s overlapping
- ii. s -  $P_x$  overlapping
- iii.  $P_x$  -  $P_x$  overlapping

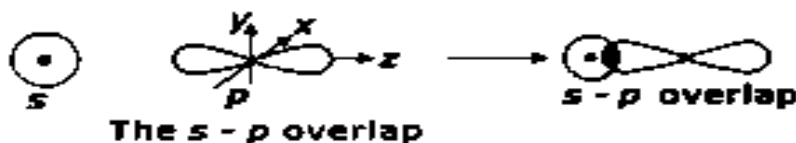
**1. S - S OVERLAPPING.**

The example of s - s overlapping  $H_2$  molecules is



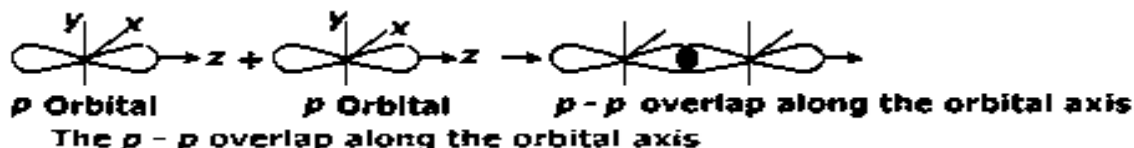
**II. S -  $P_x$  OVERLAPPING**

The examples of this overlapping are  $H$ ,  $HCl$ ,  $HBr$ .



**III.  $P_x$  -  $P_x$  OVERLAPPING**

The examples of this overlapping are  $Cl_2$ ,  $F_2$ ,  $Br_2$  etc.



## **2. PARALLEL OVERLAPPING**

The lateral overlapping of p-orbitals is called as parallel overlapping. In this types of overlapping the bonding - molecular orbital produces pi - bond ( $\pi$  - bond) and Anti-bonding molecular orbital produces pi - star bond ( $\pi^*$  - bond). This types of overlapping is taking place above and below, the inter nuclear axis. Pi ( $\pi$ ) bond is always formed between two atom, which are already linked with  $\sigma$ -bond.

The examples are.

1.  $P_y - P_y$  overlapping
2.  $P_z - P_z$  overlapping

The example of this type of overlapping is  $N_2$  molecule i.e.  $p_x$ ,  $p_y$  and  $p_z$

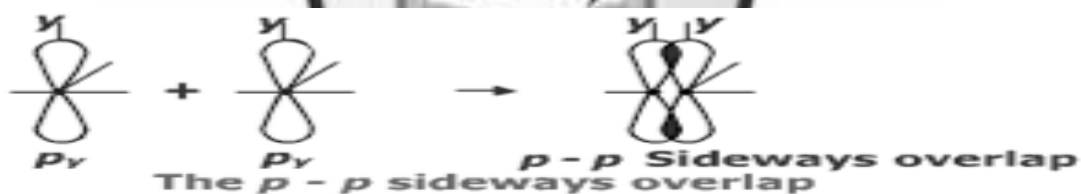
(i.e  $N = 7 = 1s^2, 2s^2, 2p_x^1, 2p_z^1$ )

$P_x$  of one nitrogen overlap with  $p_x$  of an other nitrogen is same straight line and form  $\sigma$ -bond, Whereas  $p_y$  and  $p_z$  of one nitrogen overlap with  $p_y$  and  $p_z$  of second nitrogen in parallel fashion to form two pi ( $\pi$ ) bonds.

### **SIGMA - BOND ( $\sigma$ BOND)**

#### **DEFINITION:**

The covalent bond is formed by linear overlapping of two atomic orbitals of two atoms is called as sigma bond.



#### **FORMATION:**

In this type of overlapping the resulting molecular orbitals are  $\sigma$  bonding molecular orbitals and  $\sigma^*$  - anti bonding molecular orbitals

#### **EXAMPLES:**

- i.  $s - s$  overlapping
- ii.  $s - p$  overlapping
- iii.  $p_x - p_x$  overlapping

#### **SIGMA BOND BY $s - s$ OVERLAPPING:**

The example of this type is  $H_2$  molecule in which  $1s$  atomic orbitals of one hydrogen overlaps with  $1s$  atomic orbital of other hydrogen and form  $\sigma$  or  $\sigma$ -bond.



### PROPERTIES OF $\sigma$ - BOND:

- i. It is strong bond.
- ii. The strength of sigma bond depends upon the extent of overlapping.
- iii. It is formed by linear overlapping.
- iv. Overlapping is taking place between two nuclei.
- v. Examples are  $H_2$ ,  $Hf$ ,  $HCl$ ,  $H_2O$  etc

### PI BOND ( $\pi$ - BOND)

#### DEFINITION:

A covalent bond which is formed between two atoms by side to side or parallel overlapping is called as pi-bond.

#### FORMATION:

In parallel overlapping the upper Lobes of two p-orbital, overlap above and lower lobes of p-orbitals overlap below the inter nuclear axis. Here the resulting molecular orbital are called as  $\pi$  bonding molecular orbital and  $\pi$  anti bonding molecular orbital.

**EXAMPLES:** The examples of  $\pi$  - bond are

1.  $P_y - P_y$
2.  $P_z - P_z$

#### $\pi$ - BOND BY $P_z - P_z$ OVERLAPPING.

Pi - bond is formed in  $O_2$  molecule. Oxygen atom has two half-filled atomic orbitals ( $O=8=1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$ )  $2p_y$  of atomic orbital of one oxygen will overlap with  $2p_y$  atomic orbital of one oxygen overlaps with  $2p_z$  atomic orbital of second oxygen in parallel fashion to form  $\pi$  bond. Therefore a molecule of oxygen has a double bond, out of them one is  $\sigma$  bond and other  $\pi$  bond.

$2p_x + 2p_x$  of Oxygen atom of oxygen atom  $\longrightarrow$   $2p_x + 2p_x$  and oxygen molecule  
 $2p_y + 2p_y$  overlapping

#### PROPERTIES OF $\pi$ - BOND.

1. It is weak bond.
2. The strength of  $\pi$  - bond depends upon the extent of overlapping.
3. It is formed by parallel overlapping.
4. Overlapping is taken place above and below the plane of nuclei.
5. The probability of finding the electron is maximum above or below the plane of nuclei.
6. Examples are  $O_2$ ,  $N_2$ ,  $C_2H_4$ ,  $C_2H_2$ , etc.

### THEORIES FOR THE COVALENT BONDING

There are various theories for the covalent bonding.

1. Lewis Theory
2. Valence bond theory (V.B.T)
3. Molecular orbital theory (M.O.T)
4. VSEPR theory (valence shell electron pair repulsion theory)

1) **LEWIS THEORY:** According to Lewis theory

The covalent bond is formed by sharing of electrons.

This theory fails to describe the strength of bond, geometry of compound as well as magnetic properties of molecules. These defects are removed by valence band theory and molecular orbital theory.

## **2) VALENCE BOND THEORY (VBT)**

**Introduction:** Heitler and London extended the Lewis theory in 1927 and proposed valence Bond Theory (VBT). This theory tells us about the bonding in covalent molecule with overlapping of atomic orbitals. It provides the basic information about

- Analyzing the structure and the bonding in molecule
- Strength of covalent bond
- Molecular shape on the basis of atomic orbital interaction.

**Postulates:** the main postulates of this theory are given below

1. Bond is formed due to overlapping of partially filled orbitals.
2. Overlapping orbitals have electron with opposite spin.
3. The strength of bond depends upon the extent of overlapping. Greater overlapping means greater strength.
4. After overlapping there is a maximum electron cloud somewhere between the two overlapped orbitals.
5. Valence bond theory suggests that the bonding electrons occupy the atomic orbitals of the bonded atoms.

### **LIMITATION:**

- It fails to describe the delocalization of electrons in the molecules
- It fails to describe the valencies in carbon, boron and beryllium and does not tell the paramagnetic behavior of oxygen.

## **3) MOLECULAR ORBITAL THEORY**

**Introduction** In the early 1930's Hückle, Mulliken developed molecular orbital theory.

### **Postulates**

- A covalent bond is formed by overlapping of atomic orbitals.
- It assumes that electrons occupy the molecular orbitals after overlapping.
- Molecular orbitals are classified as bonding molecular orbital and antibonding molecular orbital

**(a) BONDING MOLECULAR ORBITAL:** The molecular orbital of low energy in which electron density is maximum in between bonded nuclei is called bonding molecular orbital. The electrons of bonding molecular orbital can form covalent bond

**For example:** Sigma orbital and pi orbital

**(b) ANTI BONDING MOLECULAR ORBITAL:** The molecular orbital of high energy that moves the electron density away from center of bonded nuclei is called antibonding molecular orbital. Electrons which belong to these orbitals cannot form bonds.

- Electrons occupy the molecular orbitals in following order:

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_x, \pi 2p_y = \pi 2p_z, \pi^* 2p_y = \pi^* 2p_z, \sigma^* 2p_x$$

- The number of bonds formed between two atoms after the atomic orbitals overlap, is called the BOND ORDER.

## **4) VALENCE SHELL ELECTRON PAIR THEORY**

**Introduction** The theory was presented by Sidgwick and Powell in 1940.

### **Postulates**

- The shapes of molecules can be determined by the repulsion between the active set of electron pairs present around the central atom of the molecules.

- Electron pairs which can form geometry of molecules are called active set of electron pairs.

1. Sigma bond pair, 2. Lone pair or non bonding electron pair.


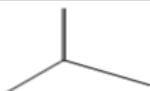
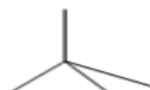


- Electrons which play no role in formation of geometry in molecule are called NON ACTIVE SET OF ELECTRON PAIRS. Pi bond pair,

- The order of repulsion between lone pairs and bond pairs is given below



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- Lone pair - Lone pair repulsion > Lone pair - Bond pair repulsion > Bond pair - Bond pair repulsion.
- In a shape of molecules depends upon total number of active set of electron pairs around central atom in a molecule.

Number of active set of electron pairs around central atom	Structure	Geometry of Molecules	Bond Angle	Example
2	Linear		$180^\circ$	$\text{BeCl}_2$ ; $\text{C}_2\text{H}_2$ ; $\text{CO}_2$ ; $\text{CS}_2$
3	Planar Trigonal		$120^\circ$	$\text{BF}_3$ ; $\text{C}_2\text{H}_4$ ; $\text{SO}_2$ ; $\text{CO}_3^{2-}$ ; $\text{BCl}_3$
4	Tetrahedral		$109^\circ$	$\text{CH}_4$ ; $\text{CCl}_4$ ; $\text{CBr}_4$ ; $\text{C}_2\text{H}_6$
4 (One lone pair of electron)	Pyramidal		$107^\circ$	$\text{NH}_3$ ;
4 (Two lone pair of electron)	Angular, Bent, Non linear		$104.5^\circ$	$\text{H}_2\text{O}$

### HYBRIDIZATION:

**INTRODUCTION:** According to this process covalent bond is formed by the overlapping of hybrid orbitals and atomic orbitals. This process was introduced by linus pauling.

#### **DEFINITION:**

The mixing of atomic orbitals of different shapes and energies to form hybrid orbitals (mixed orbitals) of same shape and energy is called as hybridization.

#### **TYPES OF HYBRIDIZATION**

There are three types of hybridization.

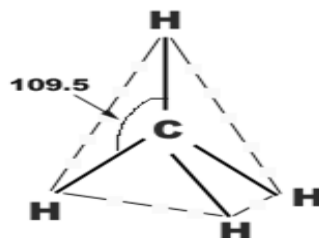
1.  $\text{Sp}^3$  hybridization
2.  $\text{Sp}^2$  hybridization
3.  $\text{Sp}$  hybridization

#### **1. $\text{Sp}^3$ HYBRIDIZATION**

In this type of hybridization the excited carbon mixes its four atomic orbital (i.e. s, px, py and pz) and four  $\text{Sp}^3$  hybrid orbitals.

$$\text{C} = 6 = 1s^2 2s^1 2p_x^1, 2p_z^1 = 4 \text{ Sp}^3 \quad \text{Four Hybrid orbital}$$

Each hybrid orbital contain one part of the properties of "s" and three part of the properties of "P". Therefore each hybrid orbital is called as  $\text{sp}^3$  hybrid orbital. Hence this process is called as  $\text{Sp}^3$  hybridization. These four  $\text{Sp}^3$  hybrids orbital are arranged in tetrahedral fashion with an angle of  $109^\circ$  as shown in figure.

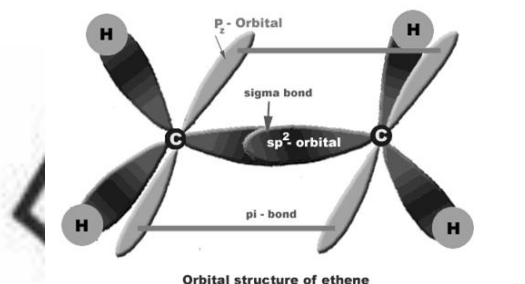


Shape of  $sp^3$  - hybridized carbon atom

This type of hybridization is taking place in alkanes i.e. methane ( $CH_4$ ) ethane ( $C_2H_6$ ) propane ( $C_3H_8$ ) etc.

## 2. $sp^2$ HYBRIDIZATION

In this type of hybridization the excited carbon mixes its three atomic orbitals ( $2s$ ,  $2p_x$ ,  $2p_y$ ) and forms three  $sp^2$  hybrid orbitals where as  $p_z$  remains same. These three hybrid orbitals are arranged in trigonal fashion with an angle  $120^\circ$  whereas  $p_z$  lie at right angles to the plain of  $sp^2$  hybrid orbitals as shown in figure.



Shape of  $sp^2$  hybridized -e- atom.

Each hybrid orbital contains one part of the properties of "s" and two parts of the properties of "p" hence called as " $sp^2$ " hybrid orbital. Thus this process is called as  $sp^2$  hybridization. This type of hybridization is taking place in unsaturated compound containing double bonds just like Ethene ( $C_2H_4$ ), propene ( $C_3H_6$ ), Butene ( $C_4H_8$ ) Pentene ( $C_5H_{10}$ ) etc. The structure of ethene  $C_2H_4$  is given below.

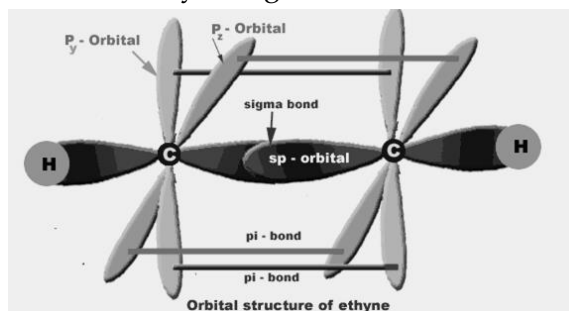
## 3. $sp$ HYBRIDIZATION

In this type of hybridization two atomic orbitals of excited carbon ( $2s$ ,  $2p_x$ ) are mixed, whereas  $p_y$  and  $p_z$  remain as such. These hybrid orbitals are collinear at an angle of  $180^\circ$  while two pure atomic orbitals  $p_y$  and  $p_z$  lie at right angles to the plane of hybridized carbon atom as shown in figure.

**SHAPE OF  $sp$  - HYBRIDIZED ATOM.**

Each hybrid contains one part of the properties of s and one part of the properties of p hence called as  $sp$  hybrid orbital and process is called as  $sp$  hybridization.

This type of hybridization is taking place in alkynes (unsaturated compounds containing triple bonds) just like ethyne ( $C_2H_2$ ) the structure of ethyne is given below.



### **SHAPE OF THE FOLLOWING MOLECULE ON THE BASIS OF HYBRIDIZATION**

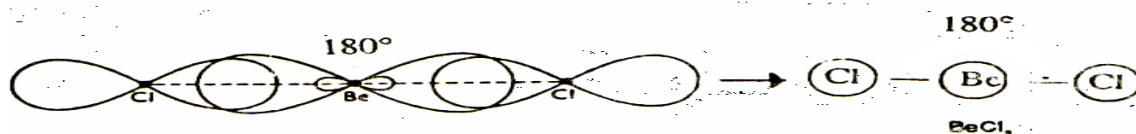
#### **(i) SHAPE OF $BeCl_2$**

In terms of hybridization, Be has  $sp$  hybridization in  $BeCl_2$ .

Be =  $1s^2, 2s^2$  (ground state)

Be =  $1s^2, 2s^2, 2p_x^1$  (excited state)

2s and 2p orbitals of beryllium are hybridized to give two new equivalent orbitals. These new orbitals are referred to as sp hybrid orbitals. The sp orbitals are identical (same energy and shape) and are arranged at an angle of  $180^\circ$  from each other.



These two hybrid orbitals overlap with 3p<sub>z</sub> orbitals of Cl atom to give two sigma bonds.

Thus according to hybridization BeCl<sub>2</sub> has linear structure.

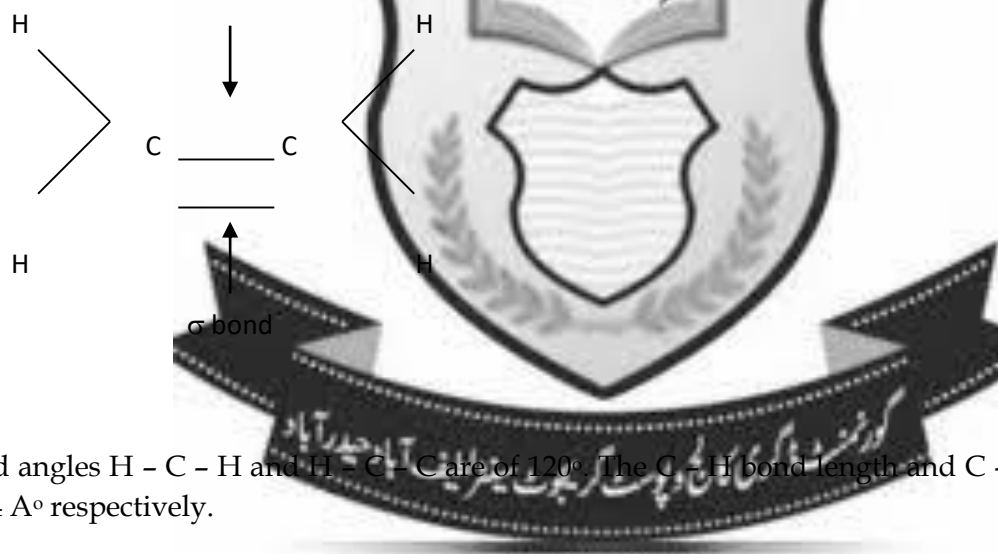
### **(ii) SHAPE OF C<sub>2</sub>H<sub>4</sub>**

In ethene molecule each "C" atom possesses three SP<sup>2</sup>-hybrid orbitals and one P<sub>z</sub> orbital.

Two SP<sup>2</sup> hybrid orbitals are used in forming sigma bonds with 1s orbitals of hydrogen atoms.

One sigma bond is formed between two carbon atoms by using their SP<sup>2</sup> orbitals. The P<sub>z</sub> orbitals of both Carbon atoms undergo parallel overlapping and form a pi-bond. The resulting structure of ethene is planar.

All bond angles H - C - H and H - C - C are equal to  $120^\circ$ . The C - H bond length and C - C bond length is 1.09 Å and 1.34 Å respectively.



All bond angles H - C - H and H - C - C are of  $120^\circ$ . The C - H bond length and C - C bond length is 1.09 Å and 1.34 Å respectively.

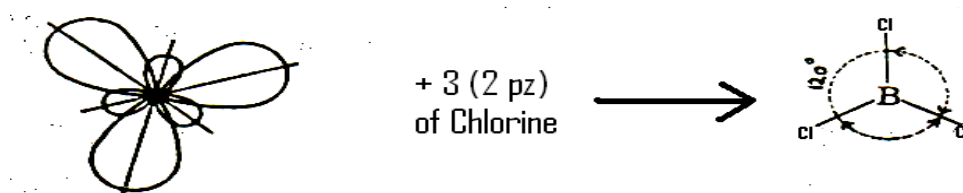
### **(iii) SHAPE OF BCl<sub>3</sub>**

In terms of hybridization, boron has sp<sup>2</sup> hybridization in BCl<sub>3</sub>.

B =  $1s^2, 2s^2, 2p_x^1$  (Ground state)

B =  $1s^2, 2s^1, 2p_x^1, 2p_y^1$  (Excited state)

SP<sup>2</sup> Orbitals of B





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One 2s and two 2p<sub>x</sub> and 2p<sub>y</sub> orbitals hybridize to form three sp<sup>2</sup> hybrid orbitals. These orbitals are co-planar and directed towards the corners of an equivalent triangle (trigonal) at an angle of 120° to each other.

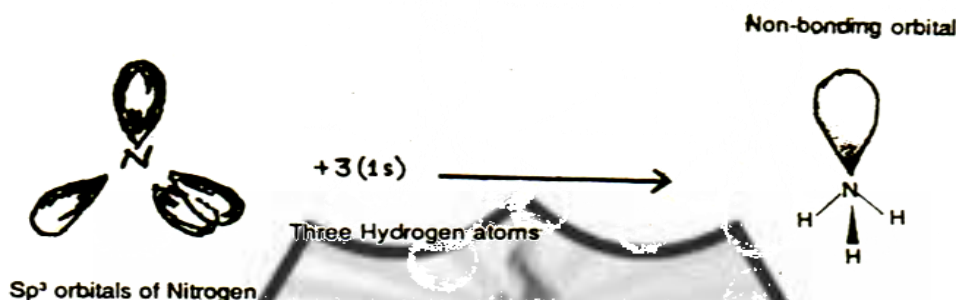
These three sp<sup>2</sup> hybrid orbitals overlap with 3p<sub>z</sub> orbitals of chlorine atoms and forms three sigma bonds.

Thus according to hybridization BCl<sub>3</sub> has trigonal structure.

### (iv) SHAPE OF NH<sub>3</sub>

In terms of hybridization, N in NH<sub>3</sub> is sp<sup>3</sup> hybridized

The 2s<sup>2</sup>, 2p<sub>x</sub><sup>1</sup>, 2p<sub>y</sub><sup>1</sup> and 2p<sub>z</sub><sup>1</sup> orbitals hybridized to give four sp<sup>3</sup> hybrid orbitals.



The three sp<sup>3</sup> hybrid orbitals overlap with 1s orbital of three H - atoms to give three sigma bonds.

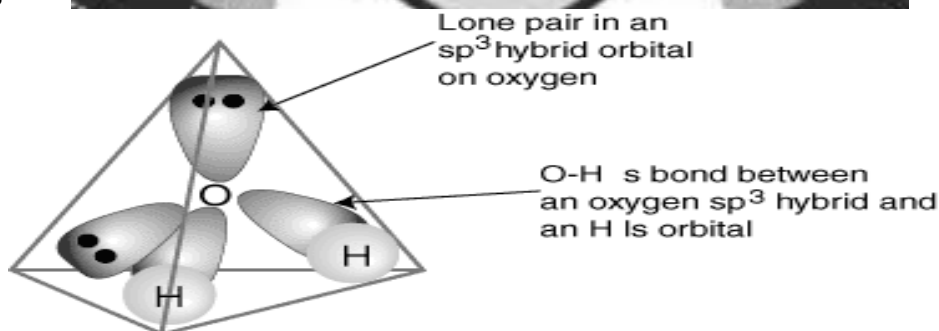
The electrons in the non - bonding sp<sup>3</sup> orbitals is associated with only one nucleus, and hence they are not hold as tightly as the electrons in the bonding orbitals. consequently the non - bonding orbital occupies large volume of space and compresses the bonding orbitals due to which bond angle in the NH<sub>3</sub> reduces to 107°.

### SHAPE OF H<sub>2</sub>O:

In water molecule oxygen atom contain four SP<sup>3</sup> hybrid orbitals. Two SP<sup>3</sup> orbitals are half filled and two are completely filled with electrons.

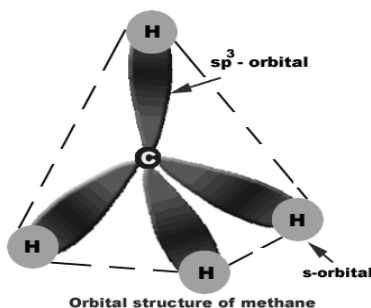
Two half filled SP<sup>3</sup> orbitals are utilized in forming sigma bonds with 1s orbitals of hydrogen atoms. These four SP<sup>3</sup> orbitals arrange themselves in four corners therefore structure of water is tetrahedral or angular.

The non bonding electron pairs in SP<sup>3</sup> orbitals cover large volume and compresses the bonding orbitals due to which bond angle in water reduces to 104.5°.



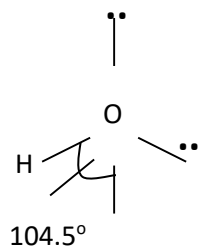
### SHAPE OF METHANE:

In methane carbon contain four SP<sup>3</sup> hybrid orbitals which are utilized in forming sigma bonds with hydrogen atoms. SP<sup>3</sup> orbitals are arranged in four corners in which each angle is of 109°28'.



**(i) H<sub>2</sub>O**

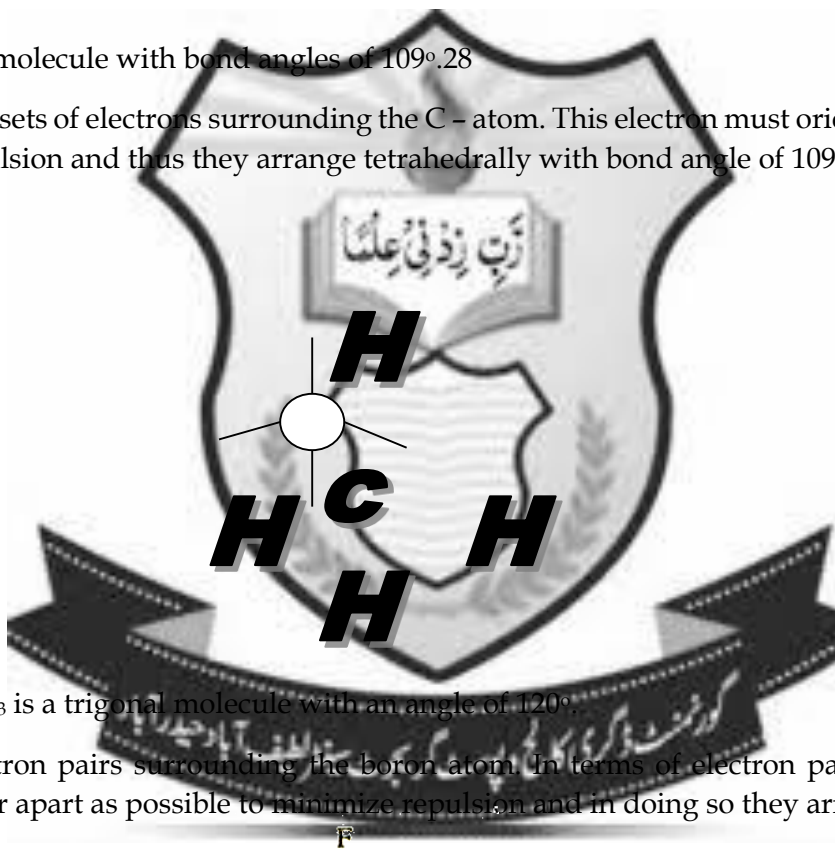
There are four active sets of electron pairs around the central oxygen atom. These electrons must orient as far apart as possible to minimize the repulsion and in doing so they arrange tetrahedrally. However, there are two lone pairs of electrons which repel each other as well as the bond pair of electrons with the result that bond angle is reduced from 109° to 104.5°.



**(ii) CH<sub>4</sub>**

CH<sub>4</sub> is a tetrahedral molecule with bond angles of 109.28°.

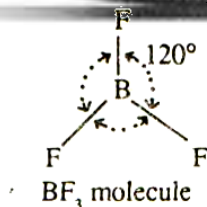
There are four active sets of electrons surrounding the C-atom. These electrons must orient as far apart as possible to minimize the repulsion and thus they arrange tetrahedrally with bond angle of 109.28°.



**(iii) BF<sub>3</sub>**

Boron trifluoride, BF<sub>3</sub> is a trigonal molecule with an angle of 120°.

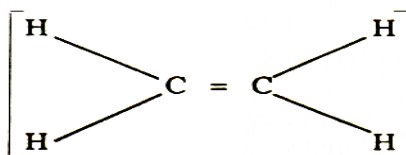
There are three electron pairs surrounding the boron atom. In terms of electron pair repulsion theory these electrons orient as far apart as possible to minimize repulsion and in doing so they arrange trigonally.



**(iv) C<sub>2</sub>H<sub>4</sub>**

C<sub>2</sub>H<sub>4</sub> is a trigonal molecule with bond angle of 120°.

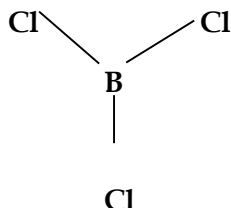
There are three active set of electrons which surround each carbon atom. These electrons must orient as far apart as possible to minimize the repulsion and thus they arrange trigonally.



**(v) BCl<sub>3</sub>**

Boron trichloride is a trigonal molecule with an angle of 120°.

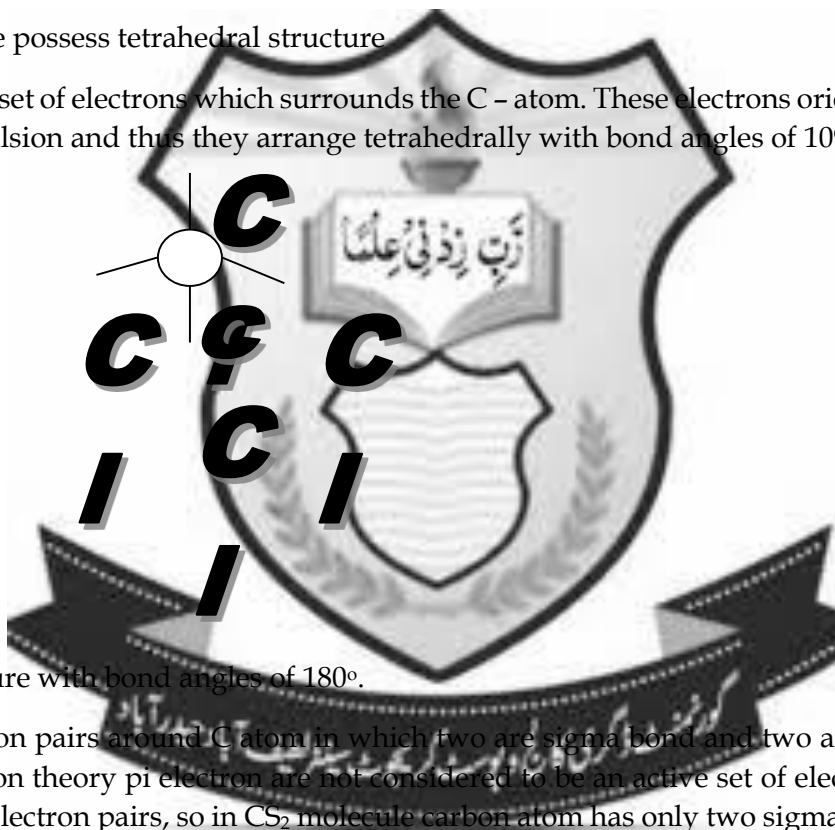
There are three active set of electron pairs which surround the boron atom. In terms of electron pair repulsion theory these electrons orient as far apart as possible to minimize repulsion and in doing so they arrange trigonally.



**(vi) CCl<sub>4</sub>**

Carbon tetra chloride possess tetrahedral structure.

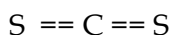
There are four active set of electrons which surrounds the C - atom. These electrons orient as far apart as possible to minimize the repulsion and thus they arrange tetrahedrally with bond angles of 109°.



**(vii) CS<sub>2</sub>**

CS<sub>2</sub> is a linear structure with bond angles of 180°.

There are four electron pairs around C atom in which two are sigma bond and two are pi bonds. According to electron pair repulsion theory pi electron are not considered to be an active set of electrons hence not included in the count of total electron pairs, so in CS<sub>2</sub> molecule carbon atom has only two sigma bonds and these electron must orient as far apart as possible to minimize the repulsion and thus they arrange linearly with bond angle of 180°.

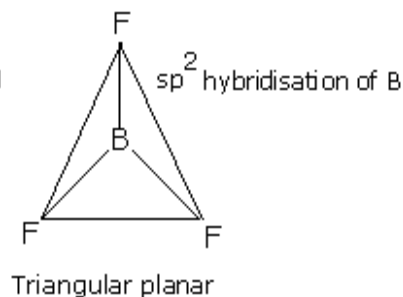
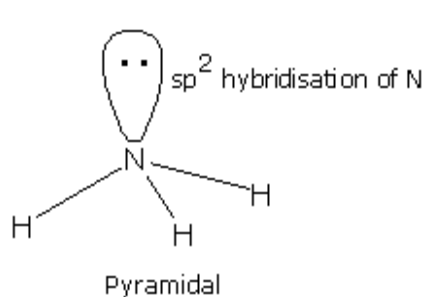


**Shape of NH<sub>3</sub>**

In ammonia, central nitrogen atom is surrounded by four active set of electron pairs which arrange themselves in four corners to minimize forces of repulsion.

Therefore structure of ammonia is pyramidal.

Due to presence of non bonding electron pairs force of repulsions increases and bond angle reduces to 107°.

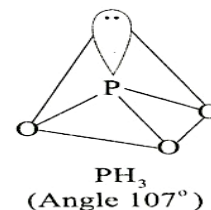


### 1. SHAPE OF PH<sub>3</sub>

No of electrons: Central P atom contains four active pairs of electron in valence orbit in which one is lone pair.

Electrons Arrangement: These four active pairs will arrange themselves on four sides of nucleus in tetrahedral pattern so that repulsion is minimized.

Shape of Molecules: Thus shape of molecules will be tetrahedral.



Geometry of molecule

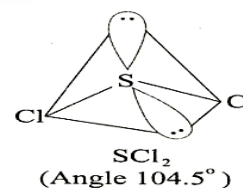
### 2. SHAPE OF SCl<sub>2</sub>

No of electrons: Central S atom contains four active pairs of electrons in valence orbit in which two are lone pairs.

Electrons Arrangement: These pairs will arrange themselves on four sides of nucleus in tetrahedral pattern so that repulsion is minimized.

Shape of molecules: Thus shape of molecules will be tetrahedral.

Bond Angle: In this case bond angle will be 104.5°.



Geometry of molecule

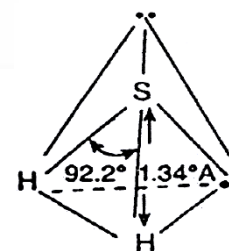
### 3. Shape of H<sub>2</sub>S

No of electrons: Central S atom contains four active pairs of electrons in valence orbit in which two are lone pairs.

Electrons Arrangement: These pairs will arrange themselves on four sides of nucleus in tetrahedral pattern so that repulsion is minimized.

Shape of molecules: Thus shape of molecules will be tetrahedral.

Bond Angle: In this case bond angle will be 92.2



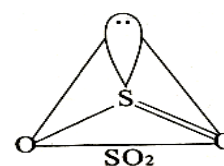
### 4. Shape of SO<sub>2</sub>

No of electron: Central S atom contains four electron pairs in the valence shell in which one is inactive  $\pi$  - pair.

Electrons Arrangement: These three active pairs will arrange themselves in three sides of the nucleus in the same plane so that repulsion is minimized

Shape of Molecules: Thus shape of molecules will be planer trigonal.

Bond Angle: In this case bond angle will be 120°



Geometry of molecule

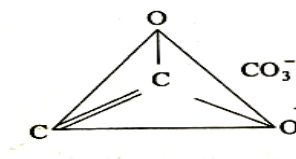
**5. Shape of  $\text{CO}_3^{2-}$**

No of electrons: Central C atom contains four electron pairs in the valence shell in which one is inactive  $\pi$  - pairs.

Electrons Arrangement: These three active pairs will arrange themselves on three sides of the nucleus in the same plane so that repulsion is minimized.

Shape of Molecules: Thus shape of molecules will be planer trigonal.

Bond Angle: In this case bond angle will be  $120^\circ$



**6. Shape of  $\text{SO}_3$**

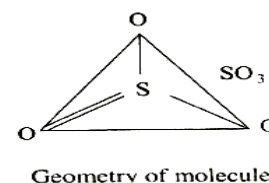
No of electron: Central S atom contains four electron pairs in the valence shell in which one is inactive  $\pi$  - pairs.

Electron Arrangement: These three active pairs will arrange themselves on three sides of the nucleus in the same plane so that repulsion is minimized.

Shape of molecules: Thus shape of molecule will be planar trigonal.

Bond Angle: In this case bond angle will be  $120^\circ$

Geometry of molecule



Geometry of molecule

**BOND ENERGY**

**DEFINITION:**

The amount of energy required to break a bond between two atoms is called as bond energy.

OR

The amount of energy required to break the one mole of bonds is called as bond energy.

OR

The amount of energy required for the breaking of  $6.02 \times 10^{23}$  bonds is called bond energy.

**UNIT:** The bond energy is expressed in KJ / mole.

**Examples**



**EXPLANATION:**

The bond energy depends upon following factors.

1. Atomic size
2. Polarity
3. Number of bonds.

**1. ATOMIC SIZE:**

Smaller the size of bonded atoms, greater will be the attraction and hence greater will be the bond energy.

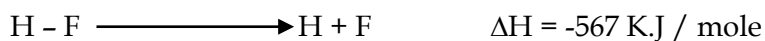


e.g



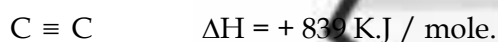
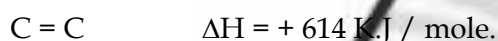
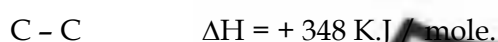
**2. POLARITY:** The polarity depends upon the difference of electronegativities. It means the higher difference of electronegativities, then greater will be the polarity and hence higher will be the bond energy.

e.g



### 3. NUMBER OF BONDS.

The bond energy increase from single bonded compounds to double bonded and then triple bonded compounds.



### DIPOLE MOMENT

**INTRODUCTION:** The polar molecules are called as dipole molecules.

e.g



These dipole molecules possess polarity and polarity of molecule is measured in a quantity which is called as dipole moment.

### DEFINITION:

The measurement of polarity of a dipole molecule is called as dipole moment.

OR

The product of charge (q) and distance (d) between atoms of a dipole molecule is called as dipole moment.

### REPRESENTATION:

The dipole moment is represented by  $\mu$  ( $\mu$ )

### MATHEMATICAL DERIVATION:

$$\mu = d \times q \quad (d = 10^{-8} \text{ cm}, \quad q = 10^{-10} \text{ e.s.u})$$

$$\mu = 10^{-8} \text{ cm} \times 10^{-10} \text{ e.s.u} = 10^{-18} \text{ e.s.u} \times \text{cm}$$

$$\mu = 10^{-18} \text{ e.s.u} \times \text{cm} = 1 \text{ debye}$$

$$(1 \text{ debye} = 10^{-18} \text{ e.s.u cm}).$$

### UNIT:

The unit for dipole moment is debye and it is represented by "D" and S.I unit is coulomb meter (Cm), where  $1 \text{ D} = 3.335 \times 10^{-30} \text{ Cm}$

**EXPLANATION:** The dipole moment depends upon following factors.

1. Polarity of the bond.
2. Geometry of the molecule
3. Symmetry of molecules.

**1. POLARITY OF THE BOND:** Greater the polarity then greater will be the dipole moment.

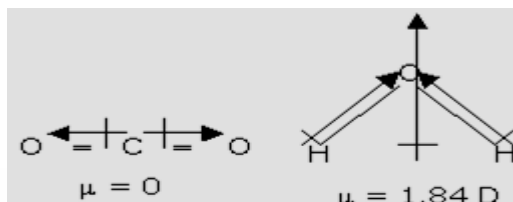
e.g

HCl = 1.03 D

HBr = 0.79 D

## **2. GEOMETRY OF THE MOLECULES:**

On the basis of geometry molecules are divided into linear molecules and angular molecules. The linear molecules have zero (0) dipole moment whereas angular molecular possess dipole moment.



## **3. SYMMETRY:**

Symmetrical molecules possess zero dipole moment, where as unsymmetrical molecules possess dipole amount e.g

Benzene = 0 D

Chloro benzene = 1.7 D

methane = 0 D

O - dichloro benzene = 2.5 D

### **SHORT QUESTION**

**QNO#01 Define the following**

(a) Bond energy

(b) Bond length

**ANS: Bond energy:**

The amount of energy required to break a bond between two atoms is called as bond energy. **OR** The amount of energy required to break the one mole of bonds is called as bond energy. **OR** The amount of energy required for the breaking of  $6.02 \times 10^{23}$  bonds is called bond energy.

(b) Bond length: the distance between the nuclei of two bonded atoms in a molecules is known as bond length.

**QNO#02: The dipole moment of water is 1.85 D but CO<sub>2</sub> has zero dipole moment. Why?**

**Ans:** The dipole moment of water and CO<sub>2</sub> both contains polar bonds but H<sub>2</sub>O has dipole moment 1.85 and CO<sub>2</sub> has zero dipole moment because H<sub>2</sub>O has angular structure and in CO<sub>2</sub> both (C=O) bonds are polar but directed equally on the opposite side at 180° angle with linear shape.

**QNO#03: Differentiate between the following**

### **Difference between bonding molecular orbitals and antibonding molecular orbital**

SNO	Bonding molecular orbital	Anti bonding molecular orbital
1	A bonding M O is generated by the addition of two atomic orbitals	A anti bonding M O is generated by the subtraction of two atomic orbitals
2	In bonding M O the electron density between the two nuclei is increased	In anti bonding M O the electron density between the two nuclei is decreased and might become zero

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3	It is formed by the overlapping of atomic orbitals which are in phase	It is formed by the overlapping of atomic orbitals which are out of phase
4	The energy of a bonding M O is lower than that of the combining orbitals	The energy of a bonding M O is higher than that of the combining orbitals
5	It is represented by Greek letters $\sigma$ or $\pi$	It is represented by Greek letters $\sigma^*$ or $\pi^*$
6	The electrons present in the bonding M O, shield both the nuclei from mutual repulsion. As a result it contributes to the process of bonding	The electrons present in the anti bonding M O, result in the increased repulsion between the two nuclei. This lowers the stability of the system. Thus the presence of electrons in an anti bonding M O does not help in bond formation.
7	It is more stable than the parent atomic orbitals	It is less stable than the parent atomic orbitals

**Difference between sigma bond and pi bond**

SNO	SIGMA BOND	PI BOND
1	It is formed by the head on (end to end ) overlapping of two half filled atomic orbitals	It is formed by the side wise (parallel) overlapping of half filled p orbitals
2	Sigma bond is considered to be strong i.e more stable and less reactive because of maximum overlapping of orbitals	Pi bond is considered to be weak i.e less stable and more reactive because of lesser overlapping of orbitals
3	Sigma bond can form between orbitals	s orbitals do not take part in pi bond formation they retain their shape
4	One lobe of p orbital take part in sigma bond formation stretches while the other lobe reduce in size	Both lobe take part in pi bond formation they retain their shape
5	It has only one region of electron cloud density around the bond axis	It has two region of electron cloud density one above and one below the $\sigma$ bond axis
6	It is formed independently because atoms always combine first with a sigma bond	It is formed only between two atoms which are already bonded by a sigma bond.
7	Only one sigma bond exists between two atoms	One or two pi bond exists between two $\sigma$ bonded atoms
8	Sigma electrons in a sigma bond are localized	Pi electrons in a pi bond may be localized and delocalized

**Difference Between Valence Bond Theory And Molecular Orbital Theory**

SNO	VBT	MOT
1	According to VBT the bonding electrons occupy the atomic orbital of the bonded atoms and the shared electrons is influenced by one nucleus (Monocentric)	According to MOT the bonding electrons occupy the molecular orbital and the shared electron is influenced by more than one nucleus (Polycentric)
2	According to VBT atomic orbital which are involved in the bond formation maintain their individual nature and identities	According to MOT atomic orbitals which form molecular orbital do not retain their individual nature

3	In VBT some of the valence electrons are indicated as unshared and uninvolved in the formation of molecule	In MOT all the valence electrons take part in the bonding of molecules
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**Q:4. Explain the following with scientific reasons.**

- (i) **Sigma bond is stronger than pi bond.**
- (ii) **HF has greater ionic character than HCl.**
- (iii) **Bond energy of molecules possessing multiple bonds is high.**

**ANS:** (i) The strength of a bond is dependent on the extent of overlapping, in case of the sigma bond, the overlapping of orbitals takes place to a larger extent. Hence the sigma bond is stronger in comparison to the pi bond because in pi bond the extent of overlapping occurs to a smaller extent.

(ii) HF has greater ionic character than HCl. Because the electronegativity difference b/w HF is greater than HCl.

E.N of H = 2.1

E.N of F = 4.0

E.N of Cl = 3.0

E.N difference of HF =  $4.0 - 2.1 = 1.9$

E.N difference of HCl =  $3.0 - 2.1 = 0.9$

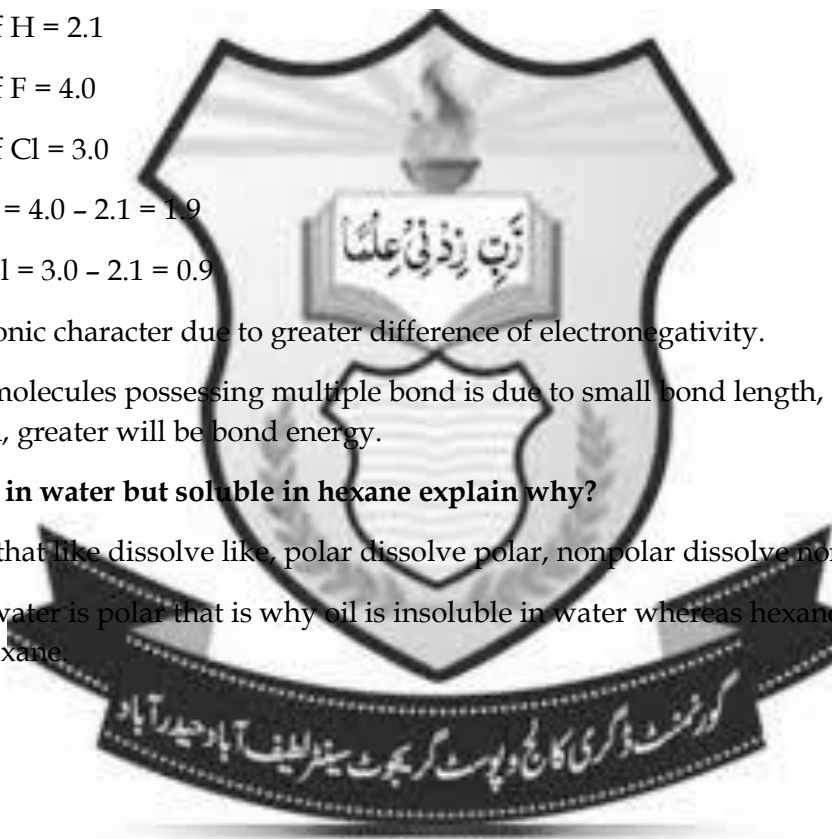
The HF has greater ionic character due to greater difference of electronegativity.

(iii) Bond energy of molecules possessing multiple bond is due to small bond length, greater the number of the bond between length, greater will be bond energy.

**Q:5. Oil is insoluble in water but soluble in hexane explain why?**

**ANS:** As we known that like dissolve like, polar dissolve polar, nonpolar dissolve nonpolar

Oil is nonpolar and water is polar that is why oil is insoluble in water whereas hexane (petrol) is nonpolar So oil is soluble in hexane.

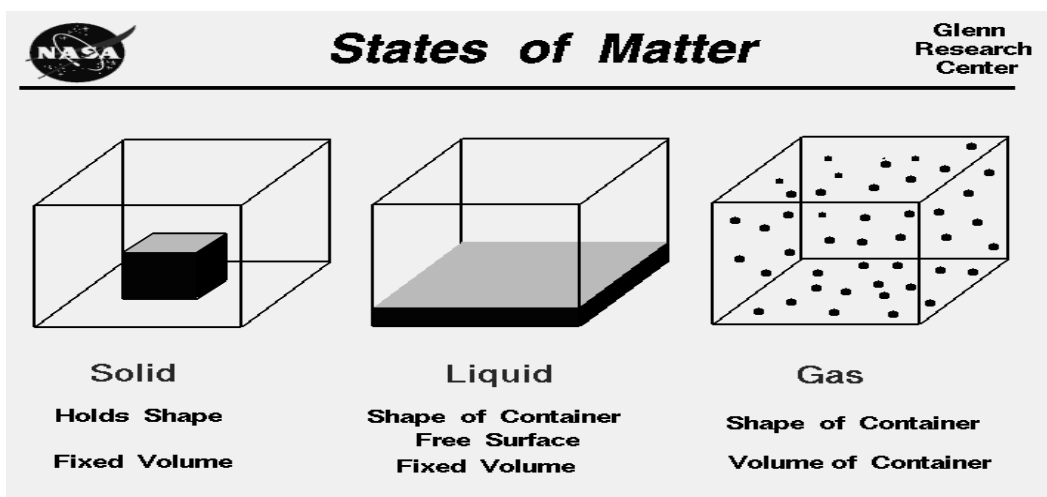
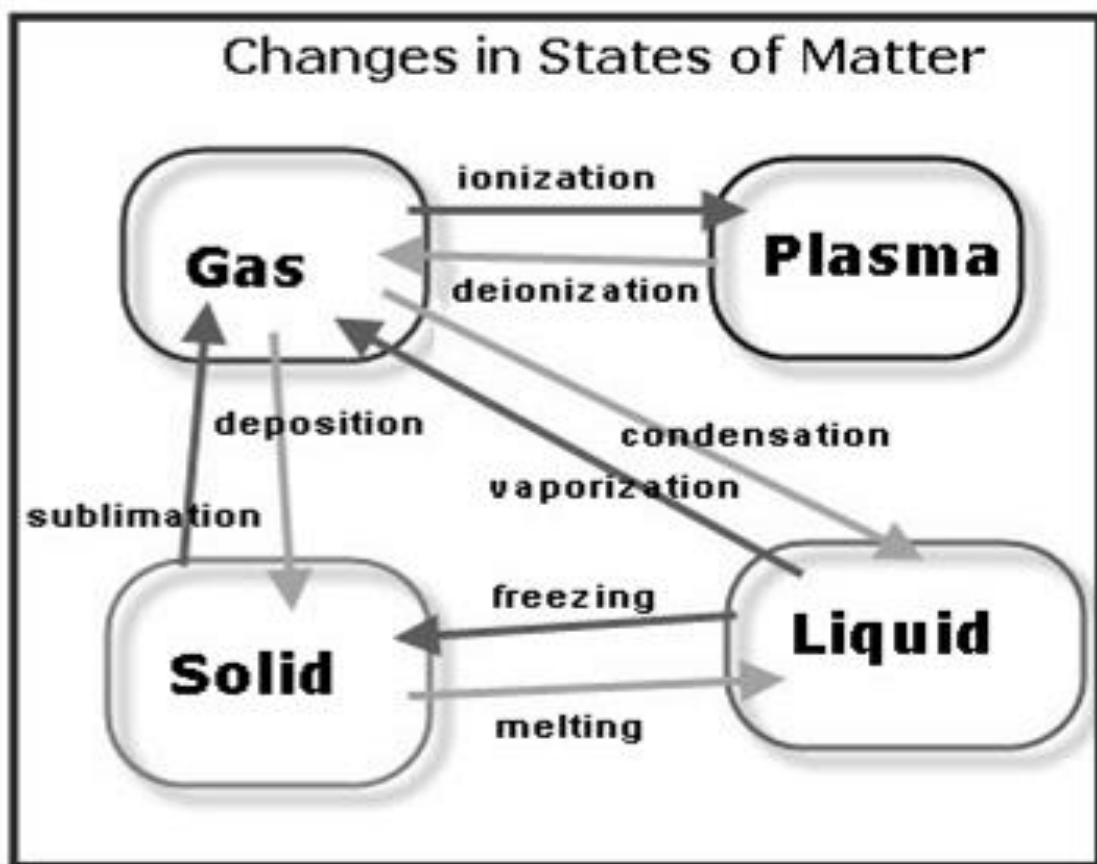


# THREE STATES OF MATTER

## GASES,

CHAPTER NO.

04





**PROF: ZUBAIR AHMED SHAIKH**  
**THREE STATES OF MATTER**  
**GASES**

**MATTER**

**DEFINITION:-** Matter is defined as anything which has weight or mass and occupying the space.

**STATES OF MATTER**

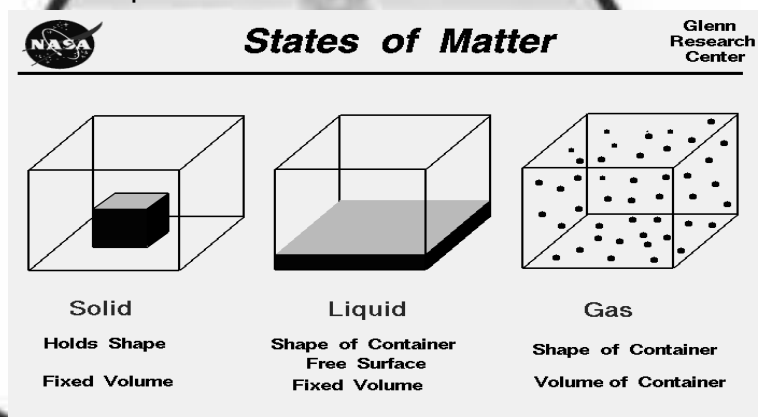
There are three states of matter.

- 1 Gas.
- 2 Liquid.
- 3 Solid.

Arrangement of particles is responsible for different behavior of water.

**PROPERTIES OF GAS:-**

- 1 A gas has no shape of its own. It acquires the shape of container.
- 2 It has no definite volume.
- 3 A gas diffuses I-e gas molecules move from one place to another place and then spread through out the space in the container.
- 4 It can be compressed and expand.



**WATER EXIST IN THREE STATES OF MATTER:-** Water can exist in three states of matter namely Solid (Ice or Snow), Liquid (Water) and Gaseous (Steam). Despite the same chemical composition, it shows different behavior in three different states.

**REASON:-** The particles (atom, molecule, ion) which constitute a substance differ in their arrangements in three states of matter. This different arrangement show different states.

**KINETIC MOECULAR THEORY OF GASES**

**INTRODUCTION:-** The kinetic theory is named because it deals with the motion of particles. The particles are in continues motion and they have kinetic energy.

**POSTULATES**

- 1 **PARTICLES:-** All gases are composed of tiny particles which are called as molecules.
- 2 **Size:-** These particles are invisible , small and widely separated from one another (distance between two molecules is 300 times greater than their sizes).
- 3 **MOTION:-** Molecules move in straight line until they collide with one another or with the wall of container
- 4 **FORCE:-** There are neither forces of attraction nor repulsion between gas molecules.
- 5 **COLLISION:-** The collision of molecules is completely elastic.
- 6 **PRESSURE:-** The gas pressure is due to collision of molecules with each other and with the

walls of container.

7 **VOLUME:-** The volume of one molecule is negligible as compared to total volume.

8 **KINETIC ENERGY:-** The molecules are in motion and they possess kinetic energy and kinetic energy is directly proportional to temperature i.e.  $K.E \propto T_{\text{absolute}}$ .

## **GASEOUS STATE**

### **(a) DIFFUSIBILITY:-**

**DEFINITION:-** The intermixing of two or more gases is called diffusion

OR

The spreading out of the gas molecules throughout the vessel is called diffusion and this property is called diffusibility.

**REASON:-** There are large spaces between the molecules of a gas. Because of these spaces, the molecules are free to move. Due to this free movement, gas molecules intermix with each other and spread out easily throughout the space available in the container.

### **(b) COMPRESSIBILITY:-**

**DEFINITION:** When pressure is applied on the gas in a closed container then it occupies smaller volume.

**REASON:-** According to kinetic theory there are very large spaces among gas molecules. Therefore they occupy very smaller space when compressed.

### **PRESSURE:-**

**DEFINITION:** The forces acting on a unit area is called pressure.

OR

It is produced by the collision of gas molecules on the object or on the walls of container.

**FORMULA:**  $\text{Pressure} = \text{Force} / \text{Area}$

**EXPLANATION:**

- All the gases and their mixture exert pressure on the walls of the container in which they are contained.
- The atmosphere around the earth (air) is a mixture of many gases, which also exerts pressure. This pressure is called "**Atmospheric Pressure**".
- The mass of atmosphere on our body at sea level and at  $0^{\circ}\text{C}$  is 14.7 psi.
- There is about 20 tons total pressure on our bodies.

**UNIT:**  $1 \text{ atmosphere} = 76 \text{ cm of Hg} = 760 \text{ mm of Hg} = 760 \text{ torr} = 14.7 \text{ PSI} = 101330 \text{ Pa} = 101330 \text{ Nm}^{-2} = 1.0133 \text{ bar}$

**APPARATUS:** The instrument used to measure atmospheric pressure is called **barometer**.

## **GAS LAWS**

**DEFINITION:-** The laws explaining the behavior of ideal gases are known as ideal gas laws.

There are three major laws about the ideal gases.

- 1 Boyle's law.
- 2 Charles's law.
- 3 Avogadro's law.

### **BOYLE'S LAW**

**INTRODUCTION:-** In 1660, Robert Boyle explained the relationship between the volume of given mass of a gas and pressure at constant temperature called Boyle's law.

**STATEMENT:-** The volume of a given mass of a gas is inversely proportional to pressure exerted on it at a given temperature.

### **EXPERIMENTAL VERIFICATION**

- 1 Robert Boyle took a J- shaped tube closed at smaller end.
- 2 A scale was fixed at smaller limb.
- 3 He inserted mercury from the open (longer) end and the gas (air) which was inside the tube was captured in the smaller end. He noted the volume of air at scale.
- 4 He inserted more mercury from the open (longer) end and noted the volume of air is reduced.
- 5 He further inserted mercury from the open (longer) end and noted the further decrease in volume of air.

**CONCLUSION:-** Robert Boyle concluded from above experiment that the decrease in volume is due to the increase in pressure by the mercury.

**MATHEMATICALLY:-**

$$V \propto 1/P \quad (T \text{ is taken constant})$$

$$V = K.1/P \quad (K \text{ is constant})$$

$$PV = K$$

This shows that at constant temperature, the product of volume of a gas and pressure exerted on it is always constant.

For two conditions

$$K = P_1 V_1 = \text{Equation \# 1}$$

$$K = P_2 V_2 = \text{Equation \# 2}$$

By comparing equation # 1 and equation # 2.

$$P_1 V_1 = P_2 V_2$$

Where;

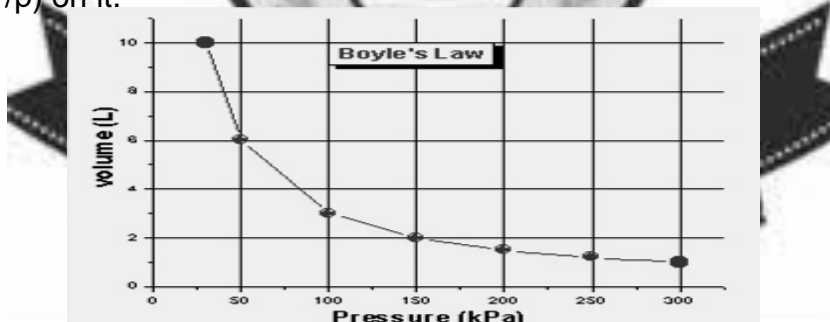
$P_1$  = Extend pressure on gas for 1<sup>st</sup> condition

$P_2$  = Extend pressure on gas for 2<sup>nd</sup> condition

$V_1$  = Volume of the gas for 1<sup>st</sup> condition

$V_2$  = Volume of the gas for 2<sup>nd</sup> condition

**GRAPHICAL REPRESENTATION:-** A hyperbolic curve is obtained when volume of a gas is plotted v/s pressure exerted on it. Straight line is obtained when volume of a gas is plotted v/s inverse of pressure exerted ( $1/p$ ) on it.



### **CHARLES LAW**

**INTRODUCTION:-** In 1787, a French Physicist Charles explained the relationship between the volume of a gas and its temperature at constant pressure called Charles law.

**STATEMENT:** The volume of a given mass of a gas is directly proportional to the temperature of that gas.

OR

The volume of a given mass of a gas increase or decrease by  $1/273$  times of its original volume at  $0^\circ\text{C}$  for every degree rise or fall of temperature at constant pressure.

**MATHEMATICALLY:-**

$$\Rightarrow V \propto T \text{ (absolute) ; if } P = \text{constant}$$

$$\Rightarrow V = KT$$

$$\Rightarrow \frac{V}{T} = K$$

T  
Suppose T changes to  $T_1$  and V changes to  $V_1$ ; then

$$\Rightarrow \frac{V_1}{T_1} = K \text{ ; similarly}$$

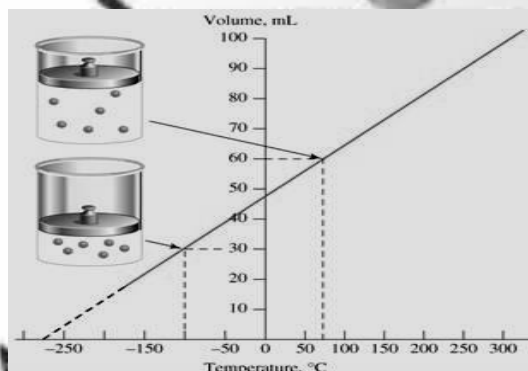
$$\Rightarrow \frac{V_2}{T_2} = K$$

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

**GRAPHICAL REPRESENTATION:-** If a graph of volume against temperature at constant pressure is plotted then it comes to be a straight line which stops in the middle of the graph. If two lines are extra plotted (shown by dotted lines) then it intercepts the temperature axis at  $(-273^\circ\text{C})$  which corresponds to zero volume. This proves that at  $(-273^\circ\text{C})$  volume of a gas should become zero. This is an imaginary temperature and is known as absolute zero i.e;  $(-273^\circ\text{C} = 0 \text{ kelvin})$ .

**EXAMPLE:-** If the volume of the gas is 25 liters at  $0^\circ\text{C}$ , its volume will be  $(1/273 \times 25) + 25$  liters at  $0^\circ\text{C}$ .

If the volume of a gas is 25 liters at  $0^\circ\text{C}$ , its volume will be  $(1/273 \times 25) - 25$  liters at  $0^\circ\text{C}$ .



### AVOGADRO'S LAW:-

**INTRODUCTION:-** In 1811, Amadeo Avogadro explained the relationship between the volume of given mass of a gas and the no. of molecules at constant pressure and temperature, called Avogadro's law.

**STATEMENT:-** Equal volumes of all gases at same temperature and pressure contain the same no. of molecules.

**MATHEMATICALLY:-**

$$V \propto n \quad (T \text{ and } p \text{ are constant})$$

$$V = K n \quad (K = \text{constant, } n = \text{no. of moles/ molecules})$$

$$K = V/n$$

### **CONCEPT OF MOLAR VOLUME**

The volume of one mole of a gas at S.T.P is called molar volume or molar gas volume i-e;  $(22.4 \text{ dm}^3)$ .

	Oxygen ( $\text{O}_2$ )	Sulfur trioxide ( $\text{SO}_3$ )	Carbon dioxide ( $\text{CO}_2$ )	Hydrogen ( $\text{H}_2$ )
Mass of one mole (a.m.u)	32	80	44	2

Volume (dm <sup>3</sup> )	22.4	22.4	22.4	22.4
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### GENERAL GAS EQUATION

**DEFINITION:** The equation which describes the relationship between four variables  
I-e Volume, temperature, pressure, and number of moles is called as general gas equation  
OR

The combination of Boyle's law, Charles law & Avogadro's law is called general gas equation.

#### **MATHEMATICALLY:-**

According to Boyle's law	$V \propto P$	(If T is constant)
According to Charles law	$V \propto T$	(If P is constant)
According to Avogadro's law	$V \propto n$	(If T & P is constant)

By combination of these laws we get :

$$\begin{aligned} V &\propto nT / P \\ V &= R nT / P \\ V &= R nT / P \quad (\text{equation of state}) \\ \boxed{PV} &= nRT \end{aligned}$$

V = Volume of given mass of a gas.

P = Pressure, n= number of moles, T= absolute temperature

R = General gas constant.

For one mole of a gas (n=1)  $PV=RT$

$$\boxed{\frac{PV}{T} = R}$$

Suppose P changes to  $P_1$ , T changes to  $T_1$ , V changes to  $V_1$

Then:  $\frac{P_1 V_1}{T_1} = R$

Similarly  $\frac{P_2 V_2}{T_2} = R$

By comparing these two equations.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

### GRAHAM'S LAW OF DIFFUSION

**INTRODUCTION:-** This law was introduced by Graham in 1881. This law describes the relationship between rate of diffusion and densities of gases.

**STATEMENT:-** The rate of diffusion of a gas is inversely proportional to the square root of its density

OR

Lighter gases diffuse faster than heavier gases.

#### **MATHEMATICALLY:-**

Let suppose;  
rate of diffusion = r  
density = d.



Then according to Graham's law, the mathematically derivation will be

$$r \propto \frac{1}{\sqrt{d}}$$
$$r = \frac{k}{\sqrt{d}} \text{----- (1)}$$

Let rate of diffusion of two gases be  $r_1$  and  $r_2$ , The densities are  $d_1$  and  $d_2$ . Then the equation for first gas will be;

$$r_1 \propto \frac{1}{\sqrt{d_1}} \quad \Rightarrow \quad r_1 = \frac{k}{\sqrt{d_1}} \text{----- (2)}$$

$$r_2 \propto \frac{1}{\sqrt{d_2}} \quad \Rightarrow \quad r_2 = \frac{k}{\sqrt{d_2}} \text{----- (3)}$$

By comparing equation (2) & (3), we get.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Because the density of gas is directly proportional to its molecular mass, the above equation becomes;

$$\Rightarrow \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

**APPLICATIONS:** - Graham's law can be used:-

**Determination:-** It is used to determine the molecular weight and density of gases.

**Dilution:-** It is used to dilute the poisonous gases and minimizing their toxic effect.

**Separation:-**

- Different isotopes of a gas.
- One gas from another gas.

### **DALTON'S LAW OF PARTIAL PRESSURE**

**INTRODUCTION:-** This law was introduced by Dalton in 1801. This law describes the relationship between partial pressure of individual gases and total pressure of all gases in the mixture.

**STATEMENT:-** In a mixture of two or more gases the total pressure is equal to the sum of partial pressure of individual gases.

**DERIVATION:-**

This law can be written as;

$$P = P_1 + P_2 + P_3 \text{-----}$$

Where;

$P$  = Total pressure exerted by all the gases.

$P_1$  = Partial pressure exerted by gas 1.

$P_2$  = Partial pressure exerted by gas 2.

$P_3$  = Partial pressure exerted by gas 3.

The general gas equation is;  $PV = nRT$   $\longrightarrow$  (a)

Therefore;

$$P_1V = n_1RT \quad \longrightarrow \quad (b)$$

$$P_2V = n_2RT \quad \longrightarrow \quad (c)$$

$$P_3V = n_3RT \quad \longrightarrow \quad (d)$$

By adding equation B,C and D; we get;

$$\Rightarrow V(P_1 + P_2 + P_3) = (n_1 + n_2 + n_3)RT \longrightarrow (e)$$

As;  $n = n_1 + n_2 + n_3$  ( $n$  = total number of moles)

By substituting the value of  $(n_1 + n_2 + n_3)$  in equation E, we get;

$$V(P_1 + P_2 + P_3) = nRT \longrightarrow (f)$$

Dividing equation B by A, we get;

$$\frac{P_1 V}{PV} = \frac{n_1 RT}{nRT}$$
$$\Rightarrow \boxed{\frac{P_1}{P} = \frac{n_1}{n}} \Rightarrow \boxed{P_1 = P \times \frac{n_1}{n}}$$

**EQUATION:-**

$$\frac{\text{Partial pressure of gas}}{\text{Total pressure}} = \frac{\text{number of moles of that gas}}{\text{Total number of moles}}$$

**APPLICATION:-** A gas collected over water also contains some of water vapour. Thus the pressure exerted by the gas would be the pressure of pure gas plus the pressure of water vapour.

Then

$$P_{\text{dry gas}} + P_{\text{H}_2\text{O(vap)}} = P_{\text{moist gas}}$$
$$P_{\text{dry gas}} = P_{\text{moist gas}} - P_{\text{H}_2\text{O(vap)}}$$

### **EXPLANATION OF GAS LAWS ON THE BASIS OF K.M.T**

**EXPLANATION OF BOYLE'S LAW:-** When pressure is increased, the gas molecules come closer to each other and thus volume is reduced, therefore decrease in volume increases the crowding of molecules. The increase in crowding of molecules increases the collision of molecules with the walls of container and thus increases the pressure. It means with the decrease of volume, pressure increases.

**EXPLANATION OF CHARLES LAW:-**

When temperature is increased, the kinetic energy of gas molecules also increases. Hence molecular velocity increases which causes expansion of gas to occupy greater volume.

**EXPLANATION OF GRAHAMS LAW:-** According to kinetic molecular theory of gases, there are large empty spaces among gas molecules. The gas molecules are always in random motion. When two gases are allowed to mix together their molecules easily enter into the empty spaces of other gas and diffuse. The entrance velocity depends upon the velocity of the molecules, lighter gases have lower velocity.

**EXPLANATION OF AVOGADRO'S LAW:-**

At same conditions (S.T.P) the kinetic energy of the molecules of all gases is same which causes same volume of the gases having same number of moles.

**EXPLANATION OF DALTON'S LAW:-**

According to K.M.T pressure is produced by the collision of gas molecules on the wall of container. The molecules do not attract or repel each other. When there are molecules of two or more gases in the same container then the molecules of each gas produce their own pressure.

Q:1. Explain the following.

(i) **Pressure and its various unit.**

(ii) **Absolute zero**

**PRESSURE AND ITS VARIOUS UNIT:**

**PRESSURE:** A force being exerted over a unit area is called pressure.

So, 
$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{F}{A}$$

Where P is measured in pascal, force in newton and the area in  $\text{m}^2$ .

**PASCAL:** A pascal (Pa) is defined as the force of one newton spread over an area of  $1\text{m}^2$ .

**a) UNIT OF PRESSURE:** SI Unit for pressure is pascal (Pa) in SI system, unit of force is newton. (N) and the unit of area is meter square ( $\text{m}^2$ ). Thus pascal is one  $\text{Nm}^{-2}$ .

1 atm = 101325 pascal

1 atm = 14.7 psi (pounds square inch)

1 atm = 760 torr = 760 mm of hg

1 joule = 1 Nm =  $10^7$  ergs =  $\text{kg m}^2\text{s}^{-2}$

1 cal = 4.18J

1 atm = 1.01325 bar

**b) ABSOLUTE ZERO:**

**INTRODUCTION:** In 1848, the Scottish Irish physicist William Thomson better known as Lord Kelvin.

**DEFINITION:** The Hypothetical temperature at which the given volume of a gas reduces to zero.

**OR**

A temperature at which volume of a gas becomes zero theoretically.

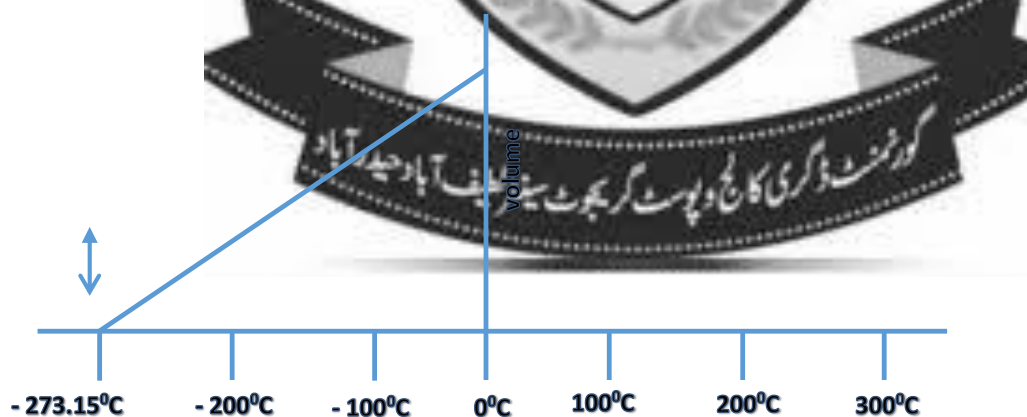
**EXPLANATION:** According to the definition of Charles's law at constant pressure, the volume of given mass of a gas increases or decreases by  $\frac{1}{273}$  of its original volume at  $0^\circ\text{C}$  by  $1^\circ\text{C}$  rise or fall of temperature, respectively.

Let the volume of an ideal gas at  $0^\circ\text{C}$  is  $V_0 \text{ cm}^3$ .

Volume at  $-1^\circ\text{C} = V_0 - \frac{1}{273} V_0$

Volume at  $-273^\circ\text{C} = V_0 - \frac{273}{273} V_0 = 0$

Thus exactly at  $-273^\circ\text{C}$  the volume of a given mass of a gas reduces to zero. A graph between volume and temperature gives a straight line and cuts the temperature axis at  $-273.15^\circ\text{C}$



Q:4. What is liquid air? Mention its three uses.

**Ans: LIQUID AIR:** Ordinary air on compression and cooling to extremely low temperature becomes liquefied and known as liquid air. It is mainly used for the cooling purpose. It absorbs the heat very rapidly and helps to convert the gases (filled in container) into solid. It is the industrial source of various gases such as oxygen, argon, nitrogen etc through a process named as air separation or fractional distillation of air.

**USES OF LIQUID AIR:**

- Liquid air is an important source of oxygen in rockets.
- Liquefied natural gas (LNG) is used as a fuel.

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- Ammonia and liquid sulphur dioxide are used as refrigerator.
- Compressed oxygen is used for welding purpose.
- Nitrogen is used in medical science.
- Liquefied petroleum gas (LPG) is a mixture of Butane and other hydrocarbons used as a fuel for portable heaters, gas cook tops and oven.

Q:5. What is plasma? Give its significance in daily life.

**Ans: PLASMA:** Plasma is the fourth state of matter. It was identified by William Crookes in 1879. He obtained it by heating molecular gas changing into atomic form and then to ionic form at higher temperature.

Molecular gas  $\longrightarrow$  Atomic gas  $\longrightarrow$  Ions.

At a higher temperature of 10000K to 100000K (10eV to 100eV) electrons are removed from the atoms to form ions. Plasma is composed of a mixture of un-ionized gas, free electrons and positively charged particles.

**PROPERTIES OF PLASMA:-** It is a substance in which many of the atoms or molecules are ionized effectively allowing charges to flow freely. It takes place at very high temperature. Plasma has the following properties.

- a) plasma consists of neutral particles, positive ions and free electrons.
- b) plasma is strongly influenced by both magnetic and electric force.
- c) plasma shows a characteristic glow depending upon the gas present in the discharge tube.

**EXAMPLE:** Oxygen gives a red glow, hydrogen green and nitrogen purple or pink glow.

### **SIGNIFICANCE:**

- It is used in television and computer chips.
- Plasma is used in rocket propulsion.
- Cleaning the environment, destroying biological hazard and healing wounds.
- It is used in laser powered power switches and diamond coated film. Neon signs are turned on as gas is excited and creates glowing plasma which lightens the surrounding.

Q:6. Derive general gas equation. Also deduce the value of R in  $\text{atm} \cdot \text{dm}^3/\text{mol} \cdot \text{K}$  and  $\text{J}/\text{mol} \cdot \text{K}$ .

**Ans: DERIVATION OF GENERAL GAS EQUATION:-** The general gas equation is a combination of three laws: Boyle's law, Charles's law and Avogadro's law.

Now according to Boyle's law,

$$V \propto \frac{1}{p} \text{ (at constant } T \text{ and } n)$$

According to Charles's law

$$V \propto T \text{ (at constant } P \text{ and } n)$$

According to Avogadro's law

$$V \propto n \text{ (at constant } T \text{ and } P)$$

Where  $n$  is the number of moles of the gas.

Combining equations 1, 2 and 3 we get.

$$V \propto \frac{1}{p} \times T \times n$$

$$V \propto \frac{Tn}{p}$$



$$V \propto R \frac{Tn}{P}$$

$$PV = nRT.$$

Where R is a general gas constant this equation is called general gas equations or ideal gas law equation or equation of state.

If  $n = 1$  then  $PV = RT$  or  $\frac{PV}{T} = R$

So  $\frac{P_1 v_1}{T_1} = R$  (for first condition of gas) and  $\frac{P_2 v_2}{T_2} = R$  (For second condition of gas)

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

**a) Value of R when pressure is in atmosphere and volume in dm<sup>3</sup>.**

We known that one mole of an ideal gas at STP(One atmosphere pressure and 273K) occupies 22.4 dm<sup>3</sup>.

$$R = \frac{PV}{nT}$$

$$R = \frac{1 \text{ atmosphere} \times 22.4 \text{ dm}^3}{1 \text{ mole} \times 273 \text{ K}}$$

$$R = 0.0821 \frac{\text{atm.dm}^3}{\text{mol.k}}$$

**b) Value of K when pressure is in N/m<sup>2</sup> and volume in m<sup>3</sup> (SI Unit):-**

According to S.I system pressure is measured in N/m<sup>3</sup> and volume in m<sup>3</sup> since 1 atm = 101325 N/m<sup>2</sup> and 1dm<sup>3</sup> = 0.00224m<sup>3</sup>

$$R = \frac{PV}{nT}$$

$$R = \frac{101325 \times 0.00224}{1 \times 273}$$

$$R = 8.313 \text{ Nm mol}^{-1} \text{ K}^{-1}$$

$$\text{OR } R = 8.313 \text{ Jmol}^{-1} \text{ K}^{-1}$$

Q:3. How an ideal gas is differentiated from real gas? What are the cause of deviation of real gas from ideal behavior? Explain this deviation at low temperature and high pressure.

**Ans:**

**IDEAL GAS**

Ideal gas which obeys the general gas equation or idea gas equation ( $PV = nRT$ ) at all temperature and pressure and all laws especially boyle's law and charle's law is called ideal gas

There are no attractive or repulsion force among the gas molecules

Actual volume of gas molecules are negligible as compared to the total volume of the gas

No such gas is exist in reality

**REAL GAS**

The gasses which do not obey general gas equation or ideal gas equation ( $PV = nRT$ ) at all temperature and pressure and all laws strictly are called real gas or non ideal gas

There are attractive or repulsion force among the gas molecules.

Actual volume of gas moleculars are not negligible as compared to the total volume of the gas.

All the gases are real gases or non – ideal gases.

E.g O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> CO<sub>2</sub> etc.

Causes of Deviation real gas from ideal behavior at low temperature and high pressure:-

The ideal condition is that the ideal gas obeys gas laws at all temperature but al low temperature and high pressure deviation cause by gases is due to the two faculty assumptions of kinetics molecules theory.



1. Inter – molecular force of attraction: There are two attractive a repulsion forces between the gas molecules.
2. Volume:- The volume of the gas molecules is negligible as compared to the volume of the container.

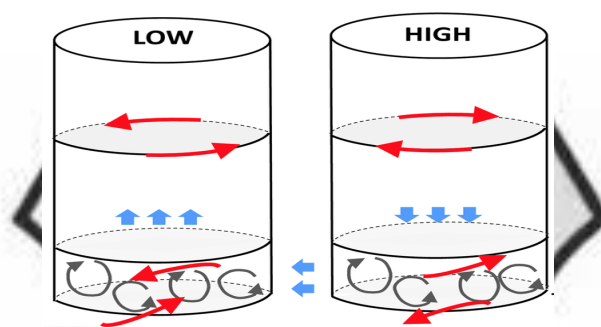
**EXPLANATION OF DEVIATION:-**

**1. AT LOWER TEMPERTURE:-** At high temperature the kinetics energy of the gaseous molecules is very high. As a result, the attractive force between them are negligible. But when temperature is decreased, the kinetics energy of the molecules deceases, The inter molecular forces become significant it means that the molecules come close to each other.

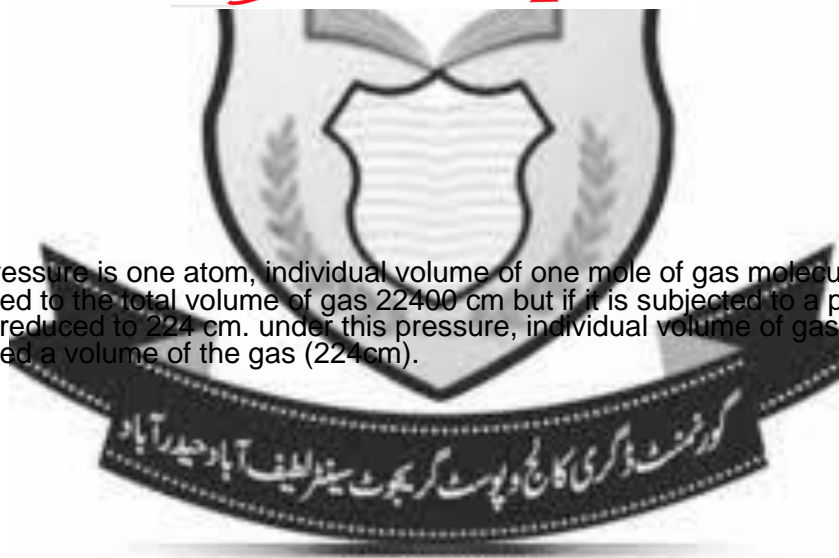
At a certain very low temperature the gases change into the liquid state. There force, attractive forces, between the gas molecules become significant near liquefying temperature that is why the ideal gases deviate from their original behavior t low temperature.

**EXAMPLE:**  $\text{SO}_2$  liquefies at  $-10^\circ\text{C}$  while  $\text{H}_2$  at  $-252.7^\circ\text{C}$ . There force attractive force between  $\text{SO}_2$  molecules cannot be considered negligible at room temperature for this reason, So gas shows non – ideal behavior at room temperature as compared to  $\text{H}_2$  gas.

**2. AT HIGH PRESSURE:** At low pressure actual volume of gas molecules is very small as compared to the volume of the container. However this volume does not remain negligible at high pressure. This can be understood from the following figure.



**SUPPOSE:** When pressure is one atom, individual volume of one mole of gas molecules say 32 cm is negligible as compared to the total volume of gas 22400 cm but if it is subjected to a pressure of 100 atom, the volume of the gas is reduced to 224 cm. under this pressure, individual volume of gas molecules (32 cm) is not negligible as compared a volume of the gas (224cm).



**STATES OF MATTER (LIQUID)**

**SHORT QUESTIONS**

**Q#01: explain the following in terms of kinetic molecular interpretation of liquids.**

- (a) Diffusion (b) compressibility  
(c) expansion (d) contraction (e) molecular motion

**DIFFUSIBILITY**

**DEFINITION:** The mixing two or more of the liquids to make homogeneous mixture is the diffusion of liquids.

For example: Mixing of colored solution with water.

Rate of diffusion of liquid is lesser than gases due to less intermolecular distances.

**REASON:-** The free movement of liquid molecules causes diffusion but the slow rate of diffusion is due to closeness of molecules.

**COMPRESSIBILITY**

**DEFINITION:** The ability of molecules of liquid to come closer on applying high pressure is called compressibility of liquid.

Liquids are very less compressible on applying high pressures.

**REASON:-** The molecules of liquid are close to another and there is not enough space between molecules to come closer on applying pressure.

**CONTRACTION**

**DEFINITION:** The decrease in volume of a liquid on decreasing temperature is called contraction.

When a liquid is cooled it contract and solidifies on further cooling.

**REASON:-** When a liquid is cooled its kinetic energy decrease so the velocity of molecules also decreases. Therefore the molecular volume decreases to give contraction.

**EXPANSION**

**DEFINITION:** The increase in volume of a liquid on increasing temperature is called expansion.

When a liquid is heated its kinetic energy increases so the velocity of molecules also increases. Therefore the molecular volume increases to give expansion.

**MOLECULAR MOTION**

**DEFINITION:** The movement of molecule of liquid is called molecular motion. Liquid molecules move randomly in all possible direction however due to small gaps and attractive force, speed of molecules is slower as compare to gas.

**Q#02: name three major kinds of intermolecular forces in liquid. Explain intermolecular force in HCl.**

The three intermolecular forces in liquids are

- (1) Dipole dipole interaction
- (2) London dispersion force
- (3) Hydrogen bond

**Intermolecular force in HCl:** HCl is a polar molecule and there is a partial positive charge on hydrogen atom and partial negative charge on chlorine atom. These opposite poles attract each other in liquid state due to dipole dipole interaction.

**Q#03: define the following:**

- (a) Molar heat of fusion (b) molar heat of vapourization (c) molar heat of sublimation

**Molar heat of fusion:** It is the amount of heat absorbed by one mole of a solid when it melts into liquid form at its melting point. The pressure, during the change, is kept at one atmosphere.

**molar heat of vaporization:** It is the amount of heat absorbed when mole of a liquid is changed into vapours at its boiling point

**molar heat of sublimation:** It is the amount of heat absorbed when one mole of a solid sublimates to give one mole of vapours at a particular temperature and one atmospheric pressure.

**Q# 4:describes hydrogen bonding in water. Explain the anomalous behavior of water due to hydrogen bonding.**

### **HYDROGEN BONDING**

**INTRODUCTION:** It is a secondary bond which is formed between different molecules of same compound and called as Intermolecular bond or **Protonic Bridge or Hydrogen bond**.

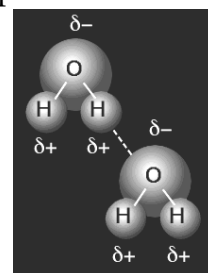
**DEFINITION:** The attractive forces between covalently bonded polarized hydrogen of one molecule and high electronegative atom of other molecule are called as Hydrogen bonding or Hydrogen Bond.

**REPRESENTATION:** This type of bond is represented by dotted lines.

**EXAMPLE:** In water molecule ( $H_2O$ ), Hydrogen acquires partial positive charge and oxygen acquires partial negative charge due to difference of electronegativity as shown below.

The partial positive hydrogen of one molecule is attracted by partial negative oxygen atom of other molecule. Due to this the attractive forces are created between two molecules. This type of attractive force which involves Hydrogen force is called Hydrogen Bond.

It is represented as shown below.



### **Anomalous Behavior Of Water**

**Definition:** When water at  $0^\circ C$  is heated, it goes on contracting till it reaches  $4^\circ C$ . After  $4^\circ C$ , it expands when heated as other liquids. This peculiar behavior of water in temperature range  $0^\circ C$  to  $4^\circ C$  is called anomalous expansion of water.

**Explanation :** when the temperature falls below the  $4^\circ C$  water molecules start arranging themselves by lining up in such a manner that each water molecule can form up to maximum number of four hydrogen bond. The increase number of hydrogen bonding, result in the freezing of water into ice. In the form of ice water molecules are arrange in the more regular hexagonal pattern in the manner that empty spaces are created in the structure of ice and its volume expands.

**Q#5:** water is more volatile than glycerin .but petrol is more volatile than water at the same temperature:

Water and glycerin both contains hydrogen bonding but glycerin contains greater number of hydrogen bond than water so water is more volatile than glycerin. Petrol is more volatile than water at the same temperature because water contains hydrogen bonding (strong intermolecular force) but petrol does not have hydrogen bond and contains weak intermolecular force.

**Q#5: Explain why?**

**Would a pressure cooker be of any value on the Mount Everest?**

**Reason:** The boiling point of water at which food is to be cooked can be increased by increasing pressure with the help of pressure cooker. At pressure 760 torr, the boiling point of water is  $100^\circ C$ . When the pressure is increased in pressure cooker, the boiling point also increased and food is cooked rapidly. On mountains, the outside pressure is less than atmospheric pressure and hence boiling point of water will be below  $100^\circ C$ , so food can not cooked without pressure cooker. Hence pressure cooker has great value at Mount Everest. .

**Why food is cooked more quickly in a pressure cooker than in a covered pot?**

**Reason:** The food is cooked more quickly in a pressure cooker than the covered pot because in a pressure cooker the molecules will evaporate from the liquid into the enclosed space and these molecules move above the liquid in cooker and can not escape and pressure increased inside the pressure cooker. Due to which the food is cooked more quickly than in a covered pot. **Evaporation is cooling process?**



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**Reason:** When liquids are heated, they evaporate and during evaporation the molecules with high energy escape from the surface of liquid, due to escape of high kinetic energy molecules, the average kinetic energy of the remaining molecules decreases. As we know that K.E is directly proportional to temperature, hence temperature of remaining liquids falls and cooling is taking place.

### **A falling drop of liquid is spherical?**

**Reason :** Surface molecules of liquid are pulled inward to decrease the surface area due surface tension, since the surface to volume ratio of sphere is small as compared to any other shape, due to which a small quantity of liquid always tend to form a spherical shape. Hence falling drop of liquid is spherical due to surface tension.

### **A drop of ink spreads on blotting paper?**

**Reason:** Surface of blotting paper is rough due to small pores. These pores have narrow channels which act as capillary tubes. When a drop of is placed on a blotting paper than due to capillary action ink rises into narrow channels of blotting paper that is why ink spreads on blotting paper rapidly.

### **Water boils at Mount Everest as 71°C while at sea level at 100°C?**

**Reason:** The normal boiling of liquid is the temperature at which its vapour pressure is equal to atmospheric pressure i-e 760 mm. The boiling of water at 760mm is 100°C. At high altitude the atmospheric pressure is less than 760 mm hence water boils at temperature below its boiling point i-e 100°C, the pressure at Mount Everest is about 540 mm therefore water boils at 71°C on it.

### **why does water spilled on a floor evaporate more rapidly than the same amount of water in a glass?**

**Reason:** The process of evaporation is affected by surface area of liquid. More evaporation is take place for larger area of surface .Water spilled on the floor spread on greater area on the floor and hence greater number of molecule are exposed for evaporation .Due this reason ,water spilled on a floor evaporate more rapidly then the some amount of water in a glass

### **Mercury has its Meniscus curved upward**

**Reason:** Meniscus is Greek word which means crescent. Mercury does not wet the surface of vessel. The nature of Meniscus depends upon interaction between liquid molecule and surface of vessel surface tension and adhesive forces. In condition of liquids which do not wet the surface of vessel the interaction is weak due to small adhesive forces and high surface tension . Thus the liquid is pushed away from the wall of vessel at the point of contact and hence its surface is curved upward

### **Honey is more viscous than water?**

**Reason :** The internal resistance of liquid to its flow is called viscosity. It depends upon inter molecular attraction forces as well as size of molecular and density etc. The intermolecular attractive forces, size, density of honey are much higher than water hence viscosity of honey is higher than water or honey is more viscous than water.

### **Viscosity of liquids decreases with the rise of temperature?**

**Reason:** As temperature increases, the molecules move more rapidly and K.E over come the forces which hold them together. Due to decrease of forces viscosity of liquid decrease..

### **Boiling point of liquid remains constant although heat is continuously supplied to the liquid**

**Reason :** On heating kinetic energy of a liquid increases because kinetic energy is directly proportional to temperature. It means by raising temperature the kinetic energy of molecules increases continuously until molecules of liquid attain their maximum energy and liquid start boiling. If heating is continued after boiling point, then the boiling point remains same but extra heat is used in the change of liquid i-e from liquid to vapour. It means extra heat is used to separate the liquid molecules and convert them at boiling point into a gas. Due to this boiling point remain same.

## **DETAILED QUESTION**

**QNO#01: What is viscosity? Explain factors affecting viscosity.**

### **VISCOSITY**

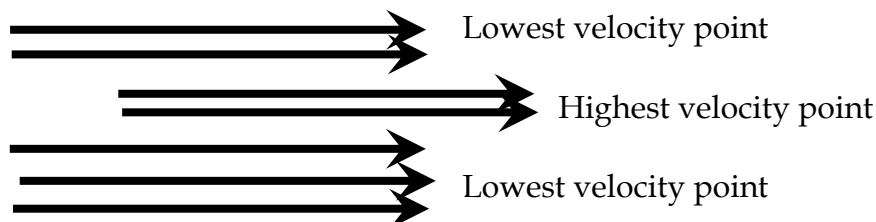
**DEFINITION:-** The internal resistance between the parallel layers to the flow of a liquid is called viscosity.

**Resistance of liquid to its flow is called as viscosity.**

**SYMBOL:** Viscosity of liquid is representing by  $\eta$ .

**EXPLANATION:-** When a liquid moves in a thin pipe, it moves in the form of layers. The layer attached to the wall of pipe is almost stationary. But when we go towards the centre of pipe, we see that the layers are moving with gradually higher velocity. Each layer experiences a friction from each side and this friction causes resistance to flow.

This resistance to flow is called viscosity of that moving liquid in the pipe.



**Flow of liquid in a pipe.**

**MOBILE LIQUIDS:-** Those liquids which have less viscosity are called thin liquids or mobile liquids or less viscous liquids.

**Example:-** Water, Ethyl alcohol etc.

**THICK LIQUIDS:-** Those liquids which have higher viscosity are called thick liquids or non mobile liquids or viscous liquids.

**EXAMPLE:-** Honey, Glycerin etc.

**UNITS OF VISCOSITY:**

**S.I UNITS:-**

Kilogram per meter per second

kg / m. Sec

Newton seconds per square meter

N. Sec / m<sup>2</sup>

Gram per centimeter per second

g / cm. sec

**CGS SYSTEMS:-**

Dynes second per centimeter square

dyne. Sec/ cm<sup>2</sup>

Poise

Poise

**UNITS EQUIVALENT:-**

1poise = 1dyne. Sec / cm<sup>2</sup>

1poise = 100 centi poise

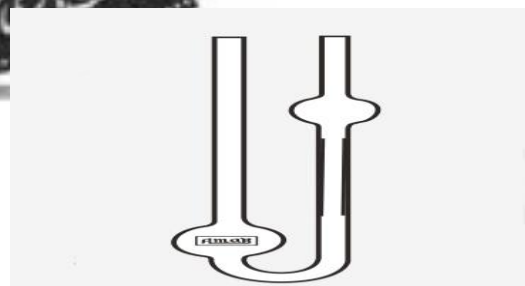
1centi poise = 0.001 (10<sup>-3</sup>) N. Sec / m<sup>2</sup>

1poise = 0.1 (10<sup>-1</sup>) N. Sec / m<sup>2</sup>

1poise = 1 g / cm. sec

**APPARATUS**

Viscosity can be measured by viscometer.



**(Viscometer)**

**FACTOR EFFECTING VISCOSITY:-**

**(a) TEMPERATURE:-** (Viscosity  $\propto 1 / \text{Temperature}$ ).

Viscosity of a liquid decreases with rise in temperature of liquid. When temperature is increased, the intermolecular distance also increases that causes less resistance between the layers of liquid to flow, hence viscosity also decreases.

**(b) INTERMOLECULAR ATTRACTION:-** (Viscosity  $\propto$  Intermolecular attractions) .

Greater will be the intermolecular attractions, higher will be the viscosity due to less intermolecular distances that causes higher resistance between liquid layers.



(c) **SIZE OF MOLECULES:-** (Viscosity  $\propto$  size of molecules)

Liquid of larger molecules have higher viscosity due to resistance to layers of molecules of liquid to flow.

(d) **SHAPE OF MOLECULES:-** Liquids of simple and spherical molecules have low viscosity due to less resistance to layers of molecules of liquid to flow but the liquids of complex, elongated and branched molecules have high viscosity due to comparatively higher resistance to layer of molecules of liquid to flow.

**QNO#02: What is SURFACE TENSION? Explain it with example. Give its uses and factors affecting on surface tension.**

**INTRODUCTION:-** All molecules of liquid are attracted by all sides; hence attraction are balanced from each side but at surface attraction are not balanced due to not having any layer of molecules at above the surface layer in liquid. This imbalanced attraction at surface of liquid is called surface tension.

**DEFINITION:-** The force per unit length acting at the surface of liquid is called surface tension  
OR

The energy per unit area acting at the surface of liquid is called surface tension.

**SYMBOL:-** Surface tension of liquid is represented by  $\gamma$ .

**EXPLANATION:-** All molecules are attracted by each other all the time from each side. The attraction in inner molecules of liquids from each side is balanced but at the top or surface layer of molecules the intermolecular attractions are balanced horizontally but are unbalanced vertically due to not having any other layer of molecules over the surface layer. This unbalanced attractive force at the liquid surface is called surface tension.

**UNITS OF SURFACE TENSION:-**

**CGS SYSTEM:-**

Dyne per centimeter (Force per unit length)      dynes / cm

Ergs per centimeter square (Energy per unit area)      ergs / cm<sup>2</sup>

**S.I SYSTEM:-**

Newton per meter (Force per unit length)      N / m

Joule per meter square (energy per unit area)      J / m<sup>2</sup>

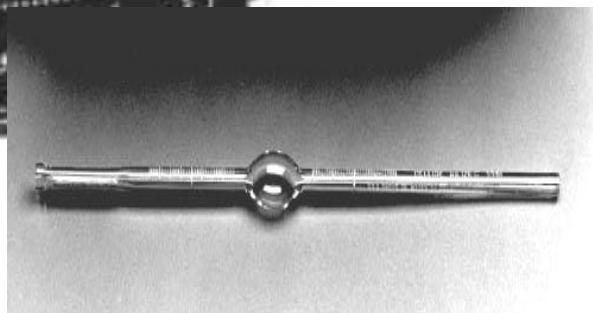
**UNITS EQUIVALENTS:-**

1 dyne / cm = 0.001 (10<sup>-3</sup>) N / m

2 dyne / cm = 1 erg / cm<sup>2</sup>

**APPARATUS:** It is measured by stalagmometer.

(Stalagomometer)



**FACTORS EFFECTING SURFACE TENSION:-**

(a) **TEMPERATURE:-** Surface tension  $\propto 1 / \text{Temperature}$

When temperature is increased, the intermolecular distances increases and intermolecular attractions decreases which causes less unbalanced pull (surface tension) at the liquid surface.

(b) **INTERMOLECULAR ATTRACTIONS:-** Surface tension  $\propto$  Intermolecular attractions

Stronger will be intermolecular attractions, higher will be surface tension due to greater unbalanced pull at the liquid surface.

**APPLICATION OF SURFACE TENSION:-** There are two major application of surface tension; Formation of drops of a liquid and capillary action.

**CAPILLARY ACTION:-** The rising of a liquid in the narrow cylindrical tube (capillary tube) is called capillary action.

**Wetting liquids** rise up in the capillary tube when it is dipped into these liquid because their cohesive forces are higher than their adhesive forces so their molecules are attracted towards the walls of container and pulled up.

**Non wetting liquids** falls down in the capillary tube when it is dipped into these liquids because their adhesive forces are higher than their cohesive forces so their molecules are attracted to each other at the greater rate to go down and do not attracted much towards the walls of container to be pulled up.

**DROP FORMATION:-** The surface tension keeps the liquid molecules together to form a drop. A falling drop is spherical because surface tension pulls up the drop but the gravity pulls it down. Hence the shape of drop becomes stretched.

**QNO#03: What is vapour pressure? Explain factors affecting vapour pressure.**

### **VAPOUR PRESSURE**

**INTRODUCTION:-** When we heat a liquid in a closed container, the liquid evaporates and condensed as well. After some time equilibrium is established between these two processes. At that time the pressure exerted by the vapours is called vapour pressure.

**DEFINITION:-** The pressure exerted by the vapours when they are at equilibrium with liquid phase

OR

The pressure exerted by the vapours when rate of expansion and rate of condensation are equal to one another

OR

The pressure exerted by the vapours when the evaporation and the condensation are at equilibrium.

**EXAMPLE:-** Liquid water  $\xrightleftharpoons[\text{Condensation}]{\text{Evaporation}}$  Water vapour

In pressure cooker the phenomena of vapour pressure is applied.

**EXPLANATION:-** When a liquid is heated in an open container, some of the vapour convert back to the liquid state but most of the vapours escape into surrounding and equilibrium is not established between liquid and vapour phase. When a liquid is heated in a closed container, about all the vapours convert back to liquid state hence condensation take place and equilibrium is established between evaporation and condensation. When liquid and vapour phases are at equilibrium to each other, at that the pressure exerted by the vapour is called vapour pressure.

### **FACTOR EFFECTING VAPOUR PRESSURE**

**(a) TEMPERATURE:-** (vapour pressure  $\propto$  Temperature)

Vapour pressures increase with the increase of temperature due to increase in average kinetic energy of liquid molecules.

**(b) INTERMOLECULAR ATTRACTION:-** Those liquids have stronger intermolecular forces will show low vapour pressure and those liquids which have weaker intermolecular forces will show high vapour pressure.

**(c) NATURE OF LIQUID:-** Vapour pressure depends upon the nature of liquid. Low boiling liquids exert more vapour pressure at a given temperature

**QNO#04: Describe the process of evaporation:**

### **EVAPORATION**

**Definition:** The conversion of a liquid into its vapour without external heating is called EVAPORATION.

**Explanation:** Evaporation is the process by which a liquid changes into a gas or vapor state. This occurs when the molecules in a liquid gain enough energy to overcome the attractive forces holding them together, and escape into the surrounding environment. The energy required for evaporation comes from the heat of the liquid, and as a result, evaporation is often accompanied by cooling.

**Factors affecting evaporation:** The numbers of molecules of a liquid converted in vapour per unit time is called rate of evaporation. The rate of evaporation depends on several factors, including the temperature of the liquid, the surface area exposed to the surrounding environment,

**Intermolecular force:** The heat of vaporization increases as intermolecular attractive forces increases and vice versa.

**Surface area:** Rate of evaporation increases with the increase in surface are and vice versa.

**QNO#05: What is meant by liquid crystal? How is it differing from liquids and crystalline solids?**

**LIQUID CRYSTALS:**

**INTRODUCTION:** The discovery of liquid crystals is attributed to Austrian botanist Friedrich Reinitzer, who observed a strange behavior of a material called cholesteryl benzoate in 1888. He noticed that the substance melted into a cloudy liquid at a certain temperature and then transformed into a clear, viscous liquid that remained cloudy even upon cooling.

**Definition:** Liquid crystals are a unique state of matter that has properties of both liquids and crystals. In a liquid crystal, the molecules are arranged in an ordered pattern like a crystal, but they can also flow and move like a liquid.

**Molecular structure:** The molecules in a liquid crystal are typically elongated and have a long axis that aligns with the long axis of neighboring molecules. This alignment gives the liquid crystal its ordered, crystalline structure. However, the molecules are not rigidly held in place like in a solid crystal, and can instead move around each other like in a liquid.

**Difference between a liquid crystal and a liquid:** difference between a liquid crystal and a liquid is that a liquid crystal has a higher degree of order, with the molecules all aligning in a particular direction. In contrast, the molecules in a liquid are more randomly arranged and do not have the same level of order.

**Difference between a liquid crystal and a solid:** A liquid crystal differs from a crystalline solid in that the molecules in a crystalline solid are tightly packed together and held in place by strong chemical bonds. In a liquid crystal, the molecules are not rigidly fixed in place and can move around each other like in a liquid.

**Importance of liquid crystal:** Liquid crystals have a number of practical applications, including in electronic displays like LCD screens, as well as in temperature sensors and optical devices. some important uses of liquid crystal are as under:

**1 Display Technology:** Liquid crystals are commonly used in display technology, including televisions, computer screens, and mobile devices. Liquid crystal displays (LCDs) offer high contrast, low power consumption, and are thin and lightweight, making them ideal for use in modern electronic devices.

**2 Optics:** it is useful in optical devices such as polarizers, optical filters, and waveplates.

**3 Materials Science:** Liquid crystals have a unique structure that makes them interesting for materials science research.

**4 Biological Applications:** They can be used to study the orientation of molecules in biological membranes, and they have been used to develop biosensors that can detect the presence of specific molecules in biological fluids.

**QNO#06: What is hydrogen bonding? How is it established? Give its application in industrial and biochemical process.**

**INTRODUCTION:** It is a secondary bond which is formed between different molecules of same compound and called as Intermolecular bond or **Protonic Bridge or Hydrogen bond**.

**DEFINITION:** The attractive forces between covalently bonded polarized hydrogen of one molecule and high electronegative atom of other molecule are called as Hydrogen boding or Hydrogen Bond.

**REPRESENTATION:** This type of bond is represented by dotted lines.

**Application of hydrogen bonding in biochemical process:** Hydrogen bonding plays a critical role in many biochemical processes.

**Protein folding:** Hydrogen bonding is critical in the folding of proteins into their three-dimensional shapes. The folding process involves the formation of hydrogen bonds between different parts of the protein molecule, helping to stabilize the protein structure.

**DNA replication:** Hydrogen bonding plays a crucial role in the complementary base pairing of DNA during replication.

**Enzyme catalysis:** enzymes use hydrogen bonds to stabilize the transition state of a reaction, lowering the activation energy required for the reaction to proceed.



**Water solubility:** Many biomolecules, such as sugars and amino acids, are highly soluble in water due to their ability to form hydrogen bonds with water molecules.

**Industrial Application of hydrogen bonding**

**Water Treatment:** Hydrogen bonding plays an essential role in water treatment processes such as reverse osmosis and distillation.

**Adhesives and Coatings:** Hydrogen bonding is used in the formulation of adhesives and coatings. In these applications, .

**Pharmaceuticals:** Hydrogen bonding can affect the solubility, stability, and bioavailability of drugs, making it an important consideration in drug design.

**Polymers:** Hydrogen bonding is an essential factor in the formation and properties of many polymers. It can affect the strength, flexibility, and other physical properties of the material.

**Food Science:** Hydrogen bonding plays a role in the texture and stability of many food products.



## STATE OF MATTER (SOLIDS)

### SHORT QUESTIONS

**QNO#01: Define the following terms:**

**Allotropy:**

**Definition:** Different forms of the same element having different arrangement of their atoms are called allotropic modification or simply allotropy.

OR

The property by virtue of which an element exists in more than one forms is called as allotropy.

**Sublimation:**

**Definition:** There are some solids which do not melt on heating but directly convert into vapour such solids are known as sublime solids and the process itself known as sublimation.

**MELTING POINT**

**Definition:** The process of conversion of solid into liquid is called melting.

The temperature at which solid changes into molten state is called melting point.

**Unit cell**

**Definition:** The smallest volume of crystal which shows all the characters of its parent is called unit cell.

OR

A unit cell is the basic structural unit which when repeats in three dimensions to generate the crystal.

**QNO#02: Define anisotropy: what type of solids has this property.**

**Definition:** anisotropy is the unique behavior of crystalline solids. It is define as the physical properties are different in different direction in a crystal due to arrangements of particles is different directions.

**Explanation:** The certain physical properties such as refractive index, coefficient of thermal expansion, electrical and thermal conductivity are different in different direction in a crystal lattice.

**For example:** graphite conduct electricity parallel to the layer because of electron movement is not allowed on perpendicular of the layer.

**QNO#03: what is transition temperature? Explain with example:**

**Definition:** The temperature at which two allotropic forms of the same element co exist in equilibrium with each other is known as transition temperature

For example: The transformation of monoclinic sulphur to rhombic sulphur is reversible. Below 95.5°C rhombic sulphur is stable above 95.5°C monoclinic sulphur is stable. It means at 95.5°C both form of sulphur occur in equilibrium.

This temperature at which both forms of sulphur are in equilibrium is called as transition temperature i.e. is about 95.5°C.

**QNO#04: Explain why diamond is the non conductor of electricity and graphite is a conductor.**

**Reason :** In graphite, each carbon atom is  $sp^2$  hybridized the fourth electron of each carbon forms the delocalized  $\pi$  bond because the  $\pi$  electron are mobile, so graphite conducts electricity easily.

In diamond, each carbon atom is bonded strongly to four other carbon atoms which are located at the corners of regular tetrahedrons, which is  $sp^3$  hybridized and no free electrons, are left so diamond is non conductor of electricity.

**QNO#05: Define lattice energy. Explain how it is affected by size and charge of ion?**

**Definition:** The amount of energy required to break one mole of an ionic solid into its ions is called LATTICE ENERGY.

The amount of energy released when oppositely charged ions combine to give one mole of a Crystal Lattice is called LATTICE ENERGY.

For example: Lattice energy of NaCl crystal  $-787 \text{ KJ mol}^{-1}$ .

**Factors:** lattice energy is affected by size of ion and charge of ion.

(a) **Size of ions:** the smaller the size of ion , the closer the packing of oppositely charged ions and acquire high energy to break the lattice

**For example:** the lattice energy of NaF (923 kJ/ mol) is greater than KF (821 kJ/ mol) because of smaller size of  $\text{Na}^+$  ion than  $\text{K}^+$  ion

(b) **Charge of ion:** the greater the charge of ion , smaller the size of ion so higher will be the lattice energy

**For example:** the lattice energy of  $\text{BeF}_2$  is (3505 kJ/ mol) is much higher than LiF (1036 kJ/ mol) because Li carries +1 charge whereas Be carries +2 charge.



**QNO#06:** Differentiate between the following:

**DIFFERENCE BETWEEN CRYSTALLINE AND AMORPHOUS SOLID**

SNO	Crystalline Solid	Amorphous Solid
1	All crystal possess characteristics geometric shapes	Amorphous solids do not possess characteristics geometric shapes.
2	They are anisotropic	They are isotropic
3	They have sharp melting point	They do not have sharp melting point
4	The particles are arranged in almost perfect order	The particles are not arranged in perfect order
5	They break down at fixed cleavage planes	They do not break down at fixed cleavage planes
6	They are symmetrical	They are not symmetrical
7	Example : NaCl Diamond etc	Example: Plastic, glass etc

**DIFFERENCE BETWEEN isomorphism and polymorphism SOLIDS:-**

SNO	Isomorphism	Polymorphism
1	The phenomenon in which two or more compounds occur in the same crystalline structure.	It is the phenomenon in which a solid substance exists in more than one crystalline form.
2	They have different physical and chemical properties	They have same chemical properties but different physical properties
3	When their solutions are mixed, they form mixed crystal.	When their solutions are mixed, they do not form mixed crystal
4	They show the property of growth.	They do not show property of growth
5	They have same crystalline system.	They have different crystalline system
6	$\text{CaCO}_3$ and $\text{NaNO}_3$ (trigonal) $\text{ZnSO}_4$ and $\text{NiSO}_4$ (orthorhombic)	Calcite ( $\text{CaCO}_3$ ) trigonal Aragonite : ( $\text{CaCO}_3$ ) orthorhombic

**QNO#07: explain the following with scientific reason:**

**i) The compressibility of solids is nearly zero?**

**Reason:** In terms of kinetic molecular theory, the particles of solids are so tightly bound together that only slight unfilled space is left, so they can withstand considerable external stress.

**ii) Why some solids are sublime in nature?**

**Reason :** Some solids are sublime in nature because they have a high vapor pressure at room temperature and atmospheric pressure, it means that their molecules are highly volatile and easily escape from the solid into the gas phase. These solids have weak intermolecular forces

**DETAILED QUESTIONS**

**QNO#01: Define unit cell. Draw a diagram to show its axial distances and axial angles.**

**UNIT CELL**

**DEFINITION:-** The smallest volume of crystal which shows all the characters of its parent is called unit cell

**OR**

A unit cell is the basic structural unit which when repeats in three dimensions to generate the crystal.

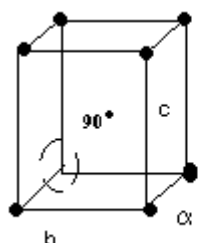
A unit cell is described by:

- (a) length of its edges, denoted by  $a, b, c$  and
- (b) angles between the edges, denoted by  $\alpha, \beta, \gamma$ ,

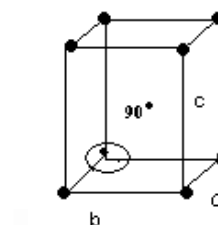
**TYPES OF UNIT CELLS**

**There are seven crystal systems as:**

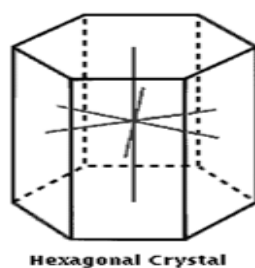
SNO	crystal	Sides	Angles	Example
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, diamond etc
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SnO <sub>2</sub> , BaSO <sub>4</sub>
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Fe SO <sub>4</sub> , Zn SO <sub>4</sub> . 7H <sub>2</sub> O, KNO <sub>3</sub>
4	Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ 90^\circ > 120^\circ$	NaNO <sub>3</sub> , KNO <sub>3</sub> , Ice.
5	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ , $\gamma = 120^\circ$	Graphite, CdS, ZnO
6	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ , $\beta \neq 90^\circ$	CaSO <sub>4</sub> , Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O



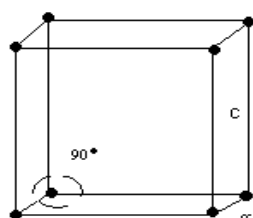
Tetragonal unit cell



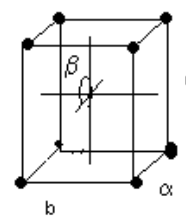
Orthorhombic unit cell



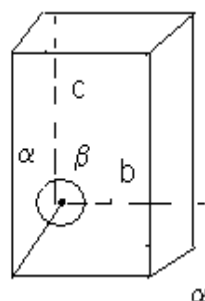
Hexagonal Crystal



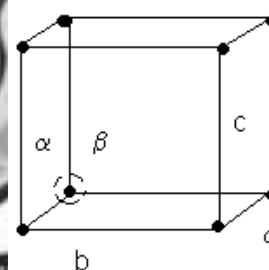
Cubic Unit cell



Monoclinic unit cell



Triclinic unit cell



Rhombohedral unit cell

**QNO#02: what is ionic crystal? Give characteristics of ionic crystal. How can you determine the number of Na<sup>+</sup> and Cl<sup>-</sup> ions in a unit cell of sodium chloride.**

**Definition:** The crystals which consist of oppositely charged ions joined by ionic bond are called IONIC CRYSTALS.

FOR EXAMPLE

NaCl, KCl, CaCl<sub>2</sub>, MgO etc.

**CHARACTERISTICS:** ionic crystals have following properties.

- (1) Ionic crystals show property of growth of crystal.
- (2) Ionic crystals are hard and brittle.
- (3) Ionic crystals are bad conductor of electricity.
- (4) Ionic crystals have high melting points.
- (5) Ionic crystals have high boiling points.
- (6) Ionic crystals have high values of lattice energy.
- (7) Ionic crystals have highest heats of fusions

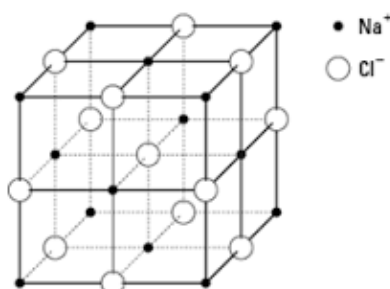
#### **STRUCTURE OF SODIUM CHLORIDE**

Sodium chloride (NaCl) has a crystal lattice structure, which means that the atoms are arranged in a repeating three-dimensional pattern. The crystal structure of sodium chloride is based on a face-centered cubic lattice. In this lattice, each ion (sodium or chloride) is located at the center of a cube, and the nearest neighbors of each ion are located at the corners of adjacent cubes.

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The ions are held together by strong electrostatic attractions between the positive and negative charges. The overall structure of sodium chloride can be visualized as a three-dimensional network of ions, with sodium ions surrounded by six chloride ions, and chloride ions surrounded by six sodium ions.

The crystal structure of NaCl is as follows:



In summary, the structure of sodium chloride is a face-centered cubic lattice in which each sodium ion is surrounded by six chloride ions, and each chloride ion is surrounded by six sodium ions.

### QNO03: Give a brief account of metallic solid. Why they conduct heat and electricity:

Definition: The crystals in which metal atoms are joined by metallic bond are called METALIC CRYSTALS.

FOR EXAMPLE

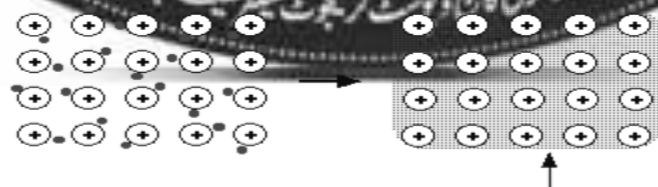
Na, Fe, Cu etc

#### CHARACTERISTICS

1. They are good conductor of heat because the free electrons absorb heat and their kinetic energy increases these free electrons then tends to move towards the other ends of metal which is relatively cooler.
2. They are good conductor of electricity because of free movement of delocalized electron in electric field.
3. They are hard, ductile and malleable.
4. They have high melting and boiling point.
5. They have high tensile strength.
6. They have high heat of fusion and lattice energies.

**Definition:** Metallic bonding constitutes the electrostatic attractive forces between the delocalized electrons, called conduction electrons, gathered in an electron cloud, and the positively charged metal ions.

**Explanation:** Force of attraction operating in a metal that holds the atoms together in a metallic structure. In metallic bonding, metal atoms form a close-packed, regular arrangement. The atoms lose their outer-shell electrons to become positive ions. The outer electrons become a 'sea' of mobile electrons surrounding a lattice of positive ions. The lattice is held together by the strong attractive forces between the mobile electrons and the positive ions.



### QNO04: what is meant by polymorphism? How it is related to allotropy. Give your answer with examples.

#### POLYMORPHISM

**DEFINITION:-** It is the phenomenon in which a solids substance exist in more than one crystalline forms under a given set of temperature and pressure.

**POLYMORPHOUS SUBSTANCE:-** It is a substance, which can exist in more than one crystalline forms.

#### PROPERTIES:

1. They have same formula having same type of composition.
2. They have same properties.
3. They have different crystalline system.s

**EXAMPLE:-**Calcium carbonate exist in two different crystalline structures i-e

Calcite : It has trigonal structure.      Aragonite : It has orthorhombic structure.

in terms of element polymorphism is called allotropy which is define as

**Definition:** Different forms of the same element having different arrangement of their atoms are called allotropic modification or simply allotropy.      OR

The property by virtue of which an element exists in more than one forms is called as allotropy.

Example: The important crystalline forms of sulphur.

(i) Rhombic sulphur.

(ii) Monoclinic sulphur.

**QNO05: Molecular solids are soft and possess low melting point. How can you justify this statement?**

The crystals consist of molecules that are held together by weak attractive forces are called molecular solids. Molecular solids are soft and possess low melting point because molecule are held together by weak Vander Waal forces.

**QNO06: Describe types of crystal in detail:**

### **TYPES OF CRYSTAL**

Types of crystals are based upon the bonding between the particles; the crystals are divided into four types.

- (1) **ATOMIC CRYSTALS:-** The crystals consist of atoms packed together by metallic bond are called atomic crystals or metallic crystals. In metals the valence electron are loosely held and move freely from one atom to another. They create negative charge atmosphere around the positively charged metals ions. This negative charge atmosphere is called electron cloud.

#### **PROPERTIES:**

1. They are good conductor of heat and electricity.
2. They are lustrous.
3. They possess high melting points.
4. They are ductile and malleable.

- (2) **IONIC CRYSTALS:-** The crystals consist of oppositely charged ions are called ionic crystals. These oppositely charged ions are held together by electrostatic force of attraction.

#### **PROPERTIES :**

1. They are hard and brittle.
2. They have high melting point.
3. They conduct electricity in molten state.

- (3) **COVLENT CRYSTALS:-** The crystals consist of atoms, which are held, together by covalent bonding, are called covalent crystals. These covalent bonds are strong and require high energy to break.

#### **PROPERTIES:**

1. They are usually non-conductor of heat and electricity.
2. They have high melting points.
3. They have low densities.
4. They have high value of refractive index.

- (4) **MOLECULAR CRYSTALS:-** The crystals consist of molecules that are held together by weak attractive forces are called molecular crystals. In these crystals following attractive forces are present.

- (a) **HYDROGEN BONDING:-** It is the electrostatic force of attraction between partially positive hydrogen of one molecule and the electronegative atom of other molecule.

- (b) **VANDERWAAL'S FORCES:-** It is the attractive forces develop between the atomic nuclei of one atom and electrons of other molecule.

#### **PROPERTIES:**

1. They are soft.
2. They have low melting point.
3. They are usually non-conductors of heat and electricity.

**QNO07: What is isomorphism? Write down its characteristics:**

### **ISOMORPHISM**

**DEFINITION:-** The phenomenon in which two or more compounds occur in the same crystalline structure.

#### **Characteristics:**

1. They have different physical and chemical properties.
2. They have same empirical formula.



3. When their solutions are mixed, they form mixed crystal.

4. They show the property of our growth.

**EXAMPLE:-** Following are the pairs of isomorphous substances:

1  $\text{CaCO}_3$  and  $\text{NaNO}_3$  : Both have trigonal structure.

2  $\text{ZnSO}_4$  and  $\text{NiSO}_4$  : They have orthorhombic structure.

## **CHAPTER# 07**

# **CHEMICAL EQUILIBRIUM**

**INTRODUCTION:-** Equilibrium is a Latin word and is composed of Aequos + Libra, where aequos means equal and Libra means (state of balance).

**TYPES OF REACTIONS:-** All the chemical reactions do not proceed to the same extent, some proceed to completion and some never go to completion, thus they are of two types.

❖ REVERSIBLE REACTION

❖ IRREVERSIBLE REACTION

## **REVERSIBLE REACTION**

**DEFINITION:-** The reaction which proceeds in both directions is called reversible reaction.

OR

The reaction in which forward and reverse reactions occurs are called reversible reactions and these reactions never proceeds to completion.

**EXPLANATION:-**

❖ The term reversible is taken from reverse which means back.

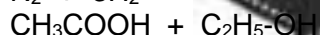
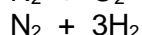
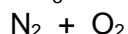
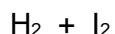
❖ These are two way reactions.

❖ The products of these reactions can be converted into reactants back.

❖ These reactions never go to completion.

**REPRESENTATION:-** It is represented by double half arrows (  $\rightleftharpoons$  ).

**EXAMPLE:-**



## **IRREVERSIBLE REACTIONS**

**DEFINITION:-** Those reactions which proceeds in only one direction are called irreversible reactions

OR

The chemical reactions in which products are not able to react to form original reactants under same set of conditions

OR

Those reactions which proceed to completion in a definite direction are called irreversible reactions.

**EXPLANATION:-**

❖ The term irreversible is composed of two words (ir) means not and (reverse) means back.

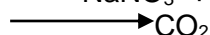
❖ These are one way reactions.

❖ The product of these reactions cannot be converted into the reactants back.

❖ These reactions go to completion.

**REPRESENTATION:-** These reactions are represented by a single headed arrow (  $\longrightarrow$  ).

**EXAMPLE:-**



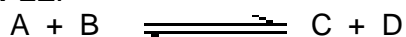
## **CHEMICAL EQUILIBRIUM OR EQUILIBRIUM STATE**

**DEFINITION:-** The state in reversible reaction at which the rate of forward direction becomes equal to the rate of backward direction is called chemical equilibrium or equilibrium state.



**REPRESENTATION:-** The chemical equilibrium is represented by double half arrows pointing in opposite direction.

**EXAMPLE:-**



**EXPLANATION:-** Consider the following general reaction.



In beginning, the rate of forward reaction is greater but as (C) and (D) are formed then the reverse reaction also starts. Due to the increase in rate of forward reaction a stage is reached, where forward as well as backward reaction proceeds with the same rate, this state is called equilibrium state. This chemical equilibrium is the example of dynamic equilibrium because in this equilibrium the constant interchange of substances is taking place at constant rate.

### **LAW OF MASS ACTION OR LAW OF EQUILIBRIUM**

**INTRODUCTION:-** This law was introduced by Guldberg and wage in 1864. It is applicable to reversible reactions only and is also known as law of equilibrium.

**STATEMENT:-** The rate of chemical reaction is directly proportional to the concentration of the reactants.

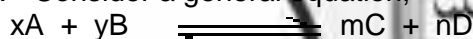
**OR**

Rate of chemical reaction is directly proportional to the product of active masses of reactants (active masses means the concentration of reactants in moles per cubic decimeter and is represented by square brackets [ ]).

**EXPLANATION:-**

- ❖ Those concentrations which take part in a chemical reaction are called active masses.
- ❖ The active masses are represented by square brackets [ ].
- ❖ The unit used for active masses is moles per litre or moles per cubic decimeter.

**DERIVATION:-** Consider a general equation;



where;

- x => number of moles of A.
- y => number of moles of B.
- m => number of moles of C.
- n => number of moles of D.

According to the law of mass action;

$$\begin{aligned} \text{Rate of forward reaction} &\propto [A]^x [B]^y \\ \text{Rate of forward reaction} &= K_1 [A]^x [B]^y \quad \dots\dots\dots 1 \\ \text{Rate of backward reaction} &\propto [C]^m [D]^n \\ \text{Rate of backward reaction} &= K_2 [C]^m [D]^n \quad \dots\dots\dots 2 \end{aligned}$$

At equilibrium state, the rates of forward and backward reaction are equal

$$\begin{aligned} \text{Rate of forward reaction} &= \text{Rate of reverse reaction} \\ K_1 [A]^x [B]^y &= K_2 [C]^m [D]^n \end{aligned}$$

$$\frac{K_1}{K_2} = \frac{[C]^m [D]^n}{[A]^x [B]^y}$$

$$K_c = \frac{[C]^m [D]^n}{[A]^x [B]^y}$$

- ❖  $K_c$  is the equilibrium rate constant that is defined as the ratio between the concentration of reactants and products raised by their number of moles.
- ❖  $K_c$  is the ratio between the forward and backward rate constant ( $K_1 / K_2$ ).
- ❖  $K_c$  is the overall rate constant of a reversible reaction.
- ❖  $K_c$  can be represented for both gaseous and non-gaseous reactions.

### **THE EQUILIBRIUM CONSTANT OF GASEOUS REACTIONS**

When reactants and products are in a gaseous state, their partial pressures are used instead of their concentrations, because at a given temperature partial pressure of a gas is directly proportional to its concentration.



According the law of mass action;

$$K_P = \frac{[P_C]^m [P_D]^n}{[P_A]^x [P_B]^y}$$

Where;

$P_A$  => Partial pressure of gas A.

$P_B$  => Partial pressure of gas B.

$P_C$  => Partial pressure of gas C.

$P_D$  => Partial pressure of gas D.

$K_P$  => Equilibrium rate constant for gaseous reactions.

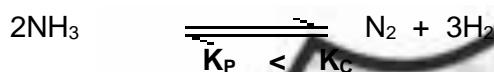
There are

**K<sub>p</sub>**:- It is defined as the ratio between the ratio of reactants and the products raised by their number of moles.

- ❖ If volume of reactants is equal to the volume of products then the value of  $K_C$  will be equal to  $K_P$ .  
$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K_P = K_C$$

- ❖ If volume of products is greater than the volume of reactants then the value of  $K_P$  will be greater than  $K_C$ .



$$K_P < K_C$$

- ❖ If volume of reactants is greater than the volume of products then the value of  $K_P$  will be smaller than  $K_C$ .



### **APPLICATION OF LAW OF MASS ACTION**

The value of equilibrium constant in the reversible reaction predicts, as follows;

- ❖ The direction of reaction.
- ❖ The extent to which a reaction proceeds.

### **PREDICTION OF DIRECTION OF A REACTION:-**

There are three possibilities.

- ❖ If calculated value of  $K_C$  is greater than the actual value of  $K_C$  then reaction will shift towards backward direction.
- ❖ If calculated value of  $K_C$  is smaller than the actual value of  $K_C$  then reaction will shift towards forward direction.
- ❖ If calculated value of  $K_C$  is equal to the actual value  $K_C$ s then reaction is at equilibrium.

### **PREDICTION OF EXTENT OF A REACTION:-**

- ❖ If value of  $K_C$  is very large then forward reaction is almost complete OR reactants are unstable. For example;  $O_3$  quickly decomposes to  $O_2$  because  $K_C$  is very large and  $O_3$  is unstable.



- ❖ If  $K_C$  is very small then forward reaction proceeds with negligible rate or reaction are fairly unstable and backward reaction is almost complete. For example; HF in water dissolving only 8% that is why  $K_C$  is very small.



- ❖ If value of  $K_C$  is moderate then the reaction will proceed in both directions.



### **LE-CHATLIER'S PRINCIPLE**

### **(FACTORS EFFECTING BALANCE OF CHEMICAL EQUILIBRIUM)**

**INTRODUCTION:-** This principle was introduced by Le-chatlier in 1881. This principle studies the effect of concentration, temperature and pressure on equilibrium.

**STATEMENT:-** When the stress is applied to a system at equilibrium, then the equilibrium tries to minimize or undo the effect of that stress, this phenomenon is regarded as Lechatlier's principle.

#### **EFFECT OF CHANGE OF CONCENTRATION:-**

SPECIES	CHANGE IN CONCENTRATION	EFFECT ON THE REACTION TO RE ESTABLISH EQUILIBRIUM
REACTANTS	Increase	Reaction will go forward
	Decrease	Reaction will go backward
PRODUCTS	Increase	Reaction will go backward
	Decrease	Reaction will go forward

**EFFECT OF CHANGE OF TEMPERATURE:-**

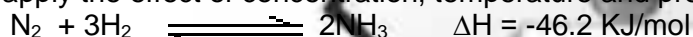
NATURE OF REACTION	CHANGE IN TEMPERATURE	EFFECT ON THE REACTION TO RE ESTABLISH EQUILIBRIUM
<b>ENDOTHERMIC</b> $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$	Increase	Reaction will go forward
	Decrease	Reaction will go backward
<b>EXOTHERMIC</b> $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$	Increase	Reaction will go backward
	Decrease	Reaction will go forward

**EFFECT OF CHANGE OF PRESSURE:-**

VOLUME	CHANGE	EFFECT ON THE REACTION TO RE ESTABLISH EQUILIBRIUM
$V_R > V_P$ $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}$	Increase	Reaction will go forward
	Decrease	Reaction will go backward
$V_R < V_P$ $2\text{O}_3 \rightleftharpoons 3\text{O}_2$	Increase	Reaction will go backward
	Decrease	Reaction will go forward
$V_R = V_P$ $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$	Increase	No effect on equilibrium position
	Decrease	No effect on equilibrium position

**APPLICATIONS OF LE-CHATLIER'S PRINCIPLE:-**

Let us apply the effect of concentration, temperature and pressure on following equilibrium reactions.



**EFFECT OF CONCENTRATION:-** If more nitrogen and hydrogen gases are added into the system at equilibrium then the reaction will proceed in forward direction, i.e; more ammonia will be formed until a new equilibrium is established. On the other hand if more ammonia is added then the reaction will proceed in backward direction, i.e; more nitrogen and hydrogen will form until a new equilibrium is established. It means that the increase in the concentration on ( $\text{H}_2$ ) ( $\text{N}_2$ ) increases the formation of  $\text{NH}_3$  or vice versa.

**EFFECT OF TEMPERATURE:-** There is no effect of rise of temperature on exothermic reactions but the rise of temperature will effect the endothermic reactions. In the above given example, the forward reaction is exothermic and the backward reaction is endothermic. It means that the increase in temperature favours in the increase of the rate of backward reactions and hence more ( $\text{H}_2$ ) and ( $\text{N}_2$ ) will form until an equilibrium is established.



**EFFECT OF PRESSURE:-** In the given example, the total volume on the left hand side is (4) and on the right hand side is (2). We know that with the increase of pressure, the volume decreases given by;

$$V \propto \frac{1}{P}$$

It means that the increase in pressure on above system at equilibrium favours the equilibrium to forward direction and more ammonia will form until a new equilibrium is established.

**SOLUBILITY PRODUCT**

**DEFINITION:-** It is the product of ionic concentration of a salt in its aqueous solution, when dissolved and un-dissolved ions are at equilibrium.

**OR**

The multiplication of ionic concentrations in a saturated solution of soluble salt is a constant product is called solubility product.

**SYMBOL:-** It is indicated by (ksp).

**DERIVATION:-** Consider an aqueous saturated solution of sparingly soluble salt such as ( $\text{AgCl}$ ). An equilibrium is established between solid state and its ions in solution as follows;

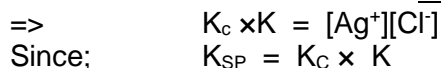


By applying law of mass action, we get;

$$\Rightarrow K_c = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

But at saturation, the concentration of solid ( $\text{AgCl}$ ) is constant.

$$\text{Since; } K = [\text{AgCl}] \quad \Rightarrow \quad K_c = \frac{[\text{Ag}^+][\text{Cl}^-]}{K}$$



$$\Rightarrow K_{SP} = [Ag^+][Cl^-]$$

( $K_{SP}$ ) is called solubility product constant or solubility product.

**UNIT:-**  $K_{SP}$  is expressed in (mole /dm<sup>3</sup>).

**APPLICATIONS:-** Solubility product is applied to know whether the salt will be precipitated out from its solution or not.

- ❖ If the product of ionic concentration is equals to ( $K_{SP}$ ), this means that the solution is saturated and no precipitation will be taken place.
- ❖ If the product of ionic concentration is greater than ( $K_{SP}$ ), this means that the solution is super saturated and precipitation will be taken place.
- ❖ If the product of ionic concentration is less than ( $K_{SP}$ ), this means that the solution is unsaturated and no precipitation will be taken place.

**USES:-** It is used to calculate the solubility of a solid. It is used to calculate the concentration of ions and quantitative analysis of salts.

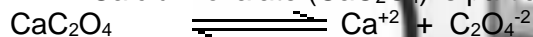
### **COMMON ION EFFECT**

**DEFINITION:-** The reduction in degree of ionization of a weak electrolyte in presence of a strong electrolyte containing one common ion is called common ion effect

**OR**

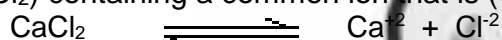
The effect by which the solubility of the salt decreases in the solution that contains already a common ion is called common ion effect.

**EXAMPLE:-** Calcium oxalate ( $CaC_2O_4$ ) is partially soluble in water, it ionize as follows;



Here;  $K_{SP} = [Ca^{+2}][C_2O_4^{-2}]$

If ( $CaCl_2$ ) containing a common ion that is ( $Ca^{+2}$ ) is added, which is highly soluble in water, it ionizes as;



Here;  $K_{SP} = [Ca^{+2}][Cl^{-2}]$

By the addition of calcium chloride ( $CaCl_2$ ) to the calcium oxalate ( $CaC_2O_4$ ) solution the solubility of ( $CaC_2O_4$ ) further reduces, this is called common ion effect.

**Why solubility of salt reduces on the addition of common ion ?**

On the basis of Le-chatlier's principle when a common ion is added to the solution of a salt, the concentration of dissolved ions increases, therefore the reaction goes backward towards undissolved particles which settles down to give precipitates of solid.

According to the theory of solubility product, when a common ion is added to the solution of a salt, the ionic product of that salt increases than its solubility product. We know that the salt precipitates out from its solution if its ionic product becomes greater than its solubility product.

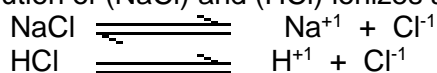
### **APPLICATIONS OF COMMON ION EFFECT:-**

**IN QUANTITATIVE SALT ANALYSIS:-** The cations of second A group are precipitated as sulphides ( $CuS$ ,  $CdS$ ,  $PbS$ ) by passing ( $H_2S$ ) gas through their solution in presence of ( $HCl$ ). ( $H_2S$ ) and ( $HCl$ ) ionizes as;



( $HCl$ ) produces ( $H^{+1}$ ) ion as common ion, thus addition of ( $HCl$ ) reduces the ionization of ( $H_2S$ ). due to this reason, the cations of second group are precipitated as ( $CuS$ ,  $PbS$ ,  $CdS$ )

**PURIFICATION OF COMMON SALT:-** The common salt is precipitated by passing out ( $HCl$ ) gas through the solution of ( $NaCl$ ) and ( $HCl$ ) ionizes as;



In this condition common ion is ( $Cl^{-1}$ ), it suppresses (decreases) the ionization of ( $NaCl$ ) and hence pure sodium chloride is precipitated. In this way common salt is purified by common ion effect.

**APPLICATIONS IN INDUSTRY:-** In industry the yields may be controlled as well as greatly increased by the use of common ion effect.



## CHAPTER# 08

### Acids, bases and salts

#### ACIDS:

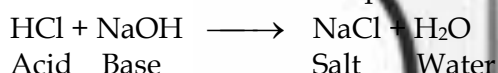
**Definition:** Those compounds which provide hydrogen ions ( $H^+$ ) in aqueous solution are called acids.

#### Physical properties:

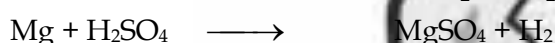
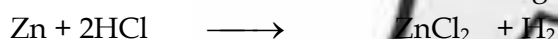
- 1-They have a sour taste.
- 2-They turn blue litmus to red.
- 3-Aqueous Solution of acids conducts Electricity.
- 4-Strong acids destroy fabrics, animal tissue and effect on skin.
- 5-It acts as an antiseptic in the stomach of human.

#### Chemical properties:

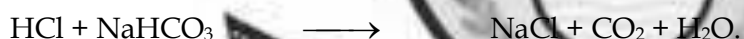
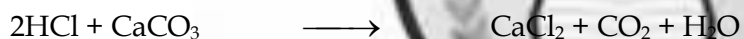
- 1- Acids neutralize bases and produce salt and water



- 2- Acid reacts with some metals like Zn, Mg, Fe etc. forming their salts and liberate  $H_2$  gas.



- 3- Most of the acids react with carbonates and bicarbonates, decomposes them and produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



#### BASE

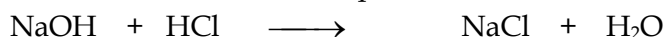
**Definition:** Those compounds which provide hydroxide ions ( $\text{OH}^-$ ) in aqueous solution are called bases.

#### PHYSICAL PROPERTIES OF BASES:

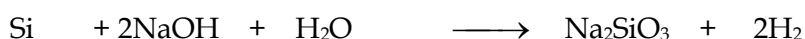
1. They have a bitter taste.
2. They have a slippery touch.
3. they turn red litmus to blue.
4. Aqueous solution of bases conduct electricity.

#### CHEMICAL PROPERTIES OF BASES:

1. Bases neutralize acids and produce salt and water.



2. Bases dissolve certain metals like Zn, Al etc and non metals like Si to liberate hydrogen gas.



3. Bases react with fats to form soaps.
4. Bases can dissolve proteins and some other organic compounds

#### THEORIES OF ACIDS AND BASES

##### 1-ARRHENIUS CONCEPT:

**Introduction:** A Swedish chemist Svante Arrhenius in 1887, proposed a theory about acids and bases. According to this concept acids and bases are define as.

**Acid:** An acid is that substance which produces hydrogen ions ( $H^+$ ) in aqueous solution.

**Bases:** Bases are those substances which produces hydroxide ions in aqueous substance.

**Example:** HCl is an acid and NaOH is a base because they produce  $H^+$  and  $\text{OH}^-$  ion in water respectively.



**Draw backs:**

1. This concept could not explain the basicity of ammonia (NH<sub>3</sub>) acidity of CO<sub>2</sub> and other similar compounds.
2. It is only applicable in aqueous solutions.

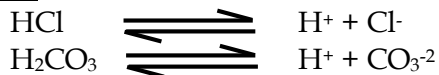
**2-LOWRY AND BRONSTED CONCEPT**

**Introduction:** Bronsted and Lowry in 1923 proposed more satisfactory definition of acids and bases.

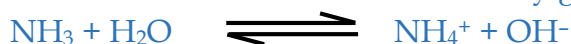
**Acids:** A species (a compound or ion) which donate or tends to donate a proton (H<sup>+</sup>) in any chemical reaction.

**Base:** A species which accepts or tends to accept a proton in any chemical reaction.

**Example:** HCl and H<sub>2</sub>CO<sub>3</sub> are Bronsted acids. Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> are Bronsted Bases.



**CONJUGATE ACID** It is the acid formed by gaining a proton from another acid.



NH<sub>4</sub><sup>+</sup> is the conjugate acid of the base NH<sub>3</sub>.

**CONJUGATE BASE**

It is the base formed by losing a proton to another base.



The anion Cl<sup>-</sup> is the conjugate base of the acid HCl.

ACID		base		Conjugated acid		Conjugated BASE
HCl	+	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	Cl <sup>-</sup>
H <sub>2</sub> SO <sub>4</sub>	+	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	HSO <sub>4</sub> <sup>-</sup>
HSO <sub>4</sub> <sup>-</sup>	+	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	SO <sub>4</sub> <sup>2-</sup>
CH <sub>3</sub> COOH	+	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	CH <sub>3</sub> COO <sup>-</sup>

**Conclusion:** In short, an acid is a proton donor and a base is a proton acceptor.

**3-LEWIS THEORY**

**Introduction:** G. N Lewis in 1923 proposed acid base theory in which, acids are electron loving (electrophile) and bases are nucleus loving (nucleophile).

**Acid:** An acid is any species (molecules or ions) which can accept a pair of electron.

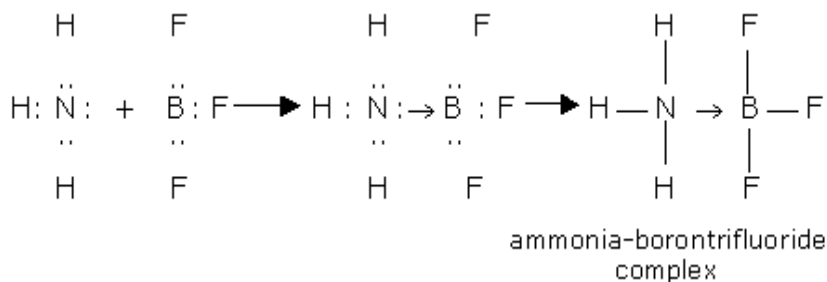
**Base:** Base is any species (molecule or ion) which can donate a pair of electrons.

**Explanation:** In 1923, an American chemist Lewis proposed electronic definition for those acids and bases which do not contain hydrogen in an acid-base reaction, the electron pair donor is base and electron pair acceptor is acid. Those species form co-ordinate bond.

**Example:** 1- Reaction of NH<sub>3</sub> with H<sup>+</sup>



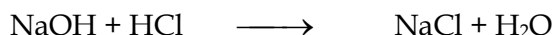
**Example:** 2- The reaction of NH<sub>3</sub> with BF<sub>3</sub>.



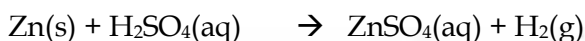
### **SALT**

**Definition:** A salt is an ionic compound, which is produced when an acid neutralized by a base.

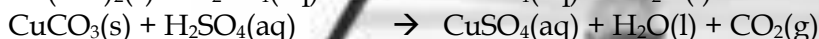
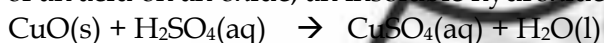
**PREPARATION:** NaOH (Sodium hydroxide or caustic soda) neutralize HCl (Hydrochloric acid) to form NaCl (Sodium Chloride) and water.



Action of an acid on a metal.



Action of an acid on an oxide, an insoluble hydroxide or an insoluble carbonate.



Action of an acid on soluble hydroxide or carbonate.



### **TYPES OF SALTS:**

Salts are divided into three groups on the basis of their chemical nature.

**1- Normal Salt:** The salts which are formed by the complete neutralization of an acid by base are called normal salts: e.g NaCl, NaNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>.

**2- Acidic Salt:** The salts which are formed by the partial neutralization of an acid by base are called acidic salt. e.g NaHSO<sub>4</sub> (Sodium bi Sulphate) KHCO<sub>3</sub> (Potassium bi carbonate) .These salts contain replaceable hydrogen ion.

**3- Basic Salt:** The salts which are formed by the partial neutralization of a base by an acid e.g Mg(OH)Cl, Zn(OH)Cl are the examples of basic salt. These salts have replaceable

### **pH (POWER OF HYDROGEN ION)**

**INTRODUCTION:-** PH means power of hydrogen ion where (P) stands for power and (H) stands for hydrogen ion.

In 1909, Sorensan suggested a simple method for expressing the concentration of hydrogen ion in terms of PH.

**DEFINITION:-** PH is a convenient method of expressing the acidity or basicity of dilute aqueous solution

OR

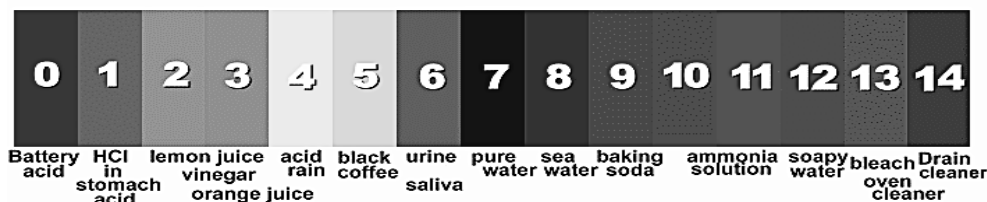
It is the negative logarithm to the hydrogen ion concentration.

**FORMULA:-**

$$\text{PH} = -\log [\text{H}^{+1}]$$

or  $\text{PH} = \log [1 \setminus \text{H}^{+1}]$

**EXPLANATION:** - PH is a simple way for expressing the acidity or basicity of solutions. PH for neutral solutions is (7), for acidic solutions it is less than (7) and for basic solutions is greater than (7). Usually acidity or basicity is measured on a scale from (0-14), this is called as PH scale.



**EXAMPLE:-**

- ❖ PH of HCl = 01 (very acidic).
- ❖ PH of CH<sub>3</sub>COOH = 2.9 (weak acidic).

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- ❖ PH of milk = 6.6 (very slightly acidic).
- ❖ PH of NaOH = 13 (very alkaline or basic).
- ❖ PH of  $\text{Na}_2\text{CO}_3$  = 11.6 (weak basic).
- ❖ PH of sea water = 08 (very slightly basic).

### USES OF PH:-

- ❖ It controls the clinical analysis.
- ❖ The control of PH in living system is very essential for their health. For example; PH of blood is constant and its value is about (7.3), if it drops below (7) or rises above (7.8) a person may die.

### BUFFER SOLUTIONS OR BUFFERS

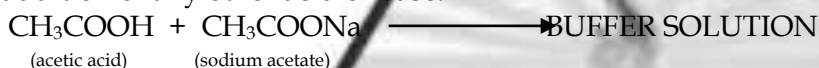
**DEFINITION:-** A solution which has reserved acidity or basicity is called as buffer solution  
**OR**

Buffers are those solutions which resist in the change of PH.

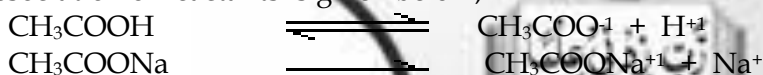
**BUFFER ACTION:-** Resistance of the solution to change in hydrogen ion concentration upon the addition of small amount of acid or base is known as buffer action.

**EXPLANATION:-** The buffer solutions are usually prepared by mixing a weak acid and its salt or a weak base and its salt, such type of mixture is called buffer mixture.

For example; The solution of  $(\text{CH}_3\text{COOH})$  and  $(\text{CH}_3\text{COONa})$  is buffer solution because it resist the change in its PH by addition of any other acid or base.



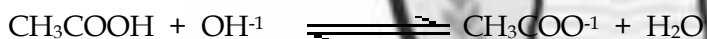
The dissociation of reactants is given below;



- ❖ If small amount of acid is added, the additional  $(\text{H}^{+1})$  ion in the solution will combine with  $(\text{CH}_3\text{COO}^{-1})$  ion to form unionized acetic acid and PH will remain at original level.

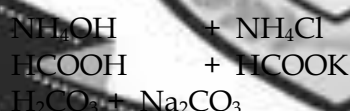


- ❖ If base is added then additional  $(\text{OH}^{-1})$  ion will be neutralized by the reaction with weak acid  $(\text{CH}_3\text{COOH})$  and hence PH remains same.



It means, this solution resists change in its PH by the addition of acids or bases, hence it is buffer solution.

### OTHER EXAMPLES:-



### PROPERTIES OF BUFFERS:-

- ❖ It has a definite PH value.
- ❖ It resists change in PH value.
- ❖ Its PH value does not change on dilution.

### IMPORTANCE OF BUFFERS:-

- ❖ It is useful in agriculture for healthy seeding and growth of crops.
- ❖ Buffers are used in the manufacturing of leather, photographic materials, dies and electroplating.
- ❖ It is used in the manufacturing of paper ink, pens, drugs etc.
- ❖ The control of PH in living system Is essential for their health. For example; the PH of blood is constant and it is about (7.3), this is because human blood is buffered with bicarbonates and phosphates etc.

### HYDROLYSIS

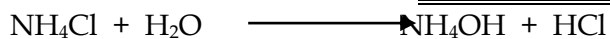
**DEFINITION:-** The reaction in which the cations and anions of a salt reacts with ions of the solvent (water) to produce acidic-basic solution is called hydrolysis **OR** The reactions of cations and anions with water so as to change the salt (PH) is called hydrolysis.

**EXPLANATION:-** The aqueous solution of normal salts may be neutral, acidic or alkaline depending the nature of the salt. For example; aqueous solution of ammonium chloride is acidic, sodium carbonate is alkaline and sodium chloride is neutral.

**REASON:-** Hydrolysis occurs only when bonds between (H-O-H) are broken and when change in the PH of the solution takes place.

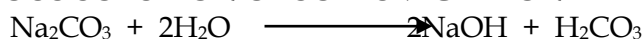
### EXAMPLE:-

**AQUEOUS SOLUTION OF AMMONIUM CHLORIDE IS ACIDIC:-**



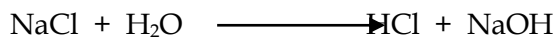
As a strong acid (HCl) is formed which has higher concentration of ( $\text{H}^+$ ) ions So PH of the solution is changed towards acid, therefore the resulting solution of ammonium chloride and water becomes acidic.

**AQUEOUS SOLUTION OF SODIUM CARBONATE IS BASIC:-**



As a strong base (NaOH) is formed which has higher concentration of ( $\text{OH}^-$ ) ions so PH of the solution is changed towards base. Therefore the solution of sodium carbonate in water is basic.

**AQUEOUS SOLUTION OF SODIUM CHLORIDE IS NEUTRAL:-**



When water is added to (NaCl), no hydrolysis takes place because there is no change in PH of the solution due to the formation of strong acid (HCl) and strong base (NaOH).

## SHORT QUESTION

**Q1: Show that  $\text{pH} + \text{pOH} = 14$**

We know that dissociation constant of water is  $K_w$  which is equal to

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$K_w = 1 \times 10^{-14}$$

$$1 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$$

Applying negative logarithm on both side  $-\log(1 \times 10^{-14}) = -\log[\text{H}^+][\text{OH}^-]$

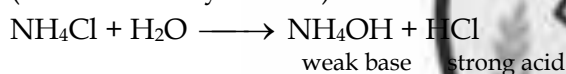
We know that  $\log a \times b = \log a + \log b$

$$-(-14) = \{-\log[\text{H}^+] + (-\log[\text{OH}^-])\}$$

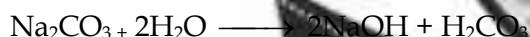
$$\text{pH} + \text{pOH} = 14 \quad \text{As } -\log[\text{H}^+] = \text{pH} \text{ and } -\log[\text{OH}^-] = \text{pOH}$$

**Q2: Why the aqueous solution of  $\text{NH}_4\text{Cl}$  is acidic and  $\text{Na}_2\text{CO}_3$  is alkaline.**

1. The aqueous solution of  $\text{NH}_4\text{Cl}$  produces strong acid HCl (Hydrochloric acid) and weak base  $\text{NH}_4\text{OH}$  (Ammonium hydroxide) with water



2. The aqueous solution of  $\text{Na}_2\text{CO}_3$  is basic because  $\text{Na}_2\text{CO}_3$  produce strong base NaOH and weak acid  $\text{H}_2\text{CO}_3$  with water



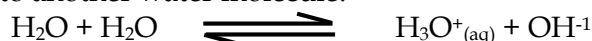
**Q3: Write down the conjugate base of the following acid**

Acid	Conjugate base
$\text{H}_2\text{SO}_4$	$\text{SO}_4^{2-}$
$\text{H}_2\text{S}$	$\text{S}^{2-}$
$\text{NH}_4^+$	$\text{NH}_3$
$\text{HCOOH}$	$\text{HCOO}^-$

**Q4: What is meant by self Ionization of water? Write the expression of  $K_w$ . What is its value at  $25^\circ\text{C}$ .**

**SELF IONIZATION OF WATER**

Water conducts electricity due to very small extent due to self ionization ability. Proton from one water molecule is transferred to another water molecule.



Equilibrium expression

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

$$K = [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Hence  $K = [\text{H}_2\text{O}]^2 = K_w \longrightarrow$  dissociation constant for water

Now equation become  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

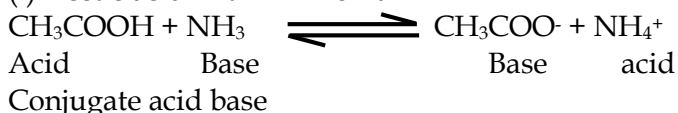
At  $25^\circ\text{C}$ , value of  $K_w$  is  $1.0 \times 10^{-14}$ , small value of  $K_w$  shows that self ionization of water occurs to very small extent.



Water is amphoteric So  $[H^+] = [OH^-] = 1 \times 10^{-7}$

**Q5: write equation and indicates the conjugate acid base pairs for the following**

(i) Acetic acid with Ammonia



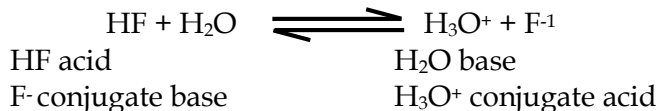
$\text{CH}_3\text{COOH}$  acid

$\text{CH}_3\text{COO}^-$  conjugate base

$\text{NH}_3$  base

$\text{NH}_4^+$  conjugate acid

(ii) Hydrofluoric acid & water



## **CHAPTER# 09**

# **INTRODUCTION TO CHEMICAL KINETICS**

### **SHORT QUESTIONS**

**Q#1: Define the following**

**(a) CHEMICAL KINETICS:** The word kinetics was derived from a Greek word Kinetic which means moving. The study of rate of chemical reaction and the mechanism by which the reaction takes place is called chemical kinetics

OR

The study of rate of chemical reaction and the factors which influence the rate of reaction is called chemical kinetics.

**(b) RATE OF A REACTION**

**DEFINITION:** - The amount of reactants consumed per unit time is called rate of reaction

OR

The amount of product formed per unit time is called rate of reaction.

**FORMULA: -**

$$\text{Rate of reaction} = \frac{\text{Amount of reactants consumed}}{\text{Time taken}}$$

$$\text{Rate of reaction} = \frac{\text{Change of concentration of reactant or product}}{\text{Time taken}}$$

**(C) VELOCITY OF A REACTION:**

**DEFINITION:** - It is defined as the rate of a reaction at a particular moment i.e.; at a specific time.

**EXPLANATION:** - Let us consider a very small interval of time (dt) in which the change in concentration is (dx) and it is taken constant. Therefore, the velocity of reaction will be representing following expression.

$$\text{Velocity of reaction} = \frac{\Delta x}{\Delta t}$$

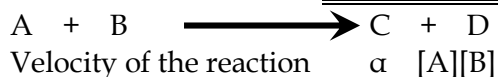
For the purpose of simplicity, we may not differentiate between rate and velocity of a reaction up to this level, hence both represented by (dx / dt).

**UNIT OF RATE OF REACTION:** - The concentration of reactants or products is expressed in (moles / dm<sup>3</sup>) and time is expressed in seconds. Therefore, the unit for rate of reaction will be (moles / dm<sup>3</sup> / sec) or (moles / dm<sup>3</sup>.sec).

**(c) RATE CONSTANT**

According to the law of mass action rate or velocity of a reaction is directly proportional to active mass or molar concentration of the reactants.

Let us apply this law to the following general reaction;



But velocity of the reaction =  $dx / dt$ ;

$$\Rightarrow \frac{\Delta x}{\Delta t} \propto [\text{A}] \times [\text{B}]$$

$$\Rightarrow \frac{\Delta x}{\Delta t} = K [\text{A}] \times [\text{B}]$$

Here (K) is rate constant;

$$\Rightarrow K = \frac{\text{Rate}}{[\text{A}] \times [\text{B}]}$$

**SPECIFIC RATE CONSTANT:** - It Is defined as the rate of reaction when molar concentration of each reactant is unity (1 mole / dm<sup>3</sup>).

For the reaction;



If;  $[\text{A}] = [\text{B}] = 1 \text{ moles per dm}^3$

Then;

$$\Rightarrow \frac{dx}{dt} (r) = K [\text{A}] \times [\text{B}]$$

$$\Rightarrow K = \frac{r}{[\text{A}] \times [\text{B}]} = \frac{r}{1 \times 1} = r \text{ or } \frac{dx}{dt}$$

Q#3 how can you define order of reaction? What are the units of zero order, first order and second order reaction?

### ORDER OF THE REACTION

**DEFINITION:** - The number equals to the sum of all the exponents of the concentration in terms of the reactants involves in the rate equations known as order of a reaction.

**EXAMPLES:** -



$$dx / dt (r) = K [\text{N}_2\text{O}_5]^1; \text{ (the reaction is of first order).}$$



$$dx / dt = K [\text{CH}_3\text{CHO}]^2; \text{ (the reaction is of second order)}$$



$$dx / dt = K [\text{NO}]^2 \times [\text{O}_2]^1; \text{ (the reaction is of third order as } (2 + 1 = 3)).$$

**EXPLANATION:** - The order of reaction is assigned to a reaction only on the basis of experiments and not by considering total number of molecules present in the reaction. It is because in a reaction there may be more reacting molecules but the concentration of only one or two molecules may change during the reaction. For photo chemical reactions, rate of reaction is independent of the concentration of the reacting molecules, therefore such reactions are of zero order. For a reaction, minimum order of reaction is zero order and maximum may be third order.

**UNITS OF K:**

- The unit of K for zero order reaction is mol l<sup>-1</sup> sec<sup>-1</sup> OR mole dm<sup>-3</sup> sec<sup>-1</sup>
- The unit of K for first order reaction is sec<sup>-1</sup>
- The unit of K for second order reaction mol<sup>-1</sup> l sec<sup>-1</sup> OR mole<sup>-1</sup> dm<sup>3</sup> sec<sup>-1</sup>
- The unit of K for third order reaction is mol<sup>-2</sup> l<sup>2</sup> sec<sup>-1</sup> OR mole<sup>-2</sup> dm<sup>6</sup> sec<sup>-1</sup>

**Q#4: Explains the following:**

**(1) powder marble reacts more rapidly than the chunk of marble  $\text{CaCO}_3$ ?**

**Reason:** The reactivity of substance depends upon its surface area, greater the surface area available for reaction than greater will be the reactivity of the substance. Powder Zinc provide more surface area than chunk of Zinc hence powdered Zinc is more reactive than chunk of Zinc

**(2) Milk sours more rapidly in summer than in winter?**

**Reason:** souring of milk in summer due to bacterial activity at high temperature.

**(3) Reactants in solution reacts faster at high concentration**

**Reason:** the concentration of substance represents the number of moles and molecules per unit volume. The higher the concentration of reactants the more is the chances of molecular collision and hence the more is the rate of reaction.

**Raise the temperature cause an increase in the rate of reaction:**

**Reason:** A rise in temperature increases the kinetic energy of reacting molecules which enhance the frequency of collision which cause an increase in the rate of reaction

**Q#5: Differentiate between the following**

**(a) Rate of reaction and rate constant**

SNO	Rate of reaction	Rate constant
1	Change in concentration of reactant or product per unit time	Rate constant is the proportionality constant
2	Depend upon the molar concentration of reactants and product	Does not depend upon the molar concentration of reactants and products
3	Depends on the temperature indirectly	Depends on the temperature directly
4	Depends on the time taken for the reaction	Does not Depends on the time taken for the reaction

**(b) Homogenous Catalysts and Heterogeneous Catalyst**

Homogeneous Catalysts	Heterogeneous Catalysts
Same phase as reaction medium. Insensitive to fatty acid and water content	Usually distinct solid phase
Often difficult to separate	Readily separated
Expensive and difficult to recycle	Readily regenerated and recycled
Often very high rates. Base catalysis highly favour kinetics	Rates not usually as fast as homogeneous
Not diffusion controlled	May be diffusion controlled
High selectivity	Lower selectivity
Short life and requires extensive purification step.	Long life and less purification step

**(c) Catalyst VS Inhibitor**

Catalyst	Inhibitor
Definition Catalyst is a chemical compound that can increase the rate of a reaction without itself being consumed	Inhibitor is a chemical compound that can either stop or decrease the reaction rate of a chemical reaction

Use	Increase the reaction rate	Either stop or decrease the reaction rate
Mechanism of action	Provides an alternative reaction pathway by producing a reaction intermediate	Either deactivates the catalyst or removes the reaction intermediates
Example	Enzymes, Raney, Nickel, Zeolite, Photocatalysts etc	Acetanilide, many drugs such as penicillin etc

**(d) Difference between elementary and nonelementary reaction**

Elementary Reaction	Nonelementary Reaction
<ul style="list-style-type: none"><li>For elementary reactions, the order of each reactant in the rate equation is identical with the stoichiometric coefficient of that species in stoichiometric equation.</li><li>These are single step reaction.</li><li>Elementary reactions are simple in nature.</li><li>For elementary reaction the order of reaction must be integer.</li><li>.</li></ul>	<ul style="list-style-type: none"><li>For nonelementary reactions, the order of each reactant in the rate equation is not identical with the stoichiometric coefficient of that species in stoichiometric equation.</li><li>These are multistep reaction.</li><li>nonelementary reactions are complex in nature.</li></ul>

**DESCRIPTIVE QUESTIONS**

**Q1: Enlist various factors which influence on the rate of chemical reactions and describe the effect of concentration and surface area of reactants on the reaction rate.**

**FACTORS EFFECTING RATE OF A REACTION**

The rate of chemical reaction depends upon following factors.

- ❖ Concentration of the reactants.
- ❖ Surface area of reactants.
- ❖ Temperature
- ❖ Catalyst.
- ❖ Light or radiation.

**1- CONCENTRATION OF REACTANTS:** - The rate of reaction depends upon the concentration of the reactants, greater the concentration then higher will be the rate of reaction.

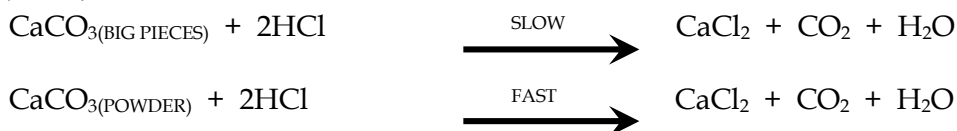
This may be explained as given below;

By increasing the concentration of the reactants, the number of effective collisions increases. Due to increase of effective collisions more product will be formed.

**EXAMPLE:-** If we put small piece of sodium in water the reaction will be slow but if a big piece of sodium is put in water the reaction becomes violent (vigorous).

**2- SURFACE AREA:-** The rate of reaction depends upon the surface area of the solid reactants or on the size of solid particles. Smaller the size of solid particles greater will be the surface area and hence faster will be the reaction.

**EXAMPLE:-**



It means we can say that by increasing surface area the rate of reaction increases, similarly amorphous boron is much more reactive than crystalline boron.

**3- TEMPERATURE:** - The rate of chemical reaction is directly proportional to the temperature because at higher temperature greater fraction of colliding molecules possess activation energy which is necessary for reaction.

**EXAMPLE:** - Lime stone ( $\text{CaCO}_3$ ) does not produce ( $\text{CO}_2$ ) gas at room temperature but it gives it on heating. Generally, rate of reaction becomes double for rise in ( $10^\circ\text{C}$ ).



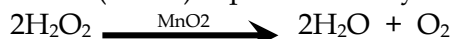
**4- CATALYST:** - Catalyst is that reaction which alters the rate of reaction without undergoing a chemical change or remain unchanged at the end of a reaction **OR** A substance which changes (mostly increases) the rate of chemical reaction without undergoing a permanent change in itself is called catalyst.

Basically they are classified as;

- ❖ Positive catalyst.
- ❖ Negative catalyst.

**POSITIVE CATALYST:** - Positive catalyst increases the rate of reaction by lowering the energy of activation (minimum energy required for reaction). As a result the number of effective collisions increases and hence increases the rate of chemical reaction.

**EXAMPLE:** - ( $\text{MnO}_2$ ) is positive catalyst for the decomposition of ( $\text{H}_2\text{O}_2$ ) i.e; it increases the rate of reaction.



**NEGATIVE CATALYST:** - Negative catalyst decreases the rate of reaction by increasing the energy of activation.



**5- LIGHT (RADIATION):** - There are certain reactions which proceed only under the influence of light (sunlight etc). These chemical reactions are called photo-chemical reactions.

In these reactions, the concentration of reactants does not influence the rate of reaction but the rate alters due to light and hence such reactions are called zero-order reactions.

**EXAMPLE:-** Photo chlorination of ( $\text{CH}_4$ ) is the example of zero order reactions and is influenced by light only.



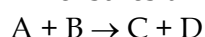
Radiation of light consists of photons only ( $h\nu$ ). When photons strike the reactant molecules, then they provide necessary activation energy to the reactant molecules to react.

**Q2: Explain in terms of collision theory how the reaction rate increases with rise of temperature**

### **COLLISION THEORY**

According to this theory:

1. A chemical reaction takes place only by collisions between the reacting molecules.
2. Only a small fraction of the collisions produces a reaction.
3. The two main conditions for a collision between the reacting molecules to be productive are:
  - (a) The colliding molecules must possess sufficient kinetic energy to cause a reaction.
  - (b) The reacting molecules must collide with proper orientation. The correct orientation is that which ensures direct contact between the atoms involved in the breaking and forming of bonds.



$$\text{Rate} = f \times p \times z$$

$f$  = fraction of molecules which possess sufficient energy to react

$p$  = probable fraction of collisions with effective orientations

$z$  = collision frequency.

**Q3: What is meant by energy of activation and activated complex, explain with the help of potential energy diagram:**

### **ENERGY OF ACTIVATION**

**INTRODUCTION:** - The rate of chemical reaction depends upon energy of activation. The reaction which possess low energy of activation are fast while the reactions with high energy of activation are slow it means that by changing the energy of activation the reaction may be made fast or slow.

**DEFINITION:** - The minimum energy required for a collision to be effective, to produce molecules of the product is called activation energy.

**OR**

The minimum amount of energy required in addition to average energy (average + access energy) which is sufficient to convert reactants into products is called activation energy.

**OR**

The access energy that the reacting molecule having average energy less than threshold energy must acquire in order to react and change into products is called activation energy.

**EXPLANATION:** - Chemical reactions occur when reacting molecules come into actual contact through collision. However, all collisions do not form products, but only few effective collisions are responsible for a chemical reaction (formation of products).

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It is found that only those collisions are effective in which colliding molecules possess threshold energy.

Before collision, molecules of reactants possess certain energy which is called average internal energy but this average internal energy is less than threshold energy. When molecules collide then they acquire certain access energy. The sum of average internal energy and access energy in effective collision is responsible for the formation of products and is called threshold energy.

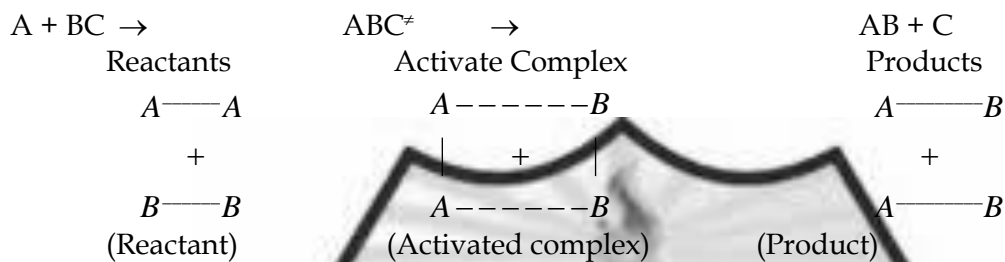
The difference of average threshold energy and average internal energy is called activation energy.

Activation energy = Threshold energy - average internal energy.

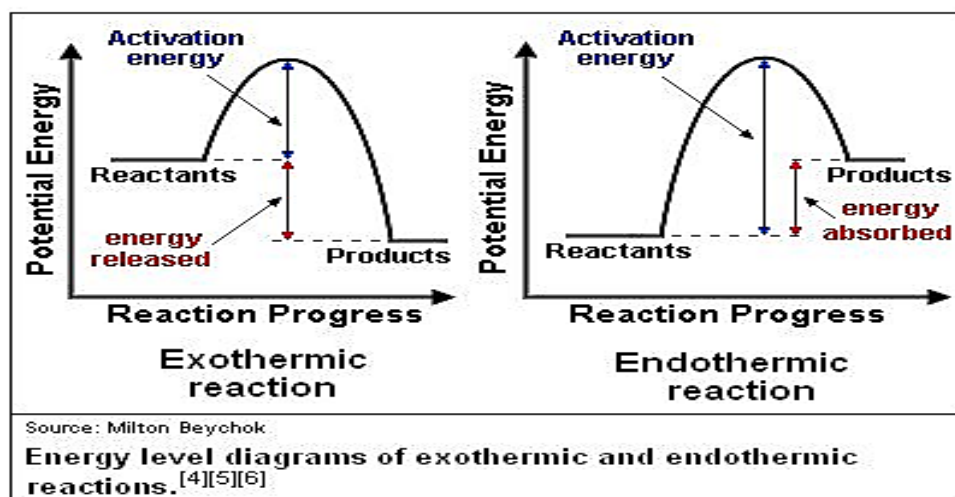
### TRANSITION STATE THEORY OR ACTIVATE COMPLEX THEORY

This theory assumed that simply

1. a collision between the reactant molecules does not really cause a reaction.
2. The reactant molecule forms a transition state or activated complex which decomposes to give the products.



Potential diagram:



Chapter#10

SOLUTION AND COLLOIDS  
SHORT QUESTION

QNO#01: What is concentration? Define various units of concentration:

QNO#02: Define molarity and molality. Which of these depends on temperature?

**Concentration:** Concentration is the ratio between the amount of solute and the amount of solvent in which the solute is dissolved

OR

Mass or volume of a solute present in known amount of solvent or solution is called concentration.

**Example:** 5% NaCl solution means 5g of NaCl is dissolved in 95g of water.

**Unit/ Expression:** Some of the common units of concentration are;

1. Molarity (M).
2. Molality (m).
3. Mole fraction (X).
4. Percentage (%).
5. Ppm (parts per million)

**MOLARITY:**

**Definition:** The number of moles of solute dissolved in 1 liter (1dm<sup>3</sup>) of solution.

It is denoted by (M).

Molarity of the solution is temperature dependent because the volume of solution increases or decrease with temperature.

**Example:** 1 mole of NaOH (40g) is dissolved in 1 liter of solution the solution is called one molar solution. Similarly a semi molar solution of NaOH will contain 20g dissolved in 1 liter of solution.

**Formula:** 
$$\text{Molarity} = \frac{\text{no of moles of solute}}{1 \text{ litre or } 1 \text{ dm}^3 \text{ of solution}}$$

OR

$$\text{Molarity} = \frac{\text{mass of solute in grams} \times 1000}{\text{formula mass of solute} \times \text{volume of solution in ml}}$$

**MOLALITY:**

**Definition:** It is defined as number of moles of solute dissolved per 1000 g (1Kg) of solvent. It is denoted by (m).

**Example:** When 1 mole of Na<sub>2</sub>CO<sub>3</sub> (formula mass) is 106g dissolved in 1000 g. the solution is said to be one molal solution.

**Formula:**  $\text{Molality} = \frac{\text{no of moles of solute}}{\text{kilograms of solution}}$

$\text{Molality} = \frac{\text{mass of solute in grams} \times 1000}{\text{formula mass of solute} \times \text{mass of solvent in grams}}$

**MOLE FRACTION:**

**Definition:** The ratio of the moles of solute to the total no. of moles of both solvent and solute is the mole fraction of that solute **OR**

It is the ratio of the no. of moles of one substance to the total no. of moles of all the substances in the solution. It is denoted by (X).

**Formula:**

$$X_A = \frac{n_A}{n_A + n_B} \quad ; \quad X_B = \frac{n_B}{n_A + n_B}$$

**PARTS PER MILLION (Symbol, ppm)**

**Definition:** The number of parts (by weight or volume) of a solute per million parts (by weight or volume) of the solution is called parts per million.

This unit is used for very low concentrations of solutions, e.g., to express the impurities of substances in water.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

**PERCENTAGE**

**Definition:** It is the number of parts of solute present in 100 parts of solvent or solution.

There are four possible relationships in percentage composition.

**(a) VOLUME - VOLUME RELATIONSHIP (V/V)**

**Definition:** It is the number of parts by volume of solute present in 100 parts by volume of solution.

The total volume of the solution should be 100 parts.

**FOR EXAMPLE:** 10% (V/V) ethanol solution will be, 10 mL ethanol + 90 mL H<sub>2</sub>O = 100 mL solution.

**(b) WEIGHT - WEIGHT RELATIONSHIP (W/W)**

**Definition:** It is the number of parts by weight of solute present in 100 parts by weight of solution. The total weight of the solution should be 100 parts.

**FOR EXAMPLE:** 10% (W/W) glucose solution will be, 10g glucose + 90g H<sub>2</sub>O = 100g solution

**(c) WEIGHT - VOLUME RELATIONSHIP (W/V)**

**Definition:** It is the number of parts by weight of solute present in 100 parts by volume of solvent. In this case the total weight or volume of the solution is not considered.

**FOR EXAMPLE:** 25% (W/V) glucose solution will be; 25g glucose + 100 mL H<sub>2</sub>O = Whatever the weight OR volume of the solution may be.

**(d) VOLUME - WEIGHT RELATIONSHIP (V/W)**

**Definition:** It is the number of parts by volume of solute present in 100 parts by weight of solvent. In this case also the total weight or volume of the solution is not considered.

**FOR EXAMPLE** 18% (V/W) ethanol solution will be; 18 mL ethanol + 100g H<sub>2</sub>O = Whatever the weight OR volume of the solution will be

**Q.03: explain on particles bases how the vapour pressure of solution is lowered by adding non volatile solute?**

**Answer:** A nonvolatile solute is added to the solution, the vapour solution is lowered as compared to the vapour pressure of pure solvent. The escaping of pure volatile solvent is much faster since all surface molecules belongs to solvent molecules but in a solution a part of surface is also occupied by non volatile solute particles. This decreases the number of solvent molecules on the surface and reduces the escaping tendency of the solvent molecules which results in lowering of vapour pressure of solution as compare to pure solvent.



**QNO#04: What are miscible, partial miscible and immiscible liquids?**

**MISCIBLE LIQUIDS:**

**Definition:** When two liquids are mix with each other in all proportion to form homogenous mixture is called miscible liquids.

**Example:** Water and methanol are completely miscible in each other due to polar nature and molecules of these liquids possess hydrogen bonding in their pure liquids state.

Benzene and toluene are also completely miscible in each other due to non polar nature and molecules of these liquids possess London dispersion forces in their pure liquids state.

**IMMISCIBLE LIQUIDS:**

**Definition:** When two liquids do not mix with each other in all proportion and do not form homogenous mixture is called immiscible liquids.

Example: water and benzene are immiscible liquids because water is polar and benzene is non polar

**PARTIALLY MISCIBLE LIQUIDS**

**Definition:** When two liquids are mixed and form two separate phases is called partially miscible liquids.

Each phase is the saturated solution of the two liquids in which one serve as solute and other as solvent

Example: water and phenol form two phase solution in which upper layer represents 5% phenol in 95% water while lower layer consists of 70% phenol in 30% water.

**QNO: why n- hexane (petrol) is immiscible in water?**

Reason : Water and n hexane are immiscible liquids because water is polar and n hexane (petrol) is non polar

**QNO#05: solubility of oxygen in water increase with pressure but solubility of glucose in water has negligible effect of pressure why?**

Solubility of solids and liquids in liquids solvent is not affected by altering the pressure that's why solubility of glucose in water has negligible effect of pressure. Whereas increase in pressure increase the number of gas molecules in a solution so the solubility of oxygen in water increase with pressure.

**DETAILED QUESTIONS**

**Q.No. 1: state Raoult's law. Derive its mathematical expression.**

**RAOULT'S LAW**

**INTRODUCTION:** in 1887, a French chemist F.M Raoult studied lowering of vapour pressure by the effect of solute particles in a solution and formulated the law named as Raoult's law.

**STATEMENT:** The vapour pressure of a solvent above a solution is equal to the product of the vapor pressure of pure solvent and the mole fraction of solvent in solution.

**EXPLANATION:** A nonvolatile solute is added to the solution, the vapour pressure is lowered as compared to the vapour pressure of pure solvent. The escaping of pure volatile solvent is much faster since all surface molecules belongs to solvent molecules but in a solution a part of surface is also occupied by non volatile solute particles. This decreases the number of solvent molecules on the surface and reduces the escaping tendency of the solvent molecules which results in lowering of vapour pressure of solution as compare to pure solvent.

**Derivation:** according to the statement

$$P \propto X_1 \quad \Rightarrow \quad P = p^\circ x_1 \text{ -----(1)}$$

$P^\circ$  = vapour pressure of solvent above solution.  $P$  = vapour pressure of pure solvent

$X_1$  = mole fraction of solvent,

Since in binary solution  $X_1 + X_2 = 1$  hence  $X_1 = 1 - X_2$

Putting the value of  $X_1$  in equation 1 ,we get

$$P = p^\circ (1 - X_2)$$

$$P = p^\circ - p^\circ X_2$$

$$p^\circ - P = p^\circ X_2$$

$$\Delta p = p^\circ X_2 \text{ -----(2)}$$

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(The lowering of vapour pressure is directly proportional to the mole fraction of solute)

$$\Delta p / p^{\circ} = X_2 \text{ -----(3)}$$

$\Delta p / p^{\circ}$  is known as lowering in vapour pressure

The relative lowering of vapour pressure is equal to the mole fraction of solute.

**Q.No.: 2 what does an ideal solution means? Give four characteristics to distinguish between ideal and non ideal solution.**

### **IDEAL SOLUTION**

**DEFINITION:** The solution which obey Raoult's law is called ideal solution

**CHARACTERISTICS:** there are four characteristics of ideal solution which distinguish it from non ideal solution:

- (1) If the forces of interactions between the molecules of different components are same as when they were in the pure state, they are ideal solutions otherwise non-ideal.
- (2) If the volume of solution is not equal to the sum of the individual volumes of the components, the solution is non-ideal.
- (3) Ideal solutions have zero enthalpy change as their heat of solution.
- (4) it obeys Raoult's law at all temperature and concentration

**Q3: Define osmosis and osmotic pressure give four daily life examples of osmosis.**

Osmosis: the process in which solute molecules move from lower concentration to a higher concentration of solution through a semi permeable membrane is called osmosis.

**Osmotic pressure:**

It is define as the hydrostatic pressure exerted by the solution which stops the process of osmosis is called osmotic pressure.

### **EXAMPLE OF OSMOSIS IN DAILY LIFE**

- (1) Fresh water fish absorbs water through their semi permeable skin because their body fluid is much saltier than the water in which they swim
- (2) Hemolysis in endo osmosis biochemical process during which water pass through semi permeable membrane of RBCs and destroy them.
- (3) Plant absorb water by root hairs through the process of osmosis
- (4) Food after digestion change into chyme which then absorb into body tissue through the semi permeable wall of small intestine.

**Q4: What are colligative properties? Why does the boiling point of liquid get raised when non-volatile solute is added?**

**Colligative properties:**

A colligative property is a property of a solution that is dependent on the ratio between the total number of solute particles (in the solution) to the total number of solvent particles. Colligative properties are not dependent on the chemical nature of the solution's components. Thus, colligative properties can be linked to several quantities that express the concentration of a solution, such as molarity, normality, and molality. The four colligative properties that can be exhibited by a solution are given below:

Boiling point elevation

Freezing point depression

Relative lowering of vapour pressure

Osmotic pressure

### **ELEVATION OF BOILING POINT**

The elevation of boiling point refers to the increase in the temperature at which a liquid boils, as a result of the presence of a non-volatile solute, such as a salt or a sugar, dissolved in the liquid.

When a non-volatile solute is dissolved in a solvent, it lowers the vapor pressure of the solvent. This means that at a given temperature, the solvent molecules are less likely to escape into the vapor phase, as more of them are being held in the liquid phase by the solute. As a result, a higher temperature is required to reach the vapor pressure of the solvent and to boil the solution.

The magnitude of the elevation of boiling point is dependent on the concentration of the solute in the solvent, as well as the properties of the solvent and solute. The elevation of boiling point is a colligative property, which means it depends only on the number of particles (molecules or ions) of the solute present in the solution, and not on their identity or chemical nature.

**QNo5: Differentiate between solution, suspension and colloid?**

S#	SOLUTION	SUSPENSION	Colloid
1)	Solutions are homogeneous mixture.	Suspensions are heterogeneous mixture.	It is homogeneous as well heterogeneous
2)	Their particles do not settle down.	Their particles settle down.	Particles do not settle down for a long time
3)	The solutions are transparent.	The suspensions are not transparent.	Often opaque, can be transparent
4)	Their particles cannot be separated by filtration.	Their particles can be separated by filtration.	Can be separated easily
5)	Particles cannot be seen in a solution.	Particles can be seen in a suspension.	Particles can not be seen with naked eye
6)	Particle size less than 1nm	Particle size greater than 1000nm	Particle size 1nm to 100 nm

## CHAPTER# 11

### THERMOCHEMISTRY SHORT QUESTIONS

**Q#1 states precisely the meaning of each of the following:**

(a) **SYSTEM:**

Any real and imaginary portion of the universe or anything, which is under consideration or under observation, is called system.

OR

Anything under consideration or under experiment is called SYSTEM".

OR

A substance which undergoes a physical or chemical change is called SYSTEM.

Example; Reaction between 100ml of HCl with 100ml of NaOH in a beaker is called A SYSTEM.

**TYPES OF SYSTEM**

**1 ISOLATED SYSTEM:** An isolated system is one that can transfer neither matter nor energy to and from its surrounding or the system which cannot exchange mass and energy with the surrounding.

EXAMPLE: boiling water, in a thermos flask, is an example of isolated system.

**2 CLOSED SYSTEM:** A closed system is one which cannot transfer matter but can transfer energy in the form of heat, and radiation to and from its surroundings. In this system boundary is sealed but not insulated.

Example: A specific quantity of hot water contained in a sealed tube, is an example of closed system: No water vapor can escape from this systems, it can transfer heat through the walls of the tube to the surroundings.

**3 OPEN SYSTEM:** is one which can transfer both energy and matter to and from the surroundings. In this system boundary is open.

Example: Water contained in a beaker placed on laboratory table is an open system.

(b) **SURROUNDINGS.**

The environment of a system or all the remaining portion of the universe which may act on the system is known as SURROUNDINGS.

OR

Everything in the universe that is not part of system is called SURROUNDINGS.

(c) **STATES OF SYSTEM**

**DEFINITION:** - The environments of a system before and after chemical change are called as States of System. The description of a system in its surrounding at a particular moment is called state.

**TYPES OF STATES:** - There are two types of state of a system.



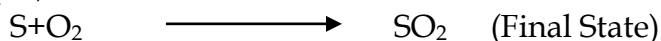
**INITIAL STATE:-**

**DEFINITION:-** The description of a system before it suffers any chemical change, for example;



**FINAL STATE:-**

**DEFINITION:-** The description of system after any chemical change is called final state, for example;



**(d) State function**

**Definition:** The physical properties which depend upon state of system (initial and final state) are called state functions.

Example: Volume, Pressure, Energy, Temperature, Enthalpy, Entropy etc.

**(e) Enthalpy**

**Definition:** It is defined as total heat content of the system. Enthalpy is the sum up of the internal energy and the product of pressure and volume.

$$H = E + PV$$

E is the internal energy, P is the pressure and V is the volume of the system.

It is written by "H". It is an extensive property and state functions of a system.

**(f) Internal energy**

**Definition:** The total energy contained in system is called internal energy.

OR

The sum of Kinetic Energy, Potential Energy etc of all particles in a system is called internal energy. It is denoted by "E". Internal Energy is the extensive property of a system and State function of a system.

The S.I. unit of internal energy is Joule (J).

**Q#2 what is meant by internal energy change ( $\Delta E$ ) and enthalpy change ( $\Delta H$ )? under what conditions are ( $\Delta E$ ) and ( $\Delta H$ ) equal?**

**Ans: Internal Energy Change  $\Delta E$ :**

The total energy content of a thermodynamic system under a given set of condition is known as Internal Energy.

Change in internal ( $\Delta E$ ) can be measured experimentally ( $\Delta E = E_2 - E_1$ ).  $\Delta E$  is a state function because it depends only upon the initial and final state and not by a path to which change occurs.

**Enthalpy change  $\Delta H$ :**

The total heat content of reaction at constant pressure is called enthalpy. Change in enthalpy of reactions are major by calorimetric method.

Enthalpy change of a reaction is a state function and it depends only on where the chemical process begins and finished.

$$\Delta E = \Delta H.$$

When a reaction is carried out at constant volume ( $\Delta V = 0$ ), no work is done on or by the system. In this condition internal energy change must equal to heat change of the reaction.

According to first law of thermodynamics

$$q_v = \Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + P(0)$$

$$\Delta H = \Delta E$$

**Q#3 how can you define standard heat of formation and standard heat of reaction?**

**HEAT OF REACTION:** The amount of heat evolved or absorbed in a chemical reaction, when molar quantities of reactants and products are used as specified in chemical reaction, is called HEAT OF REACTION.

It is also define as sum up of  $\Delta H_f$  of products minus sum up of  $\Delta H_f$  of reactants

**Equation from book page 239**

Heat of reaction is denoted by  $\Delta H$  or change in enthalpy.

**FOR EXAMPLE**



**HEAT OF FORMATION**

**DEFINITION:-** Heat of formation of a compound is defined as the enthalpy change when one mole of that compound is formed after a chemical reaction.



**STANDARD HEAT OF FORMATION:-** The standard heat of formation is the heat produced when all the substances involved in the chemical reactions are at one atmospheric pressure and 25°C.

**REPRESENTATION:-** The heat of formation is represented by  $\Delta H_f$  and can be calculated by the given heat of formations of other reactions.

**For Example:**  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H_f^\circ = -285.8 \text{ KJ/mol}$

**DETAILED QUESTIONS**

**Q#1 state and explain first law of thermodynamic. Derive pressure volume work of a system.**

**FIRST LAW OF THERMODYNAMICS**

**INTRODUCTION:-** This concept was initiated by J R Mayer in 1841 and formulated by Helmholtz in 1847. Previously this law was called "law of Conservation of Energy".

**STATEMENT:-** The energy can neither be created nor destroyed but can be converted from one form to another form.

OR

The total energy of system and surrounding remain same.

OR

Energy of initial state always equal to energy of final state

**EXPLANATION:-** First law of thermodynamics is the most fundamental of all the scientific laws. On the basis of this law, other thermodynamic laws were represented.

From the definition it is clearly understood that any gain or loss of energy by the system must be exactly equal to gain or loss of energy by the surroundings of the system.

**MATHEMATICAL DERIVATION:-** If there is a system which has initial energy  $E_1$ , it absorbs some quantity of heat 'q' from the surrounding and it can do some work on the surrounding then its energy becomes  $E_2$ . So according to first law of thermodynamics.

$$\Rightarrow E_1 + q = E_2 + w$$

$$\Rightarrow E_2 + w = E_1 + q$$

$$\Rightarrow E_2 - E_1 = \Delta E = q - w$$

Where;  $\Delta E$  = Change in internal energy

q = Heat energy evolved or absorbed

(q) Is positive when the system absorbs energy.

(q) Is negative when the system evolves energy.

w = Work done by the system or on the system.

(w) is positive when system absorbs energy by having work done on it (system) by the surroundings.

(w) is negative when system evolves energy by doing work on surroundings.

The absorption or evolution of heat during chemical reactions may take place at constant volume and at constant pressure.

**PRESSURE - VOLUME WORK: -  $(W = P \Delta V)$**

Consider a cylinder of a gas having frictionless and weightless Piston. (P).

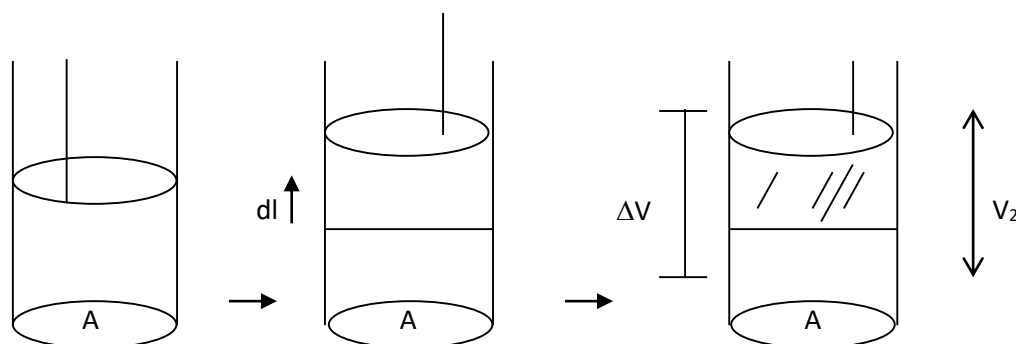
Suppose the area of cross section of the piston = A

Pressure of the piston = P

Initial volume of the gas =  $V_1$

Final volume of the gas =  $V_2$

When the pressure on the piston is released, the piston moves upward through a small distance L



So change in volume =  $V_2 - V_1 = \Delta V = A \times l$

( $A \times l$ ) represents increase in volume in the expansion process work done by the system  $W$   
= force  $\times$  distance

$$\Rightarrow W = P \times A \times l$$

$$\Rightarrow (A \times l) = \Delta V$$

$$\Rightarrow W = P \Delta V$$

Accordance to the first law of thermodynamics

$$\Rightarrow \boxed{q = \Delta E + \Delta W}$$

Since  $W = P \Delta V$

$$\Rightarrow \boxed{q = \Delta E + P \Delta V}$$

Q# 2: discuss the applications of the first law of thermodynamic at constant pressure and at constant volume.

### **APPLICATIONS OF FIRST LAW OF THERMODYNAMICS**

#### **(a) PROCESS AT CONSTANT VOLUME:**

According to the first law of thermodynamics.

Where;

$$\Rightarrow \Delta E = q - W$$

$$\Rightarrow W = P \Delta V$$

In closed vessel, the volume remains constant i.e.  $\Delta V = 0$ ,

Therefore,

$$\Rightarrow W = P \times 0$$

$$\Rightarrow W = 0$$

$$\text{But} \quad \Delta E = q_v \dots \dots \dots (3)$$

Thus in a process carried out at constant volume, the heat absorbed or evolved is equal to the energy change  $\Delta E$ ,  $q_v$  denoted the change at constant volume.

#### **(b) PROCESS AT CONSTANT PRESSURE (ENTHALPY)**

According to first law of thermodynamics

$$\Rightarrow \Delta E = q - W$$

At constant pressure it can be written,

$$\Rightarrow \Delta E = q_p - P \Delta V \text{ (Because } W = P \Delta V \text{)}$$

$$\Rightarrow q_p = \Delta E + P \Delta V \dots \dots \dots (4)$$

We know that,

$$\Rightarrow \Delta E = E_2 - E_1$$

And

$$\Rightarrow \Delta V = V_2 - V_1$$

Therefore equation (4) can be written as,

$$\Rightarrow q_p = E_2 - E_1 + P(V_2 - V_1)$$

$$\Rightarrow q_p = E_2 - E_1 + PV_2 - PV_1$$

Rearranging the above expressions,

$$\Rightarrow q_p = (E_2 + PV_2) - (E_1 + PV_1) \dots \dots \dots (5)$$

$E + PV$  is called enthalpy and is equal to  $H$ .

$$\Rightarrow \text{Enthalpy } H = E + PV$$

For two states it is written as,

$$\Rightarrow H_1 = E_1 + PV_1$$

$$\Rightarrow H_2 = E_2 + PV_2$$

The equation (5) becomes,

$$\Rightarrow q_p = H_2 - H_1 = \Delta H$$

Or

$$\Rightarrow q_p = \Delta H$$

i.e Heat Change = Enthalpy

Substituting the values in equation (4) I.e.

$$q_p = \Delta E + P\Delta V$$

We get,

$$\Rightarrow \boxed{\Delta H = q_p = \Delta E + P\Delta V} \dots\dots\dots (6)$$

Q#3 state and explain Hess's law of heat summation. Discuss its application.

**HESS'S LAW OR LAW OF CONSTANT HEAT SUMMATION**

**INTRODUCTION:-** This law was introduced by German Henry Hess (G.H.Hess) in 1840.

**STATEMENT:-** The heat is absorbed or evolved during a chemical reaction is same whether that chemical reaction is taking place in one or several steps

OR

The amount of heat evolved or absorbed in a given reaction is independent of intermediate steps involved. It depends upon initial and final states.

**MATHEMATICAL:-** According to Hess law, it is clear that enthalpy change in direct step will be equal to the sum of enthalpies in direct steps as given under.



According to Hess law

$$\Rightarrow \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

**SPECIFIC EXAMPLE:-**

**FORMATION OF SODIUM CARBONATE**

Sodium carbonate can be obtained by passing carbon-di-oxide through excess of sodium hydroxide. During the process the enthalpy change is equal to (-90 KJ/mol).



This reaction can easily be carried out in two steps.

**STEP 1:-** In the first step sodium hydroxide is converted into sodium bicarbonate by the action of carbon-di-oxide.



**STEP 2:-** In the second step sodium bicarbonate reacts with sodium hydroxide to form sodium carbonate and water.



**ACCORDING TO THE HESS'S LAW:**

$$\Rightarrow \Delta H = \Delta H_1 + \Delta H_2$$

$$\Rightarrow \Delta H = (-49) + (-41)$$

$$\Rightarrow \Delta H = -49 - 41$$

$$\Rightarrow \Delta H = -90$$

**APPLICATION OF HESS'S LAW:-**

1. It helps in calculating the heat of Reaction.
2. It helps in calculating the heat of formation, where direct measurement is not possible.
3. It helps in calculating the heat of combustion

Q#4 Explain exothermic and endothermic reactions with the help of the energy diagram

**EXOTHERMIC REACTIONS**

**INTRODUCTION:-** It is a Greek word and composed of two words.

Exo = given Out (released)

Therme = Heat.

**DEFINITION:-** The chemical reactions in which heat is given out or released or liberated are called exothermic reactions

OR

The process in which heat is transferred from system to surroundings is called exothermic reaction.

**REPRESENTATION OF CHANGE OF HEAT:-** The change of Heat is represented by  $\Delta H$  ( $\Delta$  = Delta)

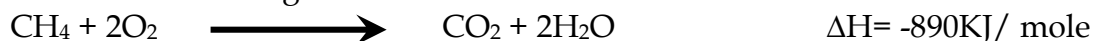
**SIGN OF  $\Delta H$ :-** The sign of  $\Delta H$  for exothermic reactions is negative (-)

**EXAMPLES:-** The examples of exothermic reaction are following.

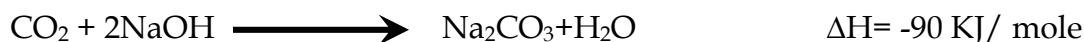
i Burning of coal.



ii Combustion of Sui gas.



iii Formation of carbonate



**ENDOTHERMIC REACTION**

**INTRODUCTION:-** It is a Greek word composed of two words

Endo = Absorbed (take in) And Therme = Heat.

**DEFINITION:-** The chemical reaction in which heat energy is absorbed or taken in is called endothermic reactions

**OR**

The process in which heat energy is transferred from surrounding into a system is called as endothermic reactions.

**REPRESENTATION OF CHANGE OF HEAT:-** The change of heat is representing by  $\Delta H$ .

**SIGN OF  $\Delta H$ :-** The sign of  $\Delta H$  for endothermic reaction is positive.

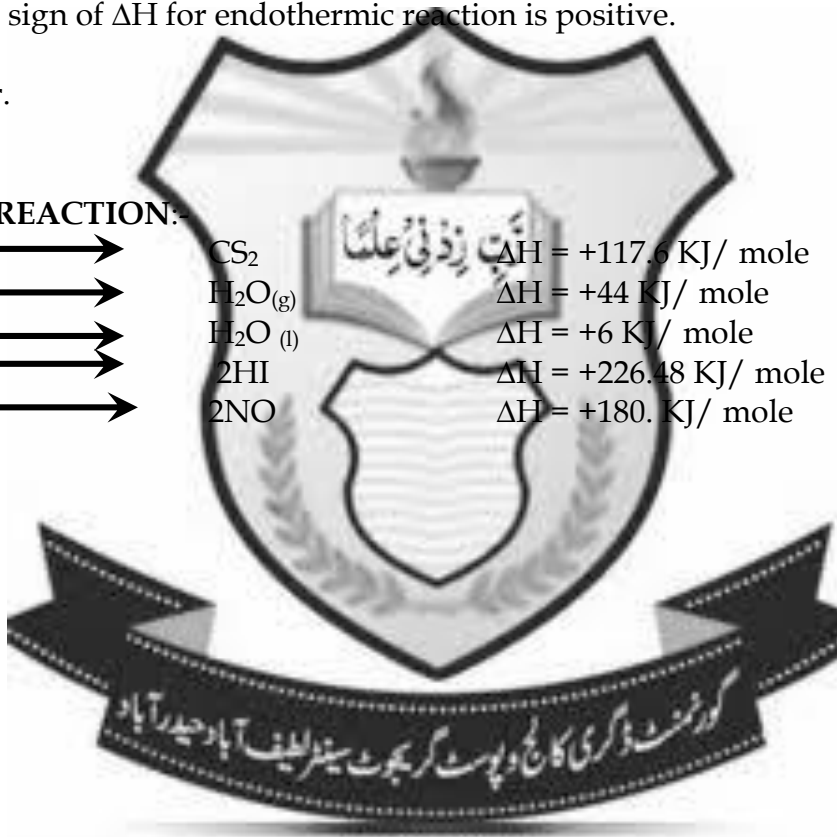
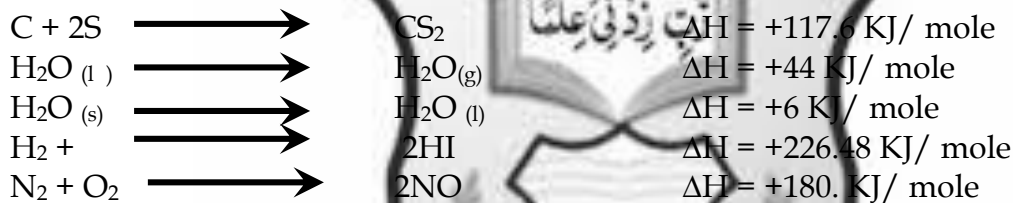
**EXAMPLES:-**

i Boiling of water.

ii Melting of ice.

iii Evaporation.

**EXAMPLE WITH REACTION:-**





## CHAPTER# 12

# ELECTROCHEMISTRY

**Q. No. 1: Defines the following terms;**

- (a) Electrochemistry      (b) Electrolysis      (c) Electrochemical cell      (d) Oxidation number  
(e) Redox reaction      (f) Primary cell      Secondary cell      (g) Electroplating      (h) Oxidation  
reduction      (i) Oxidizing and reducing agent

**A) Electrochemistry:** The branch of chemistry that deals with the relationship between electricity and chemical reactions. It is the study of conversion of electrical energy into chemical energy and chemical energy into electrical energy.

**B) Electrolysis:** The process of decomposition of an electrolyte in solution or in molten (fused) state by the process of electrical current is known as electrolysis.

OR

A process in which movement of the ions takes place towards their respective electrodes to undergo chemical change under the influence of an applied electric field is called electrolysis.

**C) Electrochemical cell:** The cell which is used to convert chemical energy into electrical energy or vice versa is called electrochemical cell.

OR

The cell in which the process of electrolysis is carried out is called electrochemical cell.

**Types of cells:**

Galvanic or voltaic cells are the types of cells which convert chemical energy into electrical energy. The simplest of the galvanic and voltaic cell is the Daniel cell.

**Very common example:** Take strips of Zinc (Zn) and copper metal; stick them into a piece of lemon. The terminal of the Zinc and Copper will join together and found producing electric current.

**D) Primary cell:** A chemical device for creating a flow of electrons in a circuit is called primary cell.

**Example:** The most common example of primary cell is dry cell.

**E) Electroplating:** It is the process of electrolysis which is used to coat one metal onto other.

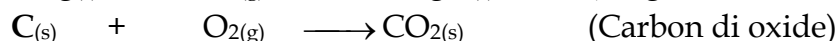
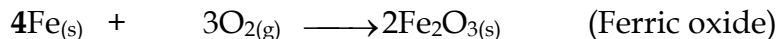
**Explanation:** The object to be electroplated is made up of cheaper or baser metal such as iron, steel. It is then coated with a thin layer of more attractive corrosion resistant and costly metal like silver, gold, nickel, chromium; tin etc. the process of electroplating has made these objects so cheaper than the original object.

**(F): OXIDATION**

Oxidation can be defined in three different ways;

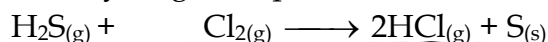
**(a) Addition of Oxygen.** Reaction in which oxygen with other elements or substances to form oxides

**For example:** rusting of iron, burning of magnesium, carbon etc



**(b) Removal of hydrogen.** It is also the loss of hydrogen atoms or removal of hydrogen from any substance

**For example,** Reaction of hydrogen sulphide and chlorine to form hydrogen chloride and sulfur



In the above chemical reaction, hydrogen sulphide has lost hydrogen, hence it has been **oxidised**

**(c) Removal or loss of electron.** The process or reaction which occurs by the loss or removal of electrons.

**For example:**



**REDUCTION**

Reduction can also be defined in three different ways

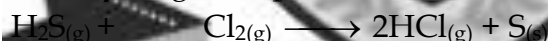
**(a) Removal of Oxygen.** It means the removal of oxygen from the substance

**For example:** CuO is reduced to Cu while H<sub>2</sub> is oxidised to H<sub>2</sub>O



**(b) addition of hydrogen.** It is the addition of hydrogen atoms from any substance

**For example,** Reaction of hydrogen sulphide and chlorine to form hydrogen chloride and sulfur



In the above chemical reaction, chlorine adds hydrogen to form HCl, hence it is **reduced**.

**(c) Gain or addition of electron.** The process or reaction which occurs by the gain or addition of electrons.

**For example:**



**OXIDISING AGENT**

**DEFINITION.** The chemical reaction in which a chemical substance helps in oxidation by accepting Electron and reducing itself is called OXIDISING AGENT.



Cl<sub>2</sub> act as oxidising Agent, because it oxidizes Zinc.

**REDUCING AGENT**

**DEFINITION.** The chemical reaction in which a chemical substance helps in reduction by losing Electron and Oxidizing itself is called REDUCING AGENT.



Zinc act as reducing agent.

**REDOX REACTION**

**DEFINITION.** Those reactions that involve both **Reduction & Oxidation** simultaneously are redox reaction.

**Explanation.** There are 4 ways to look at whether a substance has been oxidized or reduced, and they are:

1. Gain/Loss of Oxygen atoms
2. Gain/ Loss of Hydrogen atoms
3. Gain/Loss of Electrons
4. Increase/Decrease in Oxidation States/Numbers

**For example,**  $\text{Mg}_{(s)} + \text{CuO}_{(s)} \longrightarrow \text{MgO}_{(s)} + \text{Cu}_{(s)}$

From the above equation, you can see that copper (II) oxide has lost oxygen, so it has been **REDUCED**. Magnesium, on the other hand, has gained oxygen and so has been **OXIDISED**.

Now, the copper (II) oxide is said to be an **OXIDISING AGENT** because it has given oxygen to magnesium and caused the oxidation of magnesium. The magnesium, on the other hand, is said to be a **REDUCING AGENT** because it has taken oxygen from copper (II) oxide and caused the reduction of copper (II) oxide.

In the above chemical reaction, we say it is a **REDOX Reaction** since both **OXIDATION** and **REDUCTION** occurs **simultaneously**.

### **OXIDATION NUMBER**

**DEFINITION:-** It is defined as the apparent charge (+ive or -ive) which an atom would have in a compound.

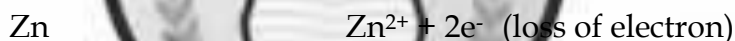
**EXAMPLE:-** The oxidation number of (Cl) in (NaCl) is (-1), in (NaOCl) is (+1) and in (NaClO<sub>3</sub>) is (+5).

**Q2: Define the term standard electrode potential and hydrogen electrode.**

#### **ELECTRODE POTENTIAL:**

**DEFINATION:** The difference of potential created between a metal and solution of its salt is called electrode potential of the metal.

**OXIDATION POTENTIAL:** Potential associated with oxidation reaction is called oxidation potential. Therefore the potential associated with the following reaction is called "oxidation potential".



Thus during oxidation its own atom lose electron and convert into Zn<sup>2+</sup> cations. Thus oxidation potential of a metal indicated electron losing tendency.

**REDUCTION POTENTIAL:** Potential associated with reduction reaction is called reducing potential. Therefore the potential associated with the following reaction is called "reducing potential".



Thus during reduction cations Zn<sup>2+</sup> present in the solution gains electrons and convert into Zn atoms. Thus reduction potential of a metal indicated the tendency to gain electron.

The oxidation and reduction potential of an electrode have the same value but differ in signs as.

$$\text{As} \quad E_{\text{ox}} = - E_{\text{red}}$$

$$E_{\text{red}} = - E_{\text{ox}}$$

**STANDARD ELECTRODE POTENTIAL (Hydrogen Electrode):** The absolute electrode potential can be measured experimentally.

It is determined by comparing with hydrogen electrode as the reference electrode which is standard electrode.

Hydrogen electrode potential under one atmospheric pressure at 25°C and one molal solution of H<sup>+</sup> is taken as zero ( 0.000 Volts).

This hydrogen electrode potential is regarded as standard electrode potential of the other electrode.

Standard electrode potential is shown as E<sup>0</sup><sub>ox</sub> and E<sup>0</sup><sub>red</sub>.

**Q3: How can you define an electrochemical series? Give its properties.**

#### **ELECTRO CHEMICAL SERIES ( E.C.S)**

**DEFINATION:**

## PROF: ZUBAIR AHMED SHAIKH

The list of elements arranged in the order of their standard potential on the hydrogen scale is known as electrochemical series of E.C.S series.

### **FACTS OF E.C.S:**

All the metals placed above the hydrogen in the series act as anode i.e they are oxidized in comparison cell. While those metals placed below the hydrogen in the series act as cathode i.e they are reduced.

When the sign of electrode potential is positive then the reaction will be reverse and the electrode will act as cathode.

The reducing strength decreases and oxidizing strength increase from top to bottom in the E.C.S on this basis lithium is the strongest reducing agent while  $F_2$  is the strongest oxidizing agent.

In E.C.S position of metals shows the order of their reactivity metal displaces metal lying below them in the series from it solution of their salts. All the metals above hydrogen have negative electrode potentials.

An important point to remember in using reducing potential value is that they relate only to standard condition i.e 1M solution of ions  $25^\circ C$  and one atmospheric pressure. Change in temperature concentration pressure will effects the value of reducing potential.

**Q4: What is Corrosion what cause it to form what can be done to prevent it formation**

### CORROSION

#### **DEFINITION**

Corrosion is a harmful reaction for metals in which the metallic material gives an undesirable reaction upon exposure to atmosphere or any chemical agent. All the metals except noble metals such as Ag, Au, Pt and Pb undergo corrosion with different rates.

#### **For example:**

- (i) The rusting of iron in moisture.
- (ii) Dry cells containing shell of zinc metal got deposition of whitish mass on its surface when exposed to atmosphere for a longer period.
- (iii) Copper utensils get the coating of green matter on their surface are the few examples of corrosion.

#### **Corrosion rate:**

Alkali metals which are highly reactive, when exposed in air, are tarnished immediately getting the coating of their oxides. Calcium quickly corrodes in air, iron corrodes slowly, and tin, lead and copper undergo corrosion very slowly.

#### **Prevention of Corrosion**

Following methods are used for the prevention of corrosion.

- (i) **Metallic Coating:** Iron can be prevented from corrosion by plating a fine film of a other metal on its surface i.e. coating thin layer of Cu or tin on its surface. Copper utensils are coated with tin metal etc.
- (ii) **Electroplating:** Noble metals Ag, Au and Pt are used to protect the highly reactive metals by electroplating.
- (iii) **Alloying:** Alloy formation also protects the metals from their corrosion. Iron can be protected on alloying it with nickel and chromium making a stainless steel.
- (iv) **Coating with non-metallic material:** Metals can also be protected by coating their surfaces with various kinds of non-metallic material such as paints, varnishes, oils, grease, plastic emulsion etc.

**Q5: In the process of electroplating the item to be plated is made cathode, give reason.**

We know that at cathode reduction occurs and at anode oxidation since the metal which has to be electroplated should not get dissolve or oxidized therefore, it is always made cathode in electroplating. The metal which is to be electroplated on the metal is taken in the solution as an electrolyte and the metal ion in it gets reduced at the cathode and form layer on it thus metal to be electroplated is always made cathode.

### **DETAIL QUESTION**

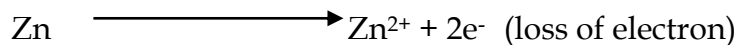


**Q1: What is mean by electrode potential and standard hydrogen electrode.**

**ELECTRODE POTENTIAL:**

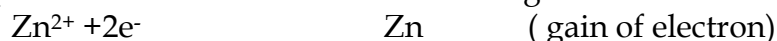
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**STANDARD ELECTRODE POTENTIAL (Hydrogen Electrode):** The absolute electrode potential can be measured experimentally.

It is determined by comparing with hydrogen electrode as the reference electrode which is standard electrode.

Hydrogen electrode potential under one atmospheric pressure at  $25^{\circ}\text{C}$  and one molal solution of  $\text{H}^{+}$  is taken as zero (0.000 Volts).

This hydrogen electrode potential is regarded as standard electrode potential of the other electrode.

Standard electrode potential is shown as  $E^{\circ}_{\text{ox}}$  and  $E^{\circ}_{\text{red}}$ .

**Q2: sketch a copper-zinc Galvanic cell, write the cell reaction and show the direction of electron flow.**

**VOLTIC CELL OR DANIELL CELL**

**Introduction:** Daniell cell is the simplest voltaic or galvanic cell. It converts chemical energy into electrical energy spontaneously.

**Construction:** Daniell cell consists of two half-cells. One half-cell is zinc rod dipped in 1M solutions. The other half-cell is copper rod dipped in a solution of 1M solutions. A porous partition or a salt bridge separates the two half-cells from each other. The two electrodes are connected together externally by a metal wire through a voltmeter are produced here so anode is the negative electrode. The copper rod acts as cathode where reduction takes place. Electrons are here so cathode is the positive electrode.

**Working:** The following reactions take place at the two electrodes.

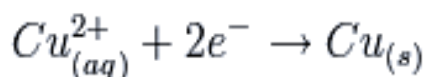
At the anode:

Oxidation ----- loss of electrons.



At cathode,

Reduction -----gain of electrons.

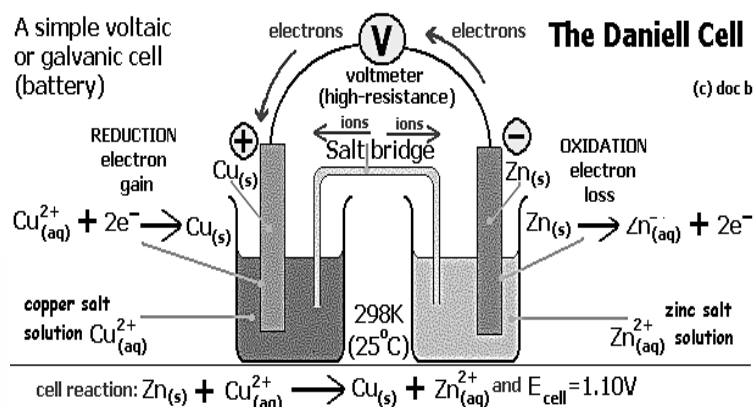


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The half reactions can be viewed as a competition between two kinds of metal atoms for electrons. In this case zinc atoms are more reactive and their tendency to lose electrons is greater than that of copper. Both the reactions take place simultaneously at both the half-cells

In this cell, electrons travel in the external circuit through the wire from the zinc anode to the copper cathode. If a bulb is in the circuit, it will light up. If there is a voltmeter, it will show the voltage. To complete the circuit, both the positive and negative ions move through the aqueous solutions via the salt bridge.

The total reaction is the sum of two half-cell reactions.



In this process, Zn electrode dissolves in the solution of  $\text{ZnSO}_4$  and reduces in size while Cu electrode grows in size due to the deposition of copper metal. Daniell cell generates an electric potential of 1.10 volt, when the solutions in the half cells are both 1M.

### Q.No. 3: What is the difference between a primary and secondary cell?

S#	PRIMARY CELL	SECONDARY CELL
01	It is non reversible cell.	It is reversible cell.
02	It cannot be recharged and cannot be used again.	It can be charges and can be used again and again.
03	It is commonly known as dry cell.	It is commonly known as accumulators.
04	Primary cell produces electricity at the expense of chemical used to make it.	In secondary cell, electrical energy is converted into chemical energy.
05	Eg; dry cell.	Eg; car battery.

### Q No.4: Sketch a diagram of dry cell and explain its working.

**Definition:** Voltaic cell in which electrolyte is a paste is known as dry cell.

**Uses:** The most commonly used dry cell is usually referred to as a flash light battery. It is commonly found in homes like battery operated clocks, torches, games, shavers and many other electrical appliances.

#### Construction:

- 1) There is an outer Zinc vessel which acts as an anode.
- 2) Inert Carbon (graphite) rod which acts as a cathode.
- 3) The graphite rod is surrounded by a mixture of manganese di oxide ( $\text{MnO}_2$ ) and carbon powder.
- 4) The electrolyte is a moist paste of Ammonium chloride and Zinc chloride.
- 5) The concentrated electrolytic solution is thickened into gel like paste by a agent such as starch.
- 6) A copper cap is fitted at the top of carbon rod to make the electrical contact.
- 7) The upper top position is sealed with wax.
- 8) The whole cell is covered with a safety cover.



**Working:** When zinc and graphite electrodes are connected by a metallic wire, Zn gets oxidized to form ( $\text{Zn}^{+2}$ ) ion which pass into the wet paste leaving behind electrons on the zinc container and the electrons move from zinc electrode to the carbon electrode through the external circuit.

**Q5: What is electrolysis discuss electrolytic cell**

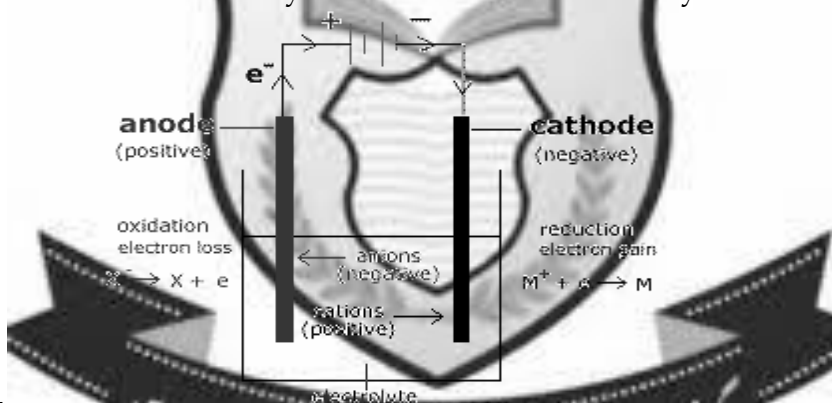
### **ELECTROLYSIS**

**DEFINITION:** - The process in which an electrolyte is decomposed into its constituent ions by passing electric current through its aqueous solution (molten state)

**OR**

The movement of cations and anions towards respected electrodes with all accompanying chemical change under the influence of electric current is called electric current.

**ELECTROLYTIC CELL:** - The electrolysis is carried out in electrolytic cell.



**CONSTRUCTION:** -

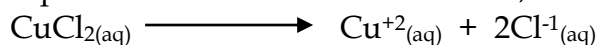
- ❖ Two metallic rods which are called as electrodes are placed in the solution inside the cell.
- ❖ The two electrodes are connected to the battery.
- ❖ The electrode attached to the positive end of the battery is called as anode.
- ❖ The another electrode connected to the negative end of the battery is called cathode.
- ❖ The complete arrangement containing the electrodes and the electrolytic solution is called as electrolytic cell.

**WORKING:** - The anode is the electrode at which oxidation occurs and cathode is the electrode at which reduction occurs.

**EXAMPLE:** -

### **ELECTROLYSIS OF CUPRIC CHLORIDE:** -

When cupric chloride is dissolved in water, it dissociates into ions.



When current is passed, ( $\text{Cu}^{+2}$ ) ions move towards cathode and ( $\text{Cl}^{-1}$ ) ions towards anode.

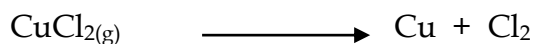
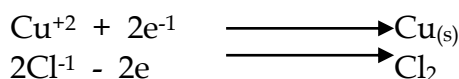
**REACTION AT CATHODE:** - At cathode ( $\text{Cu}^{+2}$ ) ions are discharged and neutralized as (Cu) atom.



**REACTION AT ANODE:** - At anode ( $\text{Cl}^{-1}$ ) ions are discharged and neutralized as ( $\text{Cl}_2$ ) gas by losing electrons.



**OVERALL REACTION:** - Thus the process oxidation and reduction are taking place in the reaction simultaneously. when the two above reactions are combined, overall reactions of electrolytes is obtained .



When ions are changed to neutral particles, current can no longer flow.

**Q6: What is oxidation number? Write down different rules for determining oxidation number.**

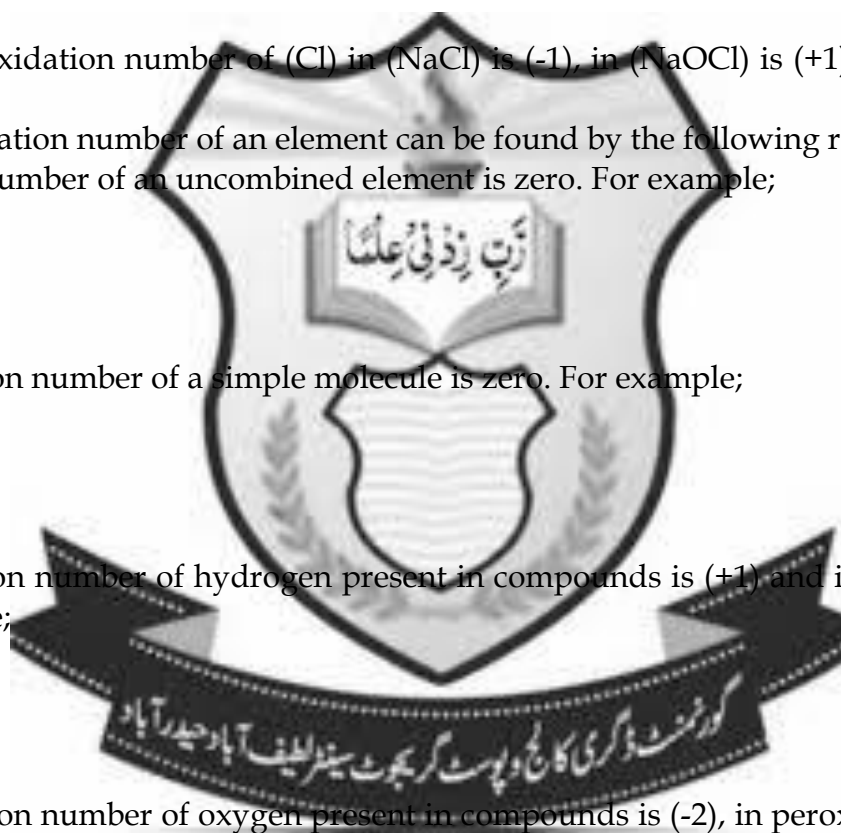
### **OXIDATION NUMBER**

**DEFINITION:-** It is defined as the apparent charge (+ive or -ive) which an atom would have in a compound.

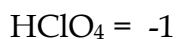
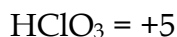
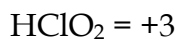
**EXAMPLE:-** The oxidation number of (Cl) in (NaCl) is (-1), in (NaOCl) is (+1) and in (NaClO<sub>3</sub>) is (+5).

**RULES:-** The oxidation number of an element can be found by the following rules.

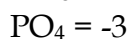
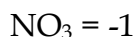
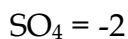
- ❖ Oxidation number of an uncombined element is zero. For example;  
Na = 0  
Cl = 0  
Zn = 0  
P = 0.
  - ❖ The oxidation number of a simple molecule is zero. For example;  
H<sub>2</sub> = 0.  
O<sub>2</sub> = 0.  
N<sub>2</sub> = 0.  
Cl<sub>2</sub> = 0.
  - ❖ The oxidation number of hydrogen present in compounds is (+1) and in hydrides it is (-1). For example;  
HCl = +1  
H<sub>2</sub>O = +1  
H<sub>3</sub>PO<sub>4</sub> = +1  
NaH = -1
  - ❖ The oxidation number of oxygen present in compounds is (-2), in peroxides it is (-1) and in (OF<sub>2</sub>) it is (+2), for example;  
H<sub>2</sub>O = -2  
CO<sub>2</sub> = -2  
HNO<sub>3</sub> = -2  
H<sub>2</sub>O<sub>2</sub> = -1
  - ❖ The oxidation number of metals present in compounds is equal to their valency. For example;  
NaCl = +1  
MgO = +2  
KBr = +1
  - ❖ The oxidation number of halogens present in a compound is (-1). For example;  
KCl = -1  
NaI = -1  
AlCl<sub>3</sub> = -1
- Some exceptions are;  
HClO = +1







- ❖ The oxidation number of radicals (poly atomic ions) is equal to the charge over them.



**Q7: write down different rules for balancing equation by ion electron method.**

**RULES TO BALANCE EQUATIONS BY ION ELECTRON METHOD**

Chemical equations in molecules or ionic form can be balanced by ion electron method, by applying following rules.

- ❖ Change the molecular equation into ionic equation (only those ions are taken in which oxidation number is changing).
- ❖ Divide the ionic equation into two half reactions, oxidation (increase in oxidation from reactants to product side) and another reduction (decrease in oxidation from reactant to product side).
- ❖ Balance other atoms leaving hydrogen and oxygen atoms.
- ❖ In acidic equations first balance oxygen atom by adding ( $\text{H}_2\text{O}$ ) and then balance hydrogen atoms by adding hydrogen ions ( $\text{H}^{+1}$ ). In basic reactions first balance oxygen atoms by adding ( $\text{OH}^{-1}$ ) and then balance hydrogen atom by adding ( $\text{H}_2\text{O}$ ).
- ❖ Balance the charge by adding electrons. In oxidation reactions, electrons are added to the product side and in reduction reactions electrons are added at the reactant side.
- ❖ Balance the number of electrons in both the half reactions, by multiplying the full equation with a required number.
- ❖ Add both the half reactions to get the final balanced equation.
- ❖ Again change the ionic equation to molecular equation.

**Q.No. 8: What is the difference between cell and battery? Cell:** A device which converts chemical energy into electrical energy is called a cell. There are two electrodes in a cell made up of two dissimilar metals.

**Battery:** Combination of cells is called a battery. An example of a battery is a lead storage battery commonly called a car battery which consists of six cells connected in series.

