

June : 2016 (CBCS)

Note :

Max. marks : 60

- (i) Attempt any five questions.
- (ii) All questions carry equal marks.

**Q.1 (a)** Explain valence bond theory (VBT).**Ans. Valence bond theory (VBT) :**

The valence bond theory was first developed by Heitler and London in 1927 to explain the stability of a hydrogen molecule. It is equally applicable to other covalent molecules containing two or more than two same or different atoms.

The theory is based on the following principles :

1. For the formation of a stable covalent molecule, atomic orbital of one atom should overlap with the atomic orbital of the other atom so that the electron density is large in between the two nuclei. This causes a decrease in nuclear repulsion and increase in the attractive forces between the electrons.
2. Overlapping occurs when atomic orbitals having unpaired electrons of anti-spin overlap with each other. After overlapping a new localized bond orbital is formed where the probability of finding electrons is maximum.
3. Greater the extent of overlapping, stronger the bond formed between the two combining atoms.
4. Greater overlapping shortens the distance between the nuclei. Thus, a stronger bond has a shorter bond length.
5. The amount of energy released per mole at the time of overlapping of orbitals to form a covalent bond is known as bond energy or stabilization energy. The electrons taking part in formation of covalent bond have almost equal energy.
6. The bond energy will be high if the valence shells are closer to nucleus.
7. After the bond formation, the combining atoms in a molecule retain their identity.

**Limitations of valence bond theory :**

1. Since the two electrons of the shared pair of electrons forming the covalent bond must come from two different atoms (which may be the same or different), it is evident that this theory throws no light on the formation of a co-ordinate bond in which one of the bonded atoms furnishes both the electrons.
2. The two atoms in O<sub>2</sub> molecule should have close concentric shells resembling those of Ne which would give no unpaired electrons to the O<sub>2</sub> molecule and thus will make it diamagnetic. Actually, experiments show that O<sub>2</sub> molecule is paramagnetic indicating the presence of unpaired electrons in O<sub>2</sub> molecule.
3. This theory does not consider the formation of odd electron molecules or ions such as H<sub>2</sub><sup>+</sup> ion where no pairing of electrons occurs.
4. This theory satisfactorily explains the formation and shapes of simple molecules but fails to give a satisfactory explanation of the geometry and shapes of the complex molecules.

**Q.1 (b)** Draw molecular orbital level diagram of oxygen (O<sub>2</sub>) molecule.

**Ans. Oxygen molecule (O<sub>2</sub>) :** The electronics configuration of oxygen  $z = 8$  is  $1s^2 2s^2 2p^4$ . The outer shell contains 6 electrons. Thus, there are 12 electrons to be accommodated in the molecular orbitals of O<sub>2</sub>.

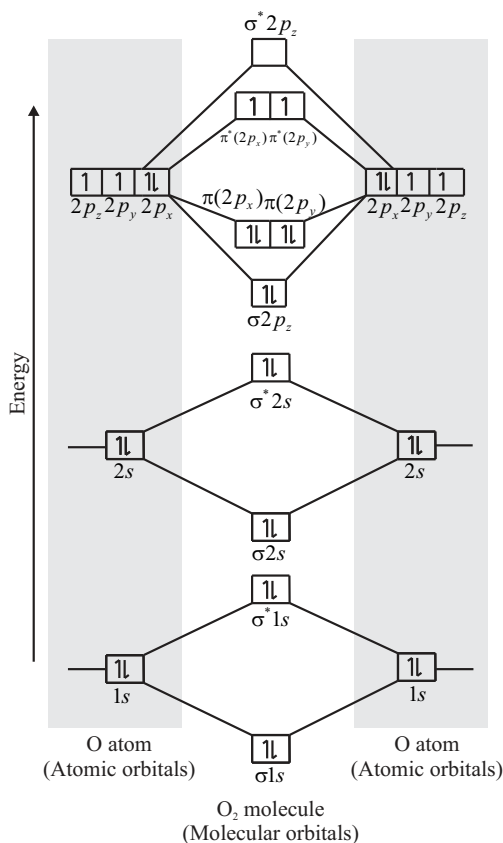
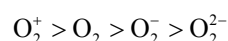


Fig. Molecular orbital energy level diagram for O<sub>2</sub> molecule

**Bond order :**

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$$

- Nature of bond :** The bond order value of 2 justifies the presence of double bond in O<sub>2</sub> molecule i.e., O = O .
- Bond strength :** As bond dissociation energies are directly proportional to the bond orders, therefore, the dissociation energies are in the order :



As greater the bond dissociation energy, greater is the stability.

- Magnetic character :** The presence of two unpaired electrons in  $\pi^*(2p_x)$  and  $\pi^*(2p_y)$  molecular orbitals shows that O<sub>2</sub> molecule is paramagnetic in nature.

**Q.2 (a)** Differentiate between bonding and antibonding molecular orbital.

**Ans. Difference between bonding and anti-bonding molecular orbital :**

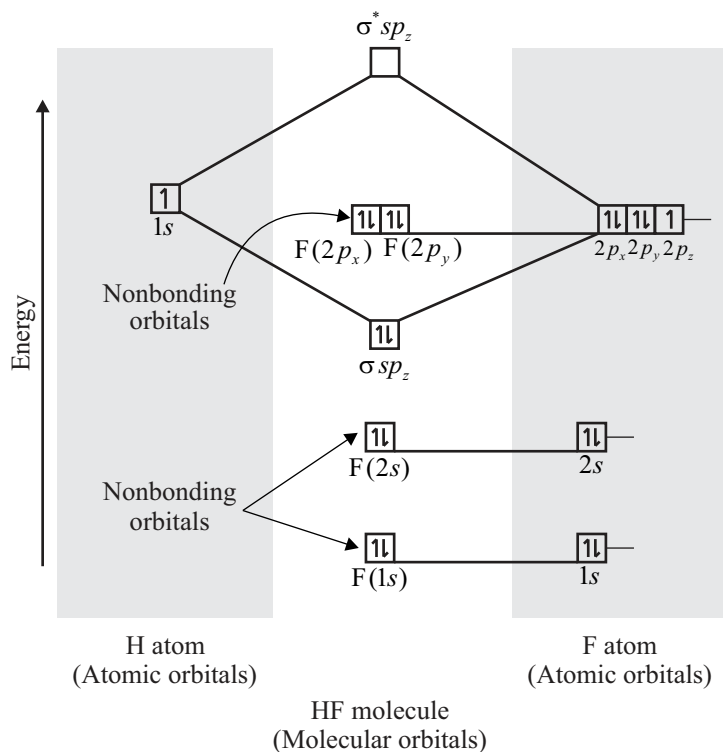
S. No.	Bonding molecular orbitals (BMO)	Antibonding molecular orbitals (AMO)
1.	They are formed by the additive effect of the atomic orbitals. $\phi_b = \psi_1 + \psi_2$ .	They are formed by the subtractive effect of the atomic orbitals. $\phi_a = \psi_1 - \psi_2$ .
2.	The electron density increases in the region between the nuclei of bonded atoms.	The electron density decreases in the region between the nuclei of the atoms and it increases in the region away from the inter-nuclear region.

S. No.	Bonding molecular orbitals (BMO)	Antibonding molecular orbitals (AMO)
3.	The electrons present in the bonding orbitals result in an attraction between the two atoms.	The electrons present in the antibonding orbitals result in the repulsion between the two atoms.
4.	Because of attractive forces involved, these molecular orbitals have lower energy than the atomic orbitals from which they are formed. This is the cause of their greater stability.	Because of the repulsive forces involved, these molecular orbitals have higher energy than the atomic orbitals from which they are formed. This is the cause of their lower stability, i.e., it does not favor bond formation and that is why the name antibonding.
5.	They are formed when the lobes of the combining orbitals have the same sign.	They are formed when the lobes of the combining orbitals have opposite sign.
6.	These molecular orbitals are represented by $\sigma$ and $\pi$ .	These molecular orbitals are represented by $\sigma^*$ and $\pi^*$ .

**Q.2 (b)** Show molecular orbital of HF molecule with help of diagram and calculate bond order.

**Ans. Hydrogen fluoride (HF) molecule :**

The electronic configurations of participating H and F atoms are



**Fig. Molecular orbital energy level diagram for HF molecule**

The formation of HF molecule occurs by linear combination of  $1s$  atomic orbital of hydrogen atom with  $2p_z$  orbital of fluorine atom. The reason behind that is the condition for the combination of atomic orbitals (AOs) is that energy should not differ much from one another and symmetry of AOs should be same.

There is the fluorine  $2s$  orbital. This has the correct symmetry to interact with the hydrogen  $1s$  orbital, but there is a very large energy gap between these two atomic orbitals. The larger the energy separation between orbitals, the smaller the interaction between them. As in this case the energy gap is very large hence there is no interaction between them.

The fluorine  $2p$  orbital is lower in energy than the hydrogen  $1s$  orbital. The fluorine  $p_z$  orbital have same symmetry as hydrogen  $1s$  orbital therefore it points towards hydrogen  $1s$  orbital, so the two orbital interact to form bonding and anti-bonding orbitals. The in-phase combination leads to a  $\sigma$ -bonding orbital and out of phase combination gives a  $\sigma^*$ -anti-bonding orbital. The bonding orbital has more fluorine character and the anti-bonding orbital has more hydrogen character.

The fluorine  $p_x$  and  $p_y$  orbitals do not have the correct symmetry to interact with the hydrogen  $1s$  orbital. Since there are no other hydrogen atomic orbitals for these orbitals to interact with them, they remain unaltered in the molecule. They are called non-bonding orbitals and take the molecular orbital label  $1\pi$ .

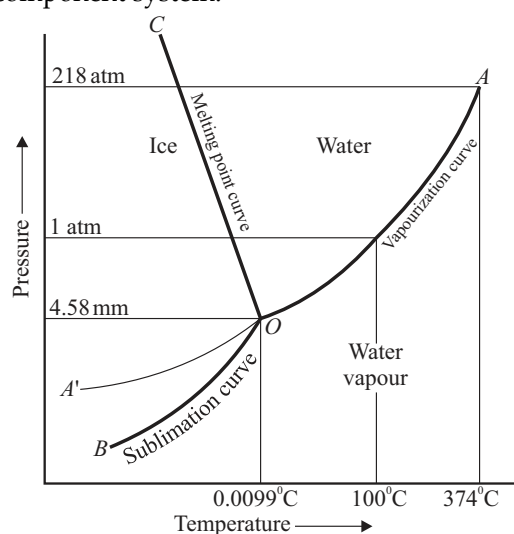
**Bond order :**

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 0) = 1$$

**Magnetic character :** Since all the molecular orbitals, are completely filled, so HF molecule is diamagnetic.

**Q.3 (a)** Draw and explain phase diagram for water system.

**Ans.** **The water system :** Under normal conditions the water system is a three phase and one component system. The three phases are liquid, ice and vapour. All these are represented by one chemical entity ( $\text{H}_2\text{O}$ ), hence it is one component system.



**Fig. Phase diagram for the water system**

The three forms of water (ice, water and vapour) constitute the following equilibrium :

**1. Single phase equilibrium :**

- Solid (ice) : represented by area  $BOC$ .
- Liquid (water) : represented by area  $AOC$ .
- Gas (vapour) : represented by area  $AOB$ .

**2. Two phase equilibrium :**

- Solid (ice)  $\rightleftharpoons$  Liquid (water) : represented by curve  $OC$ .
- Liquid (water)  $\rightleftharpoons$  Gas (water vapour) : represented by curve  $OA$ .
- Solid (ice)  $\rightleftharpoons$  Gas (water vapour) : represented by curve  $OB$ .

### 3. Three phase equilibrium :

Solid (ice)  $\rightleftharpoons$  Liquid (water)  $\rightleftharpoons$  Gas (Vapour) : represented by triple point *O*.

The phase diagram consists of :

- Three areas, *BOC*, *AOC* and *AOB*.
- Three curves, *OB*, *OA* and *OC*.
- One triple point, *O*.

For any one component system, the maximum number of degree of freedom is two. Therefore such a system can be represented completely by a two dimensional diagram. The most convenient variables are pressure and temperature. The phase diagram for water system consists of :

- Areas :** Area *BOC* represents the solid (ice) phase which is thermodynamically most stable state under these conditions. Area *AOC* represents the liquid (water) phase in the system and similarly area *AOB* represents the gas (vapour) phase in the system. Thus these areas represent one phase equilibria.

In order to define the system completely at any point in the area, it is essential to specify both the temperature and pressure. Therefore areas have two degrees of freedom and are called bivariant systems. It can also be concluded by the phase rule equation.

$$F = C - P + 2 = 1 - 1 + 2 = 2 \quad (\text{Bivariant system})$$

- Curves or boundary lines :** Separating the areas are lines *OA*, *OB* and *OC*, connecting the point at which two phases can co-exist in equilibrium. Any point on boundary lines has one degree of freedom. This follows from phase rule equation :

$$F = 3 - P = 3 - 2 = 1 \quad (\text{Univariant system})$$

(i) **The curve *OA* (Vapour pressure curve) :** Curve *OA* represents the equilibrium between the two phases, liquid water and vapour. Along this curve water and vapour coexist in equilibrium. The curve shows the vapour pressure of liquid water at different temperatures. *OA* curve is also known as vapour pressure curve of water (*l*). *A* is the critical point having temperature 374<sup>0</sup>C and pressure 218 atm. At this critical point the liquid and vapour are indistinguishable from each other and thus only one phase is left. Critical point marks the highest temperature at which the liquid can exist. Critical point is a characteristic property of pure substance.

(ii) **Curve *OB* (Sublimation curve) :** Curve *OB* represents the equilibrium between ice and vapour and it is called as sublimation curve of ice. The two phases namely ice and vapour coexist in equilibrium along this curve.

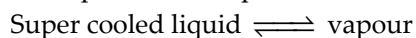
Along the curve *OC*, *OA* and *OB*, the number of phases present in equilibrium is two,

$$\therefore F = C - P + 2 = 1 - 2 + 2 = 1$$

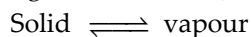
Hence system is univariant along the curve.

(iii) **Curve *OC* (Melting or fusion curve) :** The curve *OC* represents the equilibrium between ice and water (two phase equilibria) and it is known as melting point curve. The inclination of the curve *OC* towards the pressure axis indicates that melting point of ice slightly decreases by increasing pressure. The reason for this behaviour is the decrease in the volume when ice melts into water. Thus ice transforms into denser water when the pressure is raised.

(iv) **Curve  $OA'$  (Metastable curve)** : The dotted curve  $OA'$  is the continuation of vapourization curve  $OA$ . It is vapour pressure curve of supercooled water. As the water does not always freezes at  $0^{\circ}\text{C}$ , therefore if the vessel containing water and vapour is thoroughly clean and dust free, it is possible to super cool water several degrees below its freezing point.



On adding nucleus of ice (stable state) the system reverts to true stable system i.e.



3. **Triple Point** : The point  $O$  where all the three curves  $OC$ ,  $OA$  and  $OB$  meet is known as triple point. At the triple point all the three phases of water system namely solid ice, liquid water and gas vapour are in equilibrium. The equilibrium in three phases is attained at  $0.0076^{\circ}\text{C}$  temperature and 4.58 mm Hg pressure. The degree of freedom will be :

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Hence, the system is non-variant.

The main features of the phase diagram of water can be summed up as :

System	Phase	Degree of freedom
<b>Curve :</b> $OA, OB, OC, OA'$	2	1
<b>Area :</b> $AOB$ : Vapours only $BOC$ : Ice only $AOC$ : Liquid water	1	2
Triple point ( $O$ )	3	0

**Q.3 (b)** State and discuss phase rule and significance of triple point.

**Ans. Gibbs phase rule** : Gibbs phase rule states that if a heterogeneous system is influenced by temperature, pressure and concentration and not by any other action like gravity, electrical, magnetic forces or by surface action, then the sum of number of phases ( $P$ ) and degrees of freedom ( $F$ ) is greater than the number of components ( $C$ ) by two. It is expressed mathematically as follows :

$$P + F = C + 2$$

$$F = C - P + 2$$

Where,  $P$  = the number of phases

$C$  = number of components

$F$  = number of degrees of freedom

The Gibbs phase rule provides a general relationship among the degree of freedom of a system  $F$ , the number of phases  $P$  and the number of components  $C$ .

Assume that the components in the system are designated by 1, 2, 3, etc. in equilibrium between two phases  $a$  and  $b$ , then the chemical potentials of various components in the above two phases  $a$  and  $b$  may be expressed as,

$$\mu_{1(a)} = \mu_{1(b)}$$

$$\mu_{2(a)} = \mu_{2(b)}$$

$$\mu_{3(a)} = \mu_{3(b)}$$

And also  $\mu_{1(a)} = \mu_{1(b)} = \mu_{1(c)}$

In equation there are two independent equations which determine the equilibrium between the three phases. When the system is in equilibrium,  $P$  phases and  $C$  components will give a set of such equations or relationships.

$$\mu_{1(a)} = \mu_{1(b)} = \mu_{1(c)} = \dots\dots\dots\mu_{1(p)}$$

$$\mu_{2(a)} = \mu_{2(b)} = \mu_{2(c)} = \dots\dots\dots\mu_{2(p)}$$

$$\mu_{c(a)} = \mu_{c(b)} = \mu_{c(c)} = \dots\dots\dots\mu_{c(p)}$$

Here  $(P-1)$  equations are available for each constituent. Therefore for  $C$  constituent or component a total of  $C(P-1)$  independent equations are present. In this way,  $C(P-1)$  variables are automatically fixed.

$$\therefore F = [P(C-1) + 2] - C(P-1) = C - P + 2$$

In order to define the system completely therefore, this number of variables must be arbitrarily fixed, and hence will be equal to the number of degree of freedom  $F$ .

$$\therefore F = C - P + 2$$

**Triple point :** The point at which all the phases of the system coexist in equilibrium is called the triple point of the system. System is invariant at triple point (since  $F = 0$ ). If either the temperature or the pressure or both are changed, all phases would no longer coexist and at least one of them would disappear.

**Significance of triple point :** Triple point is a characteristic physical property of a pure substance. Generally, the triple point marks the lowest temperature at which the liquid can exist. As for water system, the solid-liquid phase boundary slopes in the opposite direction so the triple point criteria is not applicable with respect to temperature. But with respect to pressure, a liquid can exist as a stable phase if the pressure is above that of the triple point.

**Q.4 (a)** Differentiate between chemical corrosion and electrochemical corrosion.

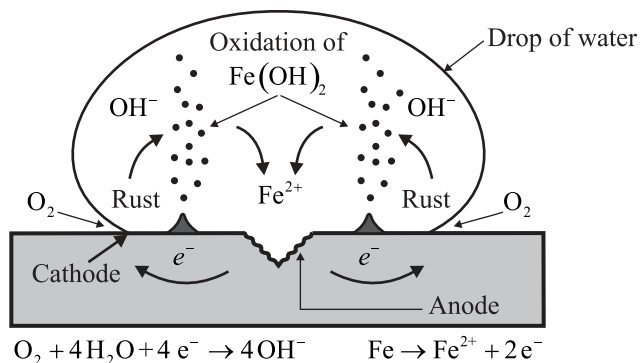
**Ans. Difference between chemical corrosion and electrochemical corrosion :**

S. No.	Chemical corrosion	Electrochemical corrosion
1.	Chemical corrosion occurs in the dry state.	Electrochemical corrosion occurs in the presence of moisture or electrolyte.
2.	It involves the direct chemical attack of the metal by the environment.	It involves the setting up of a huge number of tiny galvanic cells.
3.	It follows absorption mechanism.	It follows mechanism of electrochemical reactions.
4.	It occurs on both homogeneous and heterogeneous surfaces.	It occurs only on heterogeneous metal surface.
5.	Corrosion products accumulate at the same spot where corrosion occurs.	Corrosion occurs at the anode but products gather at the cathode.
6.	Uniform corrosion takes place.	Pitting is more frequent especially when the anode area is small.
7.	It is slow process.	It is fast process.

**Q.4 (b)** Describe the mechanism, causes and prevention of pitting corrosion.

**Ans. Pitting corrosion :** Pitting corrosion is a non-uniform corrosion resulting from a localized accelerated attack and results in the formation of pits, cavities and pin holes in the metal. Once a small pit is formed, the rate of corrosion will be increased.

Consider a drop of water resting on the surface of metal. The metal surface which is covered by the drop has low  $O_2$  concentration  $[O_2]$  and thus acts as an anode and suffers corrosion. The uncovered metal surface, due to high  $[O_2]$  acts as cathode.



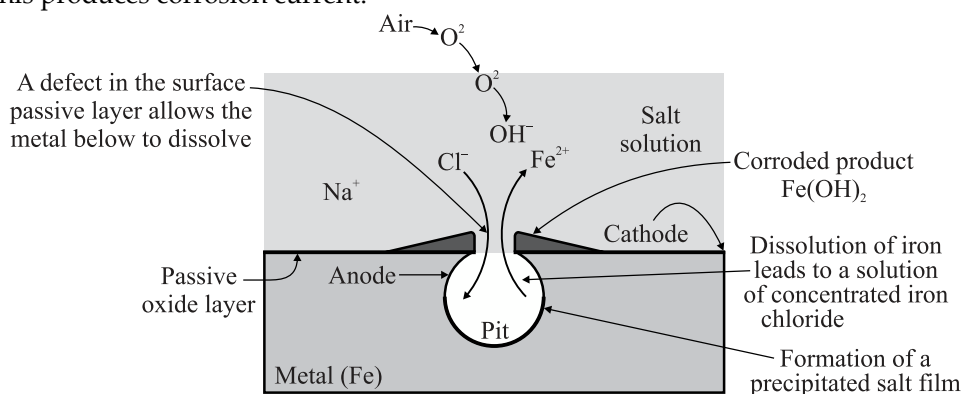
**Fig.1 Pitting corrosion**

**At anode :**  $Fe \longrightarrow Fe^{2+} + 2e^-$

**At cathode :**  $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \xrightarrow{\text{Oxidation}} Fe(OH)_3$

Formation of small anodic and large cathodic areas set up difference of potential at localized spots to pit, this produces corrosion current.



**Fig.2 Illustration of pitting corrosion**

#### Causes :

Pitting of the metal occurs when there is break in the protective layer. Breakdown of protective film may be caused by :

1. Chemical attack.
2. Turbulent flow of a solution over a metal surface.
3. Alternating stresses.
4. Sliding under load.
5. Non-uniform stresses causing straining of metal.
6. Non-uniform rough surface.
7. Scratches or cut edges.

#### Prevention :

Pitting corrosion can be prevented by :

1. The use of pure metals devoid of any impurities.
2. Proper polishing of metal surfaces.
3. Proper designing of metal structures.

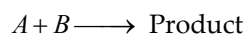


**Q.5 (a)** Discuss in detail zero order reaction along with half life period of zero order reaction.

**Ans. Zero order of reaction :**

If in a reaction, the concentrations of the reactants do not change with time and the reaction rate becomes constant and independent of the concentration, it is said to be a zero order reaction.

Alternatively, when the velocity of the reaction is proportional to the zero power of the concentration, it is called a zero order reaction. Thus for a reaction.



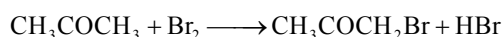
The reaction rate at a time  $t$  would be proportional to  $[A]^0$ , because it does not depend upon concentration of  $A$  or  $B$ .

$$\text{Velocity of reaction} = \frac{-d[A]_t}{dt} \propto [A]^0 [B]^0$$

$$\frac{-d[A]_t}{dt} = K_0 [A]^0 [B]^0 = K_0 \quad \left[ \because [A]^0 [B]^0 = 1 \right]$$

Where  $[A]_t$  is the concentration at time  $t$  and  $K_0$  is the velocity constant or specific reaction rate of the zero order reaction.

In such reactions, therefore, rate is not affected by concentration. The following photochemical reaction is a zero order reaction :



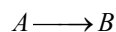
In this reaction the rate is not influenced by a change in concentration of  $\text{Br}_2$ .

For such zero order reactions,

$$\frac{dx}{dt} = \text{Constant.}$$

**Rate constant of a zero order reaction :**

When the rate of a reaction is independent of reactant concentration, the reaction is called a zero order reaction.



$$\text{The rate of reaction} \quad \frac{-d[A]_t}{dt} = K_0 [A]^0 = K_0 \quad \left[ \because [A]^0 = 1 \right] \quad \dots(\text{i})$$

At any instant  $t$ , if the amount  $x$  of  $A$  is transformed into product then the rate of reaction

$$\frac{-d[A]_t}{dt} = \frac{-d(a-x)}{dt} \quad (\text{where } a = \text{Initial concentration of reactant.})$$

$$\frac{-d[A]_t}{dt} = \frac{dx}{dt} \quad \dots(\text{ii})$$

Comparing equation (i) and (ii), we get

$$\frac{dx}{dt} = K_0 [A]^0$$

$$\frac{dx}{dt} = K_0 (a-x)^0$$

$$\frac{dx}{dt} = K_0 \quad \dots(\text{iii})$$

Separating the variable and integrating, we get

$$\int dx = \int K_0 dt$$

$$x = K_0 t + C \quad \dots(\text{iv})$$

Where,  $C$  is constant of integration.

When  $t = 0, x = 0$  [in equation (iv)]

$$C = 0$$

Hence  $x = K_0 t$  or  $K_0 = \frac{x}{t}$  ... (v)

Equation (v) is called as general rate equation for the zero order reaction.

**Unit :**  $K_0 = \frac{x}{t} = \frac{\text{concentration}}{\text{time}}$   
 $= \text{mol litre}^{-1} \times \text{time}^{-1}$

Examples of zero order reactions :

- $\text{H}_2 + \text{Cl}_2 \xrightarrow{\text{sunlight}} 2\text{HCl}$
- $2\text{N}_2\text{O} \xrightarrow{\text{hot pt wire}} 2\text{N}_2 + \text{O}_2$
- $2\text{NH}_3 \xrightarrow{W} \text{N}_2 + 3\text{H}_2$
- $2\text{HI} \xrightarrow{Au} \text{H}_2 + \text{I}_2$
- $\text{CH}_3\text{COCH}_3 + \text{I}_2 \xrightarrow{h\nu} \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$

#### Half life period for zero order reaction :

For zero order reaction the rate constant is given as,

$$K_0 = \frac{x}{t} \quad \dots (i)$$

Where,  $x$  = amount of reactant transformed into product at time  $t$ .

Let initial amount of reactant is  $a$ . If  $t_{1/2}$  is half life period of zero order reaction then according to half life reaction the concentration of reactant at half life period  $t_{1/2}$  will be  $a/2$ .

That is at  $t = t_{1/2}, x = a/2$ . Hence from equation (i),

$$K_0 = \frac{a/2}{t_{1/2}} \Rightarrow t_{1/2} = \frac{a}{2K_0}$$

The above equation shows the half life period for zero order reaction. Hence, half life period of zero order reaction is directly proportional to the initial concentration of reactant.

**Q.5 (b)** Discuss the difference between order of reaction and molecularity of reaction.

**Ans.** **Difference between molecularity and order of reaction :**

S. No.	Molecularity	Order of reaction
1.	It is the total number of atoms, ions or molecules which participate in the step leading to the chemical change.	It is the sum of the powers to which the concentration terms are raised in the rate equation for the reaction.
2.	Molecularity is always a whole number. Its zero value or negative value are not possible.	Order of reaction may be fractional, whole number or zero or negative.
3.	It can be known by writing chemical reaction.	It is determined by experiment.
4.	It is always equal to numbers of molecules participating in the reaction.	It is not always equal to the number of molecules participating in the reaction.
5.	It does not vary with conditions such as temperature, pressure or concentration.	It can vary with conditions such as temperature, pressure or concentration.

S. No.	Molecularity	Order of reaction
6.	Its magnitude cannot be changed during the reaction.	Its magnitude can be changed during the reaction.
7.	The overall molecularity of a complex reaction has no significance. Each single step has its own molecularity.	For a complex reaction, the overall order is the order of the slowest step involved in it.
8.	It provides no information about reaction mechanism.	The slowest step in the reaction can be judged by the order of the reaction and this gives further information about the mechanism.

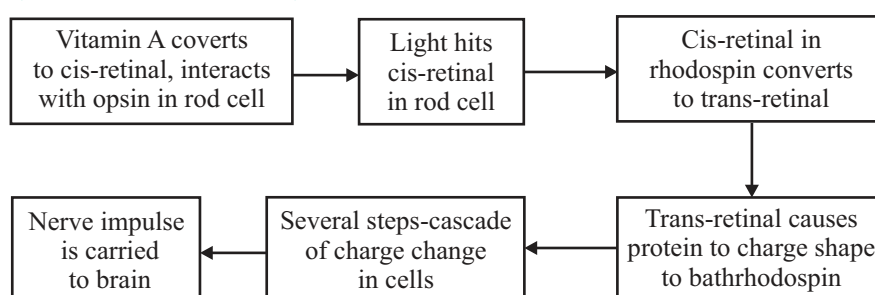
**Q.6 (a)** Give difference between electrochemical and electrolytic cell.

**Ans.** Differences between electrochemical cell and electrolytic cells :

S. No.	Electrochemical cell	Electrolytic cell
1.	It converts chemical energy (of a redox reaction) into electrical energy.	It converts electrical energy (from an external source) into chemical energy.
2.	At the electrodes, spontaneous redox reaction takes place.	At the electrodes, non-spontaneous redox reaction takes place only when electrical energy is supplied.
3.	The electrodes are made of dissimilar metals.	The electrodes may be made of same or different metals.
4.	Each electrode is dipped in electrolytic solution of its own ions.	Both the electrodes are inserted in the same electrolyte solution.
5.	Salt bridge is used.	Salt bridge is not used.
6.	Anode is negative electrode and cathode is positive electrode of the cell.	Anode is positive electrode and cathode is negative electrode of the cell.

**Q.6 (b)** Discuss chemistry of vision of human eye.

**Ans.** Chemistry of vision of human eye :

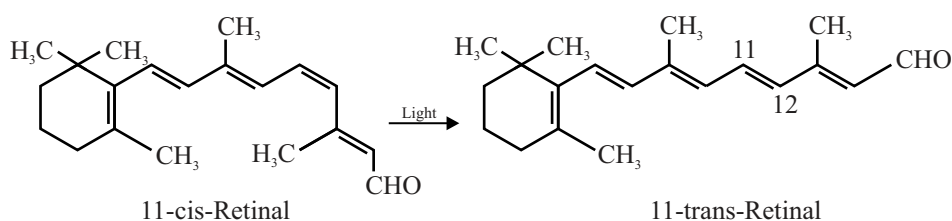


**Fig. Block diagram for vision of light through eyes**

Vision is such an everyday occurrence that we seldom stop to think and wonder how we are able to see the objects that surround us. The light image is mapped on the surface of the retina by activation of a series of light sensitive cells, known as rods and cones (photoreceptors). The rods and cones convert the light into electrical impulses, which are transmitted to the brain via nerve fibres. The

brain then determines, which nerve fibres carried the electrical impulse activated by light at certain photoreceptors and then creates an images. The tops of the rods and cones contain a region filled with membrane bound discs, which contain the molecule cis-retinal bound to protein, called opsin. The resulting complex is called rhodopsin or visual purple.

The molecule cis-retinal can absorb light at a specific wavelength when visible light hits the cis-retinal. The cis-retinal undergoes an isomerization, or change in molecular arrangement to all trans-retinal. The new form of trans-retinal does not fit as well into the protein and so a series of geometry changes in the protein begins. The resulting complex is referred to a bathrhodopsin.



As the protein changes its geometry, it initiates a cascade of biochemical reactions that results in changes in charge so that a large potential difference builds up across the plasma membrane. The potential difference is passed along to an adjoining nerve cell as an electrical impulse. The nerve cell carries this impulse to the brain, where the visual information is interpreted.

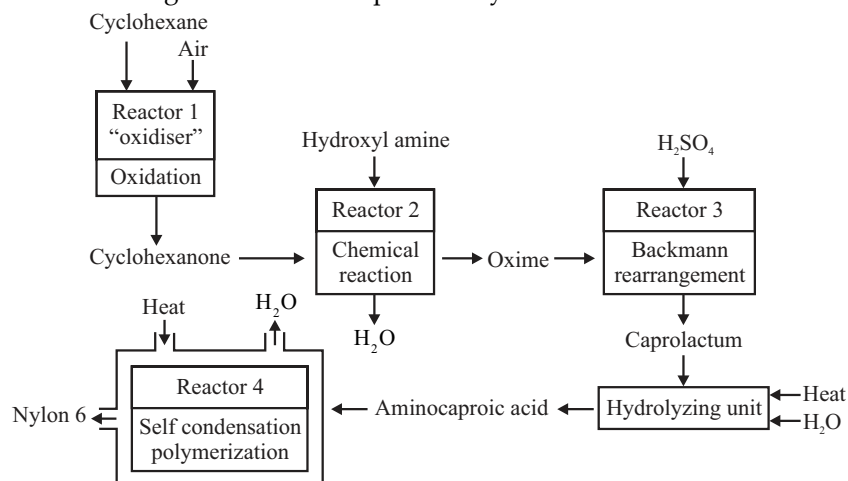
**Q.7 (a)** Write the preparation, property and uses of nylon 6.

**Ans. Nylon 6 :** Nylon is a generic designation for a family of synthetic polymers, more specifically aliphatic or semi-aromatic polyamides. They can be melt-processed into fibres, films or shapes. Synthetic fibre forming polyamides are also termed as 'Nylons'.

**Preparation :** In this method nylon 6 is obtained from petrochemical cyclohexane.

It is multi steps reaction :

**Step-I :** Cyclohexane undergoes oxidation to produce cyclohexanone.



**Fig. Flow sheet for the manufacture of nylon 6.**

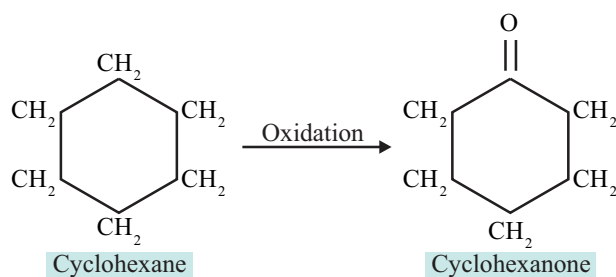
**Step-II :** Cyclohexanone reacts with hydroxyl-amine to form oxime.

**Step-III :** The oxime undergoes Beckmann rearrangement in presence of sulphuric acid to form caprolactum.

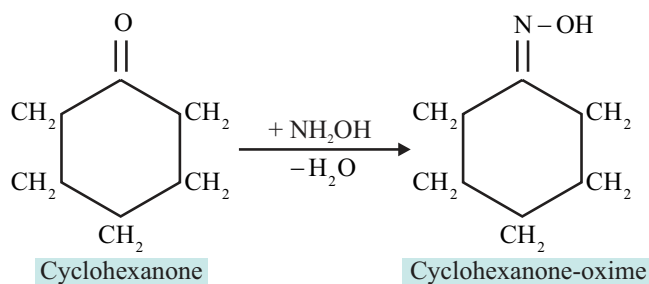
**Step-IV :** The caprolactum on heating with small amount of water undergoes hydrolysis to produce amine caproic acid which on further heating undergoes self condensation polymerization.

**Step-V :** Water is continuously removed to get continuous supply of polymer "Nylon 6".

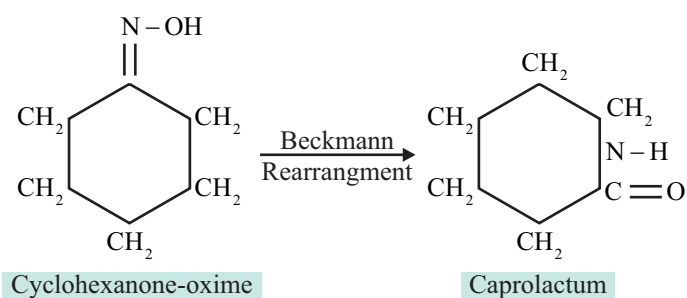
## Step-I :



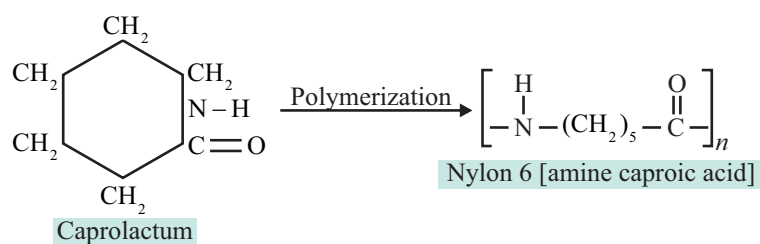
## Step-II :



## Step-III :



## Step-IV :



## Properties :

1. The structure of nylons are linear that permits side-by-side alignment.
2. Due to hydrogen bonds they have high crystallinity which imparts :
  - (a) High strength
  - (b) High melting point
  - (c) Elasticity
  - (d) Toughness
  - (e) Abrasion resistance and retention of good mechanical properties up to 125<sup>o</sup>C.
3. They are also sterilizable.
4. They have good hydrocarbon resistance.
5. They have good moisture resistance.

**Uses :**

1. It is primarily used for fibres which find use in making socks, carpets etc.
2. It is also used in mechanical engineering for well-known applications like gears, bearing, bushes, cams etc.
3. It is also used for jacketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.

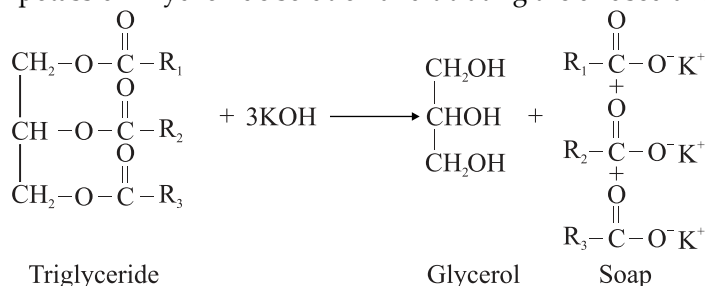
**Q.7 (b)** Explain the determination and significance of saponification numbers.

**Ans.** **Saponification value or number :** Saponification value or number of an oil is the number of milligram of potassium hydroxide required to saponify 1 gm of oil. (Saponification is the hydrolysis of an ester with KOH to give alcohol and sodium or potassium salt of the acid.)

$$\text{Saponification value} = \frac{\text{Weight of KOH in milligrams}}{\text{Weight of oil in gms}}$$

Mineral oils are the mixture of hydrocarbons and hence do not react with KOH and are not saponifiable. On the other hand, vegetable and animal oils are the mixtures of glycerol esters of fatty acids and require large amount of alkali to get hydrolyzed. Their saponification values are very high.

**Determination :** Saponification number is determined by refluxing a known quantity of oil with a known excess of potassium hydroxide solution and titrating the unused alkali against an acid.



Molecular weight of KOH = 39 + 16 + 1 = 56

For 3KOH, molecular weight = 3 × 56 = 168000 mgs .

Let molecular weight of oil or fat =  $M$

Here  $M$  gms of oil or fat require 168000 milligrams of KOH for saponification.

Therefore, one gram of fat or oil will require

$$= \frac{168000}{M} \text{ milligrams of KOH}$$

Hence, saponification number =  $\frac{168000}{M}$  mgs of KOH.

**Significance :**

- (i) As the saponification number is inversely proportional to molecular weight, hence average molecular weight of oil or fat can be found. The smaller the saponification value, the higher the molecular weight.
- (ii) It also indicates the average length of the carbon chains of the fatty acid components.
- (iii) Saponification number also gives an estimate of non-fatty impurities present in oil or fat. Thus, we can find the extent of adulteration in an oil or fat.
- (iv) As soap is formed in the product so saponification number also gives the actual amount of alkali required by triglyceride for its conversion to soap.
- (v) Mineral oils do not undergo saponification but animal and vegetables oils undergo saponification. Hence, this gives an indication of the amount of animal and vegetables oils added to mineral oils to improve oiliness. This test also helps us to ascertain whether the oil under study is animal or vegetable or mineral or compounded oil.

