

January : 2016 (CBCS)

Note :

Max. marks : 60

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

Q.1 (a) Draw molecular orbital level diagram for nitric oxide and boron molecule.

Ans. Nitric oxide (NO) :

The electronic configuration of participating N and O atoms are

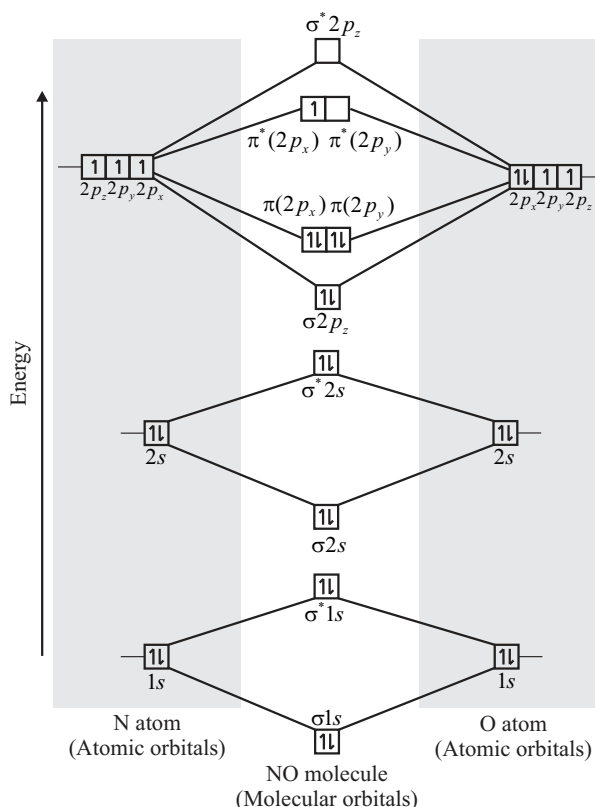
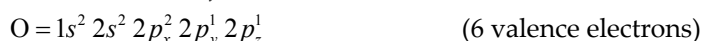


Fig.(a) Molecular orbital energy level diagram for NO molecule

Bond order :

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 5) = 2\frac{1}{2}$$

Magnetic character : NO molecule contains one unpaired electron in $\pi^* 2p_x$ orbital, hence NO molecule is paramagnetic.

Boron molecule (B_2) : For the formation of B_2 molecule, two B atoms are required. The atomic number of B is 5 and its electronic configuration is $1s^2 2s^2 2p^1$. The total of 10 electrons in B_2 molecule can be filled by following the rules : Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity. The filled molecular orbitals in B_2 molecule are shown in figure below.

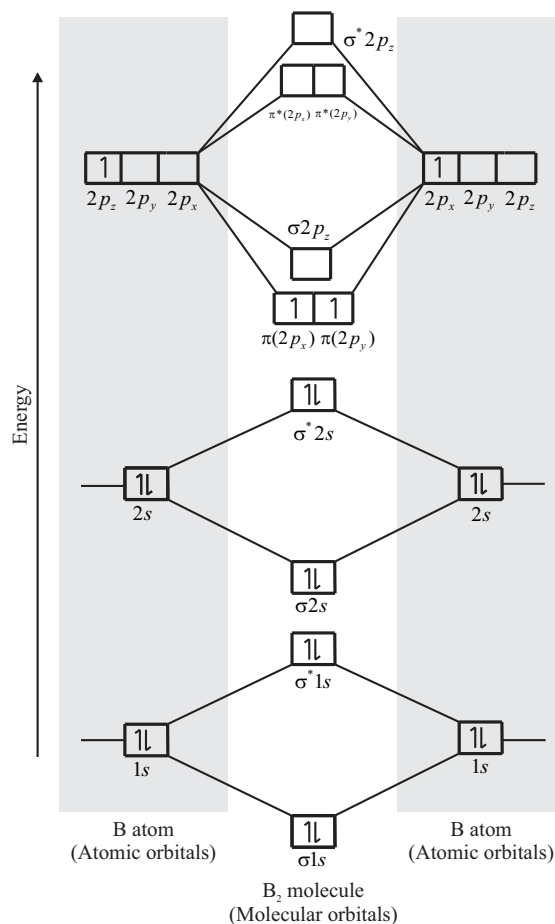


Fig.(b) Molecular orbital energy level diagram for B_2 molecule

Bond order :

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(6 - 4) = 1$$

- 1. Stability :** As the bond order is one hence B_2 molecule is stable in nature and there is single bond between two boron atoms i.e. B–B.
- 2. Nature of bond :** B_2 molecule has a weak pi bond.
- 3. Magnetic character :** As there are two unpaired electrons hence B_2 molecule is paramagnetic in nature.

Q.1 (b) Explain VSEPR model.

Ans. VSEPR theory :

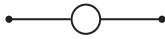
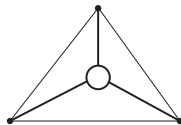
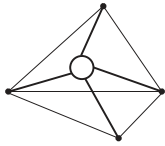
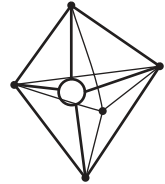
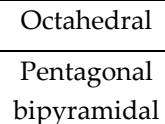

This theory was given by Sidgwick and Powell in 1940 and was further improved by Nyholm and Gillespie in 1957. The basic concept of this theory is as follows :

“The electron pair surrounding the central atom repel one another and move so far apart from one another that there are no further repulsions between them. As a result, the molecule has minimum energy and maximum stability.”

The basic postulates of the VSEPR theory which help to find the shape of a molecule are :

1. The shape of a molecule containing only two atoms is always linear.
2. For molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.

- If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons only, the repulsions between them are similar. As a result, the shape of the molecule is symmetrical and the molecule is said to have a regular geometry.
- If the central atom is linked to different atoms or is surrounded by bond pair as well as lone pairs of electrons, the repulsion between them are different. As a result, the molecule has an irregular or distorted geometry. The order of repulsions between electron pairs is as follows :
Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.
- The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

No. of atomic orbital involved	Hybridization involved	Shape of molecule	Bond angle	Example
1.	sp	Linear 	180°	$\text{BeF}_2, \text{BeH}_2, \text{CO}_2, \text{CS}_2, \text{NO}_2^+$
2.	sp^2	Planar triangular 	120°	$\text{BF}_3, \text{BCl}_3, \text{NO}_3^-, \text{CO}_3^{2-}$
3.	sp^3	Tetrahedral 	$109^\circ 28'$	$\text{CH}_4, \text{CCl}_4, \text{SO}_4^{2-}$
4.	sp^3d	Trigonal bipyramidal 	120° & 90°	$\text{PCl}_5, \text{PF}_5, \text{XeF}_2$
5.	sp^3d^2	Octahedral 	90°	$\text{SF}_6, \text{XeF}_4$
6.	sp^3d^3	Pentagonal bipyramidal 	72° & 90°	$\text{IF}_7, \text{XeF}_6$

Applications of VSEPR theory to some real molecules (shapes of molecules) :

On the basis of this theory shape of molecules can be predicted without knowing type of hybridisation.

To find the shape of a molecule, follow the steps given below :

- (i) Identify the central atom and count the number of valence electrons.
- (ii) Then find the number of electron pair shared.
- (iii) While counting the number of electron pairs for ion, value of negative charge is added and positive charge is subtracted.
- (iv) On the basis of total number of electron pairs (bond pairs + lone pairs) predict the geometry of the molecule.

Q.2 (a) Differentiate between VBT and MOT.

Ans. Difference between VBT and MOT :

S. No.	Valence bond theory (VBT)	Molecular orbital theory (MOT)
1.	After the bond formation, the combining atoms in a molecule retain their identity. Bonding is explained with the help of atomic orbitals.	After the bond formation, the combining atoms in a molecule lose their identity. Bonding is explained with the help of molecular orbitals.
2.	Only the half-filled atomic orbitals of the valence shell take part in bond formation.	It considers all the electrons in the given atoms for the prediction of number of bonds per atom.
3.	The concept of resonance is applicable only to valence bond theory.	Resonance has no role in molecular orbital theory.
4.	It fails to explain the paramagnetic character of O ₂ molecule.	It explains the paramagnetic character of O ₂ molecule.
5.	This theory finds difficulty in explaining the stability of one and three electron bond's having unpaired electrons.	The formation of one electron bond and three electron bonds can be easily explained by MOT.
6.	VBT fails to explain the formation of O ₂ ⁺ and O ₂ ⁻ ions from O ₂ has the stable octet.	MOT can explain the formation of O ₂ ⁺ and O ₂ ⁻ ions from O ₂ .

Q.2 (b) Calculate the bond order of CO and N₂.

Ans. Carbon monoxide (CO) molecule :

The electronic configurations of participating C and O atoms are



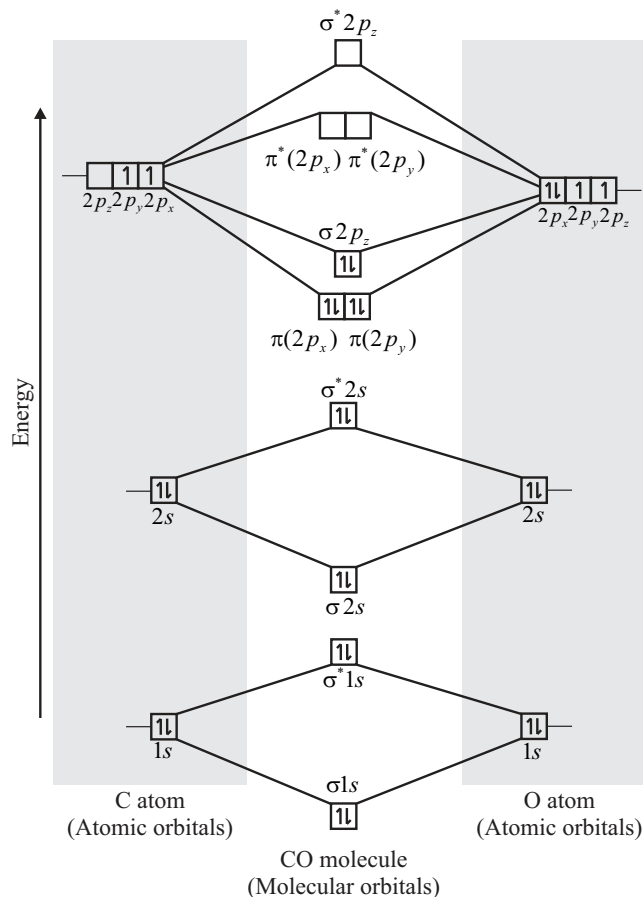


Fig.(a) Molecular orbital energy level diagram for CO molecule

It should be noted here that energy of $\sigma 2p_z$ bonding molecular orbital is higher than $\pi(2p_x)$ and $\pi(2p_y)$. Difference between energies of $2p$ orbitals of C and O is very large, therefore they can overlap only to little extent. Due to higher value of electronegativity of oxygen, energies of atomic orbitals of oxygen are lower than the energies of atomic orbitals of carbon.

Bond order :

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3$$

- Nature of bond :** This shows that carbon and oxygen atoms in CO are bonded to each other by a triple bond (one σ bond and two π bond).
- Magnetic character :** There is no unpaired electron in CO molecular and hence it is diamagnetic in nature.

Nitrogen molecule (N_2) : Electronic configuration of nitrogen $z = 7$ is $1s^2 2s^2 2p^3$. The outer shell in this case contains 5 electrons. Thus, there are 10 electrons to be accommodated in the molecular orbitals of N_2 .

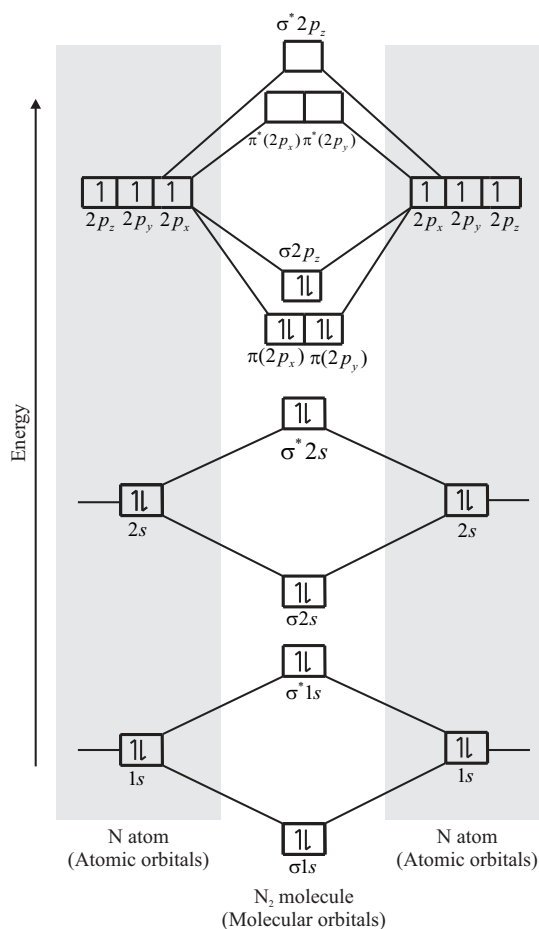


Fig.(b) Molecular orbital energy level diagram for N₂ molecules

Bond order :

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3$$

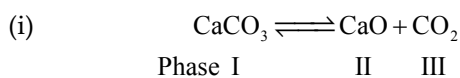
- Nature of bond :** Bond order value of 3 means that N₂ contains triple bond i.e., N ≡ N.
- Bond strength :** High value of bond order implies that it should have highest bond dissociation energy as compared to all other diatomic molecules.
- Magnetic character :** Since there are no unpaired electrons, hence N₂ is diamagnetic in nature.

Q.3 (a) Define the following term :

- Component
- Phase
- Degree of freedom

Ans. 1. Phase : A phase is defined as the part of the heterogeneous system which consists of two or more homogeneous parts which are separated from each other by definite boundaries.

Examples :



This system has three phases i.e. solid (CaCO₃), solid (CaO), gas (CO₂).

- A system consisting of water and ice : All the pieces of ice form one phase and the water another phase. Thus, there are two phases.

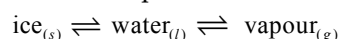
- (iii) A mixture of gases such as helium, hydrogen and argon constitutes a single phase since gases are completely miscible.
- (iv) Liquids may or may not form a single phase. It depends upon their miscibility. Completely miscible liquids constitute one phase system. For example, water and alcohol.

- 2. Component :** The component of a system in equilibrium is defined as the minimum number of independently variable constituents chosen, by means of which the composition of any phase of the system can be expressed either directly or in the form of a chemical equation.

The term component actually refers to “chemical constituents” which are present in the phases of a heterogeneous system.

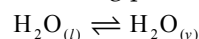
(i) Example of one component system :

- (a) Consider the case of system ice-water-vapour. At the freezing point of water, three phases are in equilibrium.



Since, the chemical composition of all the phase is H_2O , hence it is one component system.

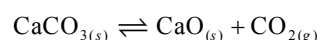
- (b) At the boiling point of water, the liquid and vapour are in equilibrium.



So in this case, number of phases are two, viz. liquid phase and vapour phase but because the chemical constituents present in either of the liquid or vapour phase is H_2O only. So this system is also a “one component system”.

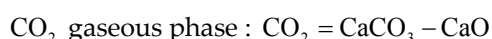
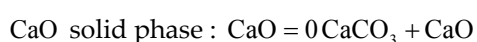
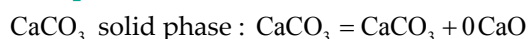
(ii) Example of two component system :

- (a) Consider the decomposition of CaCO_3 into CaO and CO_2



The composition of any phase can be expressed in terms of at least any two of the independently variable constituents CaCO_3 , CaO and CO_2 . Thus, it is a two component system.

Example :



- (b) Consider a system consisting of a solution of sugar in water. In this case the solution contains two constituents namely sugar and water. Thus, this is a two-component system.

- 3. Degree of freedom or variance :** Degree of freedom or variance of a system is defined as the minimum number of the independently variable factors such as temperature, pressure and concentration of the components which must be arbitrarily fixed in order to define the system completely.

Examples :

- (i) Consider a gaseous mixture of two gases CO_2 and N_2 in equilibrium. To define this system three variables viz. composition (35% CO_2 & 65% N_2), temperature (40°C) and pressure (760 mm) are required to be arbitrarily fixed. Hence the system has three degree of freedom.

- (ii) From definition, a gas or vapour may be completely defined by fixing two variables P and T or V because the third variable may be calculated from the equation $PV = RT$ and will have certain definite value (R is a constant), hence the degree of freedom of the system is two.
- (iii) Consider a system of two phases viz. water in equilibrium with its vapour. The vapour pressure of water will have only one fixed value at a given temperature. Thus, if temperature is arbitrarily fixed, the pressure is automatically determined and vice versa. The system will have one degree of freedom.
- (iv) For ice-water vapour system : In the system, $\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour}$, the three phases co-exist at the freezing point of water. As the freezing temperature of water has a fixed value, the vapour pressure of water also has a definite value. The system has two variables (T and P), both of which are already fixed. The system is completely defined automatically and there is no need to specify any variable. It has no degree of freedom.

Systems having degree of freedom three, two, one or zero are known as trivariant, bivariant, univariant (or monovariant) and nonvariant systems, respectively.

Q.3 (b) Draw a phase diagram of copper-silver system.

Ans. The copper-silver system : Copper and silver are completely miscible in the molten state. However, they are partially miscible in solid solution. The phase diagram of Cu-Ag system is shown in figure.

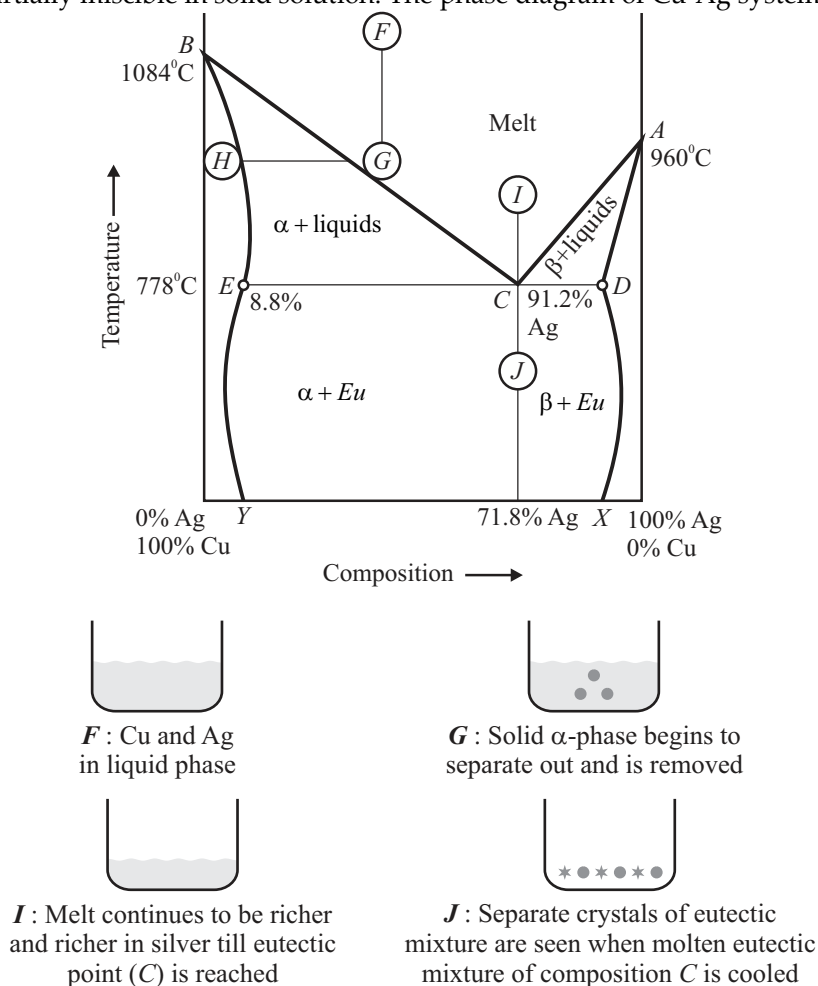


Fig. Phase diagram of copper (Cu)-silver (Ag) system

Point A = Melting point of silver ($= 960^{\circ}\text{C}$).

Point B = Melting point of copper ($= 1084^{\circ}\text{C}$).

Point C = The eutectic point of the Cu-Ag system ($= 778^{\circ}\text{C}$ and 71.8% Ag).

AC = Depression in freezing point of silver on addition of copper along AC.

BC = Depression in freezing point of copper on addition of silver along BC.

AD = The composition of β -phase a solid solution of copper in silver.

BE = The composition of the α -phase of a copper-rich solid phase of silver.

DX = The variation of β -phase with temperature below eutectic temperature.

EY = The variation of α -phase with temperature below eutectic temperature.

Area BEC = α -phase is in equilibrium with the melt.

Area ADC = β -phase is in equilibrium with the melt.

When silver is added to copper, the freezing point of copper will reduce along BC and the copper-rich solid phase of silver (α -phase) will separate from the melt. When a melt of overall composition F is slowly cooled, at the point G, a solid of α -phase will separate having composition given by H. In consequence, the melt would be silver rich. On further cooling, the composition of the liquid will proceed along GC until the point C is reached.

When copper is added to silver, the freezing point of silver will reduce along AC.

At point C, the liquids AC and BC meet and three phase (viz., α , β and liquid phase) co-exist in equilibrium.

$$\therefore P = 3$$

Applying reduced phase rule equation for two component ($C = 2$) copper-silver system

$$F + P = C + 1$$

$$F + 3 = 2 + 1$$

$$F = 0$$

Point C is the eutectic point of the Cu-Ag system. The composition of eutectic mixture is 71.8% Ag and 28.2% Cu. The eutectic temperature is 778°C , below point C, only solid phase can exist.

Eutectic mixture of Cu and Ag will melt or solidify at 778°C like a pure metal. A melt of composition less than 71.8% silver will give (on cooling below 778°C) a heterogeneous mixture of α -phase with temperature below eutectic temperature and is represented by EY.

On cooling below eutectic temperature (778°C), a melt of composition higher than 71.8% Ag will produce a heterogeneous mixture of β -phase with eutectic. The variation of composition of β -phase with temperature below 778°C is represented by DX.

Q.4 (a) What are the consequences of corrosion?

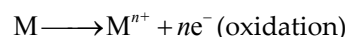
Ans. Consequence of corrosion :

1. Plant shutdown due to failure.
2. Replacement of corroded equipment.
3. Preventive maintenance (such as painting).
4. Necessity for over design to allow for corrosion.
5. Loss of useful properties of metal and thus loss of efficiency.
6. Contamination or loss of the product.
7. Decrease in production rate, because efficiency is less and replacement or repair in corroded equipment is time-consuming.
8. Increase in maintenance and production cost.

Q.4 (b) Write mechanism of electrochemical corrosion.

Ans. **Electrochemical or wet corrosion :**

- (i) It takes place mostly under wet or moist conditions through the formation of short-circuited galvanic cells.
- (ii) Separate 'anodic' and 'cathodic' parts are formed, between which current flows through the conducting medium.
- (iii) Occurrence of oxidation (corrosion) at anodic area which generates metallic ions.



- (iv) Non-metallic ions like OH^{-} or O^{2-} are formed at cathodic areas.
- (v) Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion product somewhere between anodic and cathodic areas.

Example : Fe^{2+} ions originate at anode and OH^{-} ions originate at cathode. Smaller Fe^{2+} ions diffuse more rapidly than the larger OH^{-} ions, so corrosion occurs at the anode, but rust is deposited near cathode.

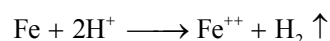
- (vi) The electrons released at the anode are conducted to the cathode and are responsible for various cathodic reactions such as :

(a) **Evolution of hydrogen :** This type of corrosion occurs usually in acidic environment.

Example : The anodic reaction is dissolution of iron as ferrous ions with the liberation of Fe^{2+} electrons.



These electrons flow through the metal from anode to cathode, where H^{+} ions (of acidic media) are eliminated by hydrogen gas.



This type of corrosion causes displacement of H^{+} ion from the acidic solution by metal ions. All metal above hydrogen in the electrochemical series have tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

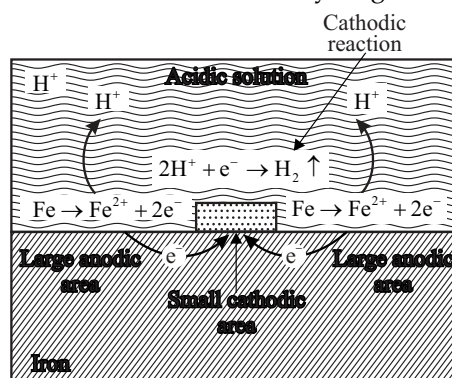


Fig.(a) Mechanism of electrochemical corrosion with evolution of hydrogen

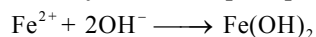
- (b) **Absorption of oxygen :** Rusting of iron in neutral aqueous solution of electrolyte (NaCl) in the presence of atmospheric oxygen is a common example of this type of corrosion. An anodic area of the metal dissolves as ferrous ion with liberation of electrons.



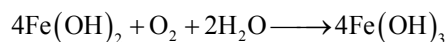
The liberated electron flows from anodic to cathodic end through iron metal,



The Fe^{2+} ions (at anode) and OH^- ions (at cathode) diffuse and when they react with each other ferrous hydroxide is precipitated.



(i) If enough oxygen is present ferrous hydroxide is easily oxidized to ferric hydroxide.



The product is formed called yellow rust.

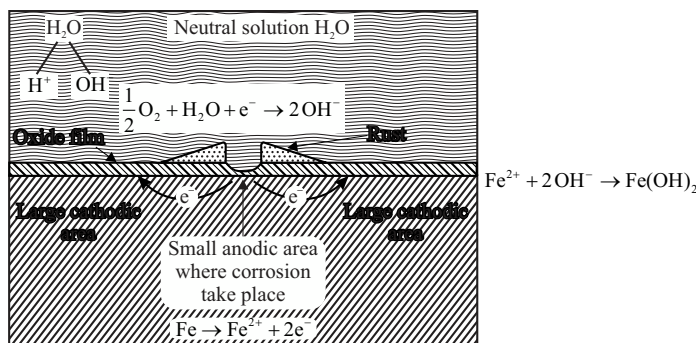


Fig.(b) Mechanism of electrochemical corrosion with absorption of oxygen

(ii) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite Fe_3O_4 . Fe^{2+} and OH^- originate from the anode and cathode respectively, but the formation of rust or deposition of rust occur near to the cathode, because the smaller Fe^{2+} diffuse more rapidly than the large OH^- ions.

Q.5 (a) Explain the following :

- (i) Transport number
- (ii) Solubility product

Ans. (i) **Transport number** : The quantity of electricity carried by an ion is proportional to its velocity or speed. The fraction of the total current carried by either ion (positive or negative), is called the transport number, transference number or Hittorf number.

Let V_a and V_c be the speeds of anion and cation respectively. Since the current carried by an ion is proportional to its speed therefore,

$$\text{Current carried by anion} \propto V_a$$

$$\text{Current carried by cation} \propto V_c$$

$$\text{The total quantity of current carried by anion and cation} \propto (V_a + V_c)$$

Therefore the fraction of total current carried by cation or the transport number of cation

$$= \frac{V_c}{V_a + V_c} = t_+ \text{ (say)}$$

Similarly the fraction of total current carried by anion or transport number of anion

$$= \frac{V_a}{V_a + V_c} = t_-$$

Hence,

$$t_+ + t_- = \frac{V_c}{V_a + V_c} + \frac{V_a}{V_a + V_c} = 1$$

$$t_+ + t_- = 1$$

Determination of transport number :

Transport number is determined by the following three methods :

1. Hittorf's method
2. Moving boundary method
3. E. M. F. method

Hittorf's method :

The principle of the method is that during electrolysis of an electrolyte the loss in weight of electrolyte around an electrode is proportional to the speed of the ion moving away from it.

$$\text{Thus, } \frac{\text{Loss around cathode}}{\text{Loss around anode}} = \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{V_a}{V_c}$$

Adding 1 to both the sides, we get,

$$1 + \frac{\text{Loss around cathode}}{\text{Loss around anode}} = \frac{V_a}{V_c} + 1 = \frac{V_a + V_c}{V_c}$$

$$\frac{\text{Loss around anode} + \text{Loss around cathode}}{\text{Loss around anode}} = \frac{V_a + V_c}{V_c}$$

Taking reciprocal, we get

$$\frac{\text{Loss around anode}}{\text{Total loss (total amount of electrolyte decomposed)}} = \frac{V_c}{V_a + V_c} = t_+$$

Thus, if the loss around anode and the total amount of electrolyte decomposed is known, the transport number of cation can be calculated.

$$\text{Similarly, } \frac{\text{Loss around cathode}}{\text{Total loss (total amount of electrolyte decomposed)}} = \frac{V_a}{V_a + V_c} = t_-$$

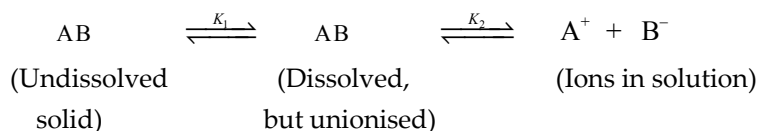
Transport number of cation and anion can also be given as,

$$t_+ = \frac{\text{Current carried by an cation}}{\text{Total current passed through the solution}}$$

$$t_- = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}}$$

(ii) Solubility product : Substances like AgCl, BaSO₄, PbSO₄, CaF₂ etc., which dissolve in water to an extremely small extent are known as sparingly soluble.

Consider the saturated solution of a sparingly soluble binary electrolyte, AB. There exist two equilibria simultaneously between undissolved solid, dissolved (but unionised) molecules and free ions i.e.



Applying the law of mass action, it follows that :

$$\frac{[\text{A}^+][\text{B}^-]}{[(\text{AB})_d]} = K_2, \quad \frac{[(\text{AB})_d]}{[(\text{AB})_s]} = K_1$$

∴ On multiplying we get :

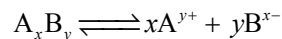
$$\frac{[\text{A}^+][\text{B}^-][(\text{AB})_d]}{[(\text{AB})_d][(\text{AB})_s]} = \frac{[\text{A}^+][\text{B}^-]}{[(\text{AB})_s]} = K_1 \times K_2$$

But the concentration of solid AB is constant so that :

$$[A^+][B^-] = \text{Constant} = K_{sp}$$

Where constant K_{sp} is known as the solubility product of AB.

In general, for an electrolyte, $A_x B_y$ which ionizes as :

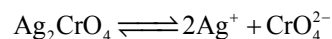


The solubility product is given by :

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Solubility product of an electrolyte may be defined as “the maximum product of the concentrations of its constituent ions (mole per litre) in its solution, when each ionic concentration term being raised to the number of times the ion occurs in the equation representing the solution of 1 molecule of the electrolyte”.

Example :



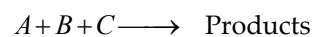
The solubility product,

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$$

Q.5 (b) Define order of reaction. How it is differ from molecularity of a reaction?

Ans. **Order of reaction :** Order of reaction is defined as the total number of reacting species (atom, ions or molecules) whose concentration actually alters during the course of chemical reaction. In other words, it is the number of concentration terms which determines the dependence of rate of reaction. For a general reaction numerical value of order of a reaction is the sum of all the exponents to which the concentrations in the rate equation are raised.

Thus, when the rate of a reaction,



is given by, $\frac{-dc}{dt} = K \cdot C_A^x \cdot C_B^y \cdot C_C^z$

Where, K = Specific reaction rate.

x, y, z = Reaction order of individual reactants A, B, C respectively.

Then order of the reaction as whole = $x + y + z$.

The sum of the powers to which the concentration terms are raised in the rate law is known as the order of the reaction.

The order of reaction can be known only experimentally and chemical equations totally fail to supply information about the order of a reaction.

Example : For the reaction $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$, the following experimental data was collected :

Experiment	[NO]	[O]	Rate (M/s)
1.	0.1	0.1	0.5
2.	0.2	0.1	2.0
3.	0.1	0.2	1.0

The general rate law for this reaction would be :

$$\text{Rate} = K[NO]^m [O_3]^n$$

In this example it can be seen that ongoing from experiment 1 to experiment 2, the [NO] doubles ($[O_3]$ is held constant) and the rate increased four-fold, which means that the reaction is second order with respect to NO i.e. $m = 2$. If experiments 1 and 3 are compared, it can be seen that the $[O_3]$ doubles ([NO] is held constant) and the rate doubled. Therefore, the reaction is first order with respect to O_3 i.e. $n = 1$ and the rate equation is,

$$\text{Rate} = k[\text{NO}]^2[\text{O}_3]$$

Hence, the overall order = $m + n = 2 + 1 = 3$.

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.
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) Describe relationship between C_p and C_v .

Ans. Relation between C_p and C_v :

Heat capacity at constant volume is given as,

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

Heat capacity at constant pressure is given as,

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Therefore, $C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_v$... (i)

Enthalpy of the system is given as,

$$H = E + PV \quad \dots(\text{ii})$$

Differentiating equation (ii) with respect to temperature at constant pressure, we get

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \quad \dots(\text{iii})$$

Combining equation (i) and (iii), we get

$$C_p - C_v = \left(\frac{\partial E}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_v \quad \dots(\text{iv})$$

If we consider V and T as independent variables out of P, V and T , then

$$E = f(T, V)$$

and therefore $dE = \left(\frac{\partial E}{\partial T}\right)_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV$... (v)

Dividing both sides by dT , and considering pressure constant, we get

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_p &= \left(\frac{\partial E}{\partial T}\right)_v \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \\ \left(\frac{\partial E}{\partial T}\right)_p &= \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \quad \dots(\text{vi})$$

This equation (vi) is now substituted in equation (iv), we get

$$C_p - C_v = \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial E}{\partial T}\right)_v \quad \dots(\text{vii})$$

$$C_p - C_v = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \quad \dots(\text{viii})$$

Here the term $\left(\frac{\partial E}{\partial V}\right)_T$ represents change in internal energy with changes in volume at constant temperature and it is known as internal pressure. Internal pressure is measure of interactions between the molecules.

$$\left[\left(\frac{\partial E}{\partial V}\right)_T\right]_{\text{solids}} > \left[\left(\frac{\partial E}{\partial V}\right)_T\right]_{\text{liquids}} > \left[\left(\frac{\partial E}{\partial V}\right)_T\right]_{\text{gases}}$$

Hence, for an ideal gas,

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad \dots(\text{ix})$$

For an ideal gas, $PV = RT$

Differentiate with respect to T at constant pressure, we get

$$P\left(\frac{\partial V}{\partial T}\right)_p = R \quad \dots(\text{x})$$

Hence, from equation (viii), (ix) and (x), we get

$$C_p - C_v = R$$

Where, R is gas constant.

Hence Proved.

- Q.6 (b) Write short note on :
- Flash and fire point
 - Viscosity index

Ans. 1. Flash and fire point :

Flash point : The flash point of an oil is the lowest temperature at which it gives off vapours that will ignite for a moment when small flame is brought near it.

Fire point : The fire point of an oil is the lowest temperature at which the vapours of the oil burn continuously for atleast 5 seconds when a small flame is brought near it.

Significance :

- An ideal lubricating oil should have a flash point which is considerably above the working temperature of machine to ensure safety against fire hazards.
- Flash point and fire point of lubricating oils help in knowing the highest temperature upto which an oil can be used as lubricant.
- Knowledge of flash and fire points in lubricating oil aids in precautionary measures against fire hazards.
- It is useful for identification and detection of contaminants in the oil.

Determination : The determination of flash and fire point can be made by using the following apparatus :

- Abel's closed cup apparatus
- Pensky Marten's apparatus
- Cleveland flash point apparatus

Pensky Marten's flash and fire point apparatus :

It consists of following parts :

- Oil cup
- Shutter
- Flame exposure device
- Air bath
- Pilot burner.

Working :

- The oil sample is filled up to the specified filling mark in the cup.
- It is then covered and positioned properly in the stove.
- The thermometer is inserted in the sample.
- The test flame is lighted while being stirred, the sample is heated at the rate of 9^oF to 11^oF per minute upto 220^oF.
- The test flame is applied at every 2^oF rise in temperature, thereafter it is applied at every 5^oF rise in temperature.
- When a distinct flash occurs in the interior of the cup at the time of the flame application, the temperature reading on the thermometer is the flash point.

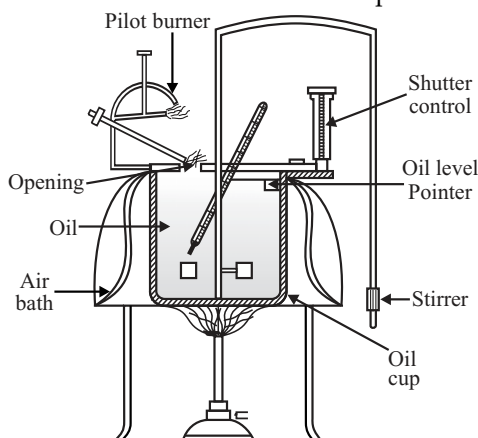


Fig. Pensky Marten's flash point apparatus

2. **Viscosity index (V.I.) :** Viscosity is the property of a fluid that determines its resistance to flow. Viscosity index is an indicator of flowability of a lubricating oil. The lower the viscosity, greater the flowability.

Significance : Viscosity helps in the selection of good lubricating oil. For instance, light oils have low densities and easy flowabilities. These oils when used on parts moving at high speed, promotes the formation of a good oil film. Moreover, light oils do not impose much drag on high-speed parts.

Determination : For determining viscosity-index, two types of standard oils are used as reference. One of these is pennsylvanian oil. The pennsylvanian oil consists mainly of paraffin and shows a small decrease in the viscosity with increase in temperature. These oils are arbitrary given a value of 100 for viscosity index. The other reference taken is naphthanic base, Gulf oils.

V.I. = 100 ; Pennsylvanian oil

V.I. = Zero ; Naphthanic base gulf oil

For the determination of viscosity index, first the viscosity of the oil under test is determined at 100^oF and 210^oF . Let it be U and V respectively.

$$\text{Then, Viscosity index} = \frac{V_L - U}{V_L - V_H} \times 100$$

Where, V_L = Viscosity at 100^oF of gulf oil which has the same viscosity at 210^oF as that of oil under test.

U = Viscosity of oil under test at 100^oF.

V_H = Viscosity at 100^oF of pennsylvanian oil which has the same viscosity at 210^oF as that of oil under test.

Q.7 (a) Write mechanism of polymerization.

Ans. Techniques of polymerization : The conversion of a monomer into a polymer is an exothermic reaction, if this heat is not dissipated or properly controlled, serious explosions will result. The main manufacturing processes are given below :

- 1. Bulk polymerization :** It is used in producing polystyrene, PVC and polymethyl methacrylate. The polymerization is carried out in two stages. In the first stage, the monomer is taken in the liquid state and the initiator is dissolved in the monomer. The reaction mass is heated for initiating the polymerization. As the proportion of the polymer increases, the temperature also increases and the reaction mixture is cooled by circulating water through cooling coils. In the second stage, the highly viscous polymerization mixture is fed into the upper end of a vertical reactor. The reaction is carried out at 110-200^oC. Almost 100% polymerization is achieved.
- 2. Suspension polymerization :** This process is largely used to manufacture PVC and polystyrene. Only water insoluble monomer can be polymerized by this technique, The monomer is dispersed as fine droplets in water containing gelatin as suspending agent to stabilise suspension, i.e. to prevent the droplets from coalescing. The polymerization is initiated by a monomer soluble initiator (benzoyl peroxide for vinyl chloride). Polymerization proceeds to 100% conversion and the product is obtained as spherical beads or pearls.
- 3. Emulsion polymerization :** It is widely used to prepare polyvinyl chloride, polyvinyl acetate, etc. the monomer is dispersed in water as droplets which are stabilized by the addition of soap. Initiators are either water soluble or monomer soluble. Normally, persulphates are used as initiators. The polymer obtained is in the form of latex. The latex can be coagulated with an acid to get the solid polymer.

4. **Solution polymerization** : It is the polymerization of one or more monomers in solution. Vinyl chloride, acrylonitrile and vinyl acetate are polymerized by this method. It is used to create polymers and copolymers by dissolving a monomer and a catalyst in a non-reactive solvent. The disadvantages of this method are that the polymer produced is of low molecular weight and is always contaminated with traces of solvent.

- Q.7 (b)** Write short note on :
 (i) Gibbs-Helmholtz equation
 (ii) Norrish type-I reaction.

Ans. (i) Gibbs Helmholtz equation : The Gibbs Helmholtz equation is a thermodynamic equation used for calculating changes in the Gibbs energy of a system as a function of temperature.

Free energy is related to enthalpy and entropy as,

$$G = H - TS$$

∴ Enthalpy of the system,

$$H = E + PV$$

∴ $G = E + PV - TS$

Differentiating G , we get

$$dG = dE + PdV + VdP - TdS - SdT \quad \dots(i)$$

From first law of thermodynamics,

$$dq + dw = dE$$

$$dq = dE - dw \quad \dots(ii)$$

If work is done only due to expansion, then

$$dw = -PdV$$

∴ $dq = dE + PdV$

For reversible process entropy change is,

$$dS = \frac{dq}{T} \Rightarrow TdS = dq \quad \dots(iii)$$

From equation (ii) and (iii), we get

$$TdS = dE + PdV \quad \dots(iv)$$

Combining equation (i) and (iv), we get

$$dG = dE + PdV + VdP - dE - PdV - SdT$$

$$dG = VdP - SdT \quad \dots(v)$$

At constant pressure, $dP = 0$ then,

$$dG = -SdT \quad \dots(vi)$$

Let, G_1 = initial free energy of a system at T ,

$G_1 + dG_1$ = Initial free energy of the system at $T + dT$, where dT is infinitesimally small and pressure is constant, then

$$G_1 + dG_1 - G_1 = dG_1 = -S_1dT \quad \dots(vii)$$

Where, S_1 is the entropy of the system in the initial state.

Now suppose that the free energy of the system in final state is G_2 at T . Let $G_2 + dG_2$ is the free energy of the system at $T + dT$ in the final state. Then,

$$G_2 + dG_2 - G_2 = dG_2 = -S_2dT \quad \dots(viii)$$

Where, S_2 is the entropy of the system in the final state.

Subtracting (vii) from (viii), we get

$$dG_2 - dG_1 = -(S_2 - S_1)dT$$

$$d(\Delta G) = -\Delta SdT \quad \dots(ix)$$

∴ At constant pressure,

$$\left[\frac{\partial(\Delta G)}{\partial T} \right]_p = -\Delta S \quad \dots(x)$$

Now, change in Gibbs free energy is,

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ -\Delta S &= \frac{\Delta G - \Delta H}{T} \quad \dots(xi) \end{aligned}$$

From equations (x) and (xi), we get

$$\begin{aligned} \frac{\Delta G - \Delta H}{T} &= \left[\frac{\partial(\Delta G)}{\partial T} \right]_p \\ \Delta G &= \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p \quad \dots(xii) \end{aligned}$$

This equation is called **Gibbs Helmholtz equation** in terms of free energy and enthalpy changes at constant pressure.

Gibbs Helmholtz equation in terms of work function :

Equation (xii) can also be written as,

$$\Delta G = \Delta E + P\Delta V + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p \quad \dots(xiii)$$

Since, Gibbs free energy and Helmholtz free energy is related as,

$$\Delta G = \Delta A + P\Delta V$$

For constant volume, $\Delta V = 0$

$$\therefore \Delta G = \Delta A \quad \dots(xiv)$$

Hence, from equation (xiii) and (xiv) it can be written as,

$$\Delta A = \Delta E + T \left[\frac{\partial(\Delta A)}{\partial T} \right]_V \quad \dots(xv)$$

(For constant volume, $\Delta V = 0$, hence $P\Delta V = 0$)

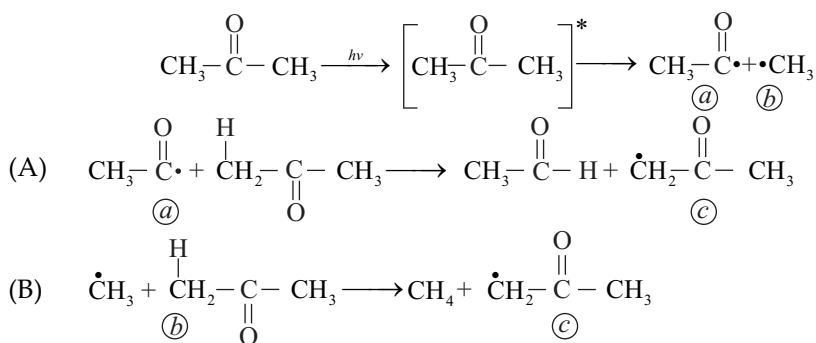
This equation is Gibbs Helmholtz equation in terms of work function.

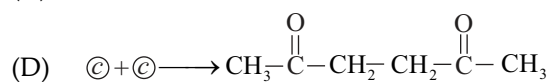
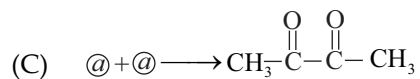
- (ii) **Norrish type - I reaction** : Ketones after photochemical excitation undergo homolytic fission at the α -carbon-carbon bond. This is because the bond dissociation energy of a carbon-carbon bond adjacent to a carbonyl is comparatively small. This process is known as α -cleavage or Norrish type - I reaction.

Example : Acetone

The decomposition of acetone via triplet state is more efficient and the quantum yield (ϕ) is almost unity.

At room temperature, the photo irradiation of acetone yield biacetyl, acetaldehyde, methane etc.





At elevated temperature, the photolysis of acetone yields carbon monoxide and ethane.

