

• Chemistry - 18CYB101J

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• Unit IV - Thermodynamics

→ The study of It simply means the flow of heat. Thermodynamics deals with the relationship between heat and work, i.e., it is the interconversion between heat and other forms of energy.

→ What is a System?
It is a body of matter confined in space by walls, which separates it from its surroundings.

→ Types of Systems:

1. Isolated System
2. Closed System
3. Open System

→ Properties of a System:

1. Intensive - are independent of the amount of mass
2. Extensive - Varies directly with the mass.

→ Thermodynamic Processes:

The operation by which the change of state occurs.

→ Types:

1. Isothermal
2. Adiabatic
3. Isochoric
4. Cyclic
5. Irreversible
6. Reversible

1. Internal Energy

2. Enthalpy

3. Entropy

4. Gibbs Free Energy

5. Helmholtz Free Energy

1. Internal Energy: (E)

It is the total energy content of a system.

Def. It is the sum of potential energy of the molecules due to their mutual attraction and KE due to their motion.

→ IE is an extensive property and a State Function.

State Function: The system is independent of the path.

→ Change in IE.

Absolute IE cannot be determined directly, that is why the change in IE (ΔE) can be calculated.

→ Expression of IE,

Consider the expansion of a gas in a closed system at constant pressure.

Suppose the heat supplied to the system is Q .

A part of their heat may be used by the system itself to increase IE (ΔE) and rest is used for doing external work.

i. Heat supplied to the system Q
 $=$ Used to increase IE (ΔE)
 + Some work.

$$Q = \Delta E + w \quad \text{--- (1)}$$

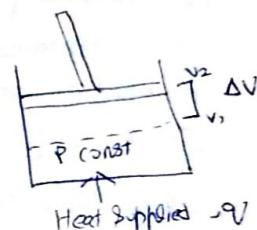
Since the expansion of gas is carried at constant pressure (P), the work done by the system

$$w = P\Delta V \quad \text{--- (2)}$$

Sub (2) in (1)

$$Q = \Delta E + P\Delta V$$

$$\Delta E = Q - P\Delta V$$



2. Enthalpy: (H)

Energy stored in the bonds of compounds

$$\Delta H = \text{Products} - \text{Reactants}$$

Def. Enthalpy of Combustion: +ve Enthalpic -ve Exothermic

The change in heat content when 1 mole of the substance is completely burnt in excess of oxygen

Enthalpy of formation:

The change in heat content when 1 mole of the compound is formed from its elements

Mathematically, this function is defined by the relation,

$$H = E + PV$$

Absolute value of enthalpy cannot be determined. However the change in enthalpy (ΔH) is determined from 1st Law of Thermodynamics,

$$Q = \Delta E + P\Delta V \quad (\text{at const. Pressure})$$

$$= (E_2 - E_1) + P(V_2 - V_1)$$

$$= E_2 - E_1 + PV_2 - PV_1$$

$$= (E_2 + PV_2) - (E_1 + PV_1)$$

$$= (H_2 - H_1)$$

$$\therefore \boxed{\Delta H = \Delta U}$$

So, the change of enthalpy ΔH is equal to the quantity of heat changes (Q) at constant pressure.

Since, E and PV are state functions, ΔH of the system is also a state function.

3. Entropy: (S)

It is the quantity that tells whether a chemical reaction can occur spontaneously in an isolated system or not.

Def. The thermal property of a substance which remains constant during an adiabatic cyclic change.

It is expressed in JK^{-1} .

The absolute value cannot be determined. The change in entropy (ΔS) during the state change can be calculated.

ΔS is defined as the integral of all terms involving heat absorbed (q_V) divided by Kelvin Temp. (T).

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

[Reversible Process]

$$\Delta S_{\text{sys}} + \Delta S_{\text{surf}} > 0$$

[Irreversible Process]

$$\boxed{\Delta S = \frac{q_{\text{rev}}}{T}}$$

It is a state function and is an extensive property.

→ Entropy change in reversible process

Consider an isothermal reversible expansion of an ideal gas at temp. T . During the expansion, let q_V be the amount of heat absorbed by the sys. from the surroundings. Change in entropy of the sys.

$$\Delta S_{\text{sys}} = \frac{q_V}{T}$$

At the same time, the surroundings release the same amount of heat q_V at same temp. (T)

$$\Delta S_{\text{surf}} = -\frac{q_V}{T}$$

∴ Total change in entropy = Change in entropy in sys + entropy of surroundings.

$$\Delta S = \Delta S_{\text{sys}} + \Delta S_{\text{surf}}$$

$$= \frac{q_V}{T} + \left(-\frac{q_V}{T} \right)$$

$\Delta S_{\text{tot}} = 0$ for a reversible process.

• Entropy is constant for a reversible process

→ Entropy Change in Irreversible Process

Let the system be at higher temp. T_1 and its surroundings at lower temp. T_2 .

q_V is the quantity of heat passing irreversibly from system to surroundings.

$$\text{Decrease in entropy of sys. } \Delta S_{\text{sys}} = -\frac{q_V}{T_1}$$

$$\text{Increase in entropy of surf. } \Delta S_{\text{surf}} = \frac{q_V}{T_2}$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surf}}$$

$$= \frac{-q_V}{T_1} + \frac{q_V}{T_2}$$

$$= q_V \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$= q_V \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

$g_{\text{gas}} > \text{liquid} > \text{solid}$

$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$

$\rightarrow T_1 > T_2$, $T_1 - T_2$ is positive.

$$\therefore \Delta S_{\text{tot}} = \text{positive (or)} \quad \Delta S_{\text{tot}} > 0$$

Hence during the irreversible process, the entropy of the system increases.

4. Gibbs Free Energy (G_f) Constant P (Net useful work)

Free energy of a system is a thermodynamic state function, which is related to enthalpy and entropy as

Extensive Property
State function

$$G_f = H - TS$$

Def. Free energy change (ΔG_f) of a system or a reaction is "a measure of energy available for doing useful work"

$$G_f = H - TS$$

(Energy available for useful work)
 \downarrow Non-available energy

The change in free energy between two states of the system,

$$\Delta G_f = G_{f2} - G_{f1} = (H_2 - T_2 S_2) - (H_1 - T_1 S_1)$$

↓
Non-spontaneous in forward direction

$$\Delta G_f = \Delta H - (T_2 S_2 - T_1 S_1)$$

↓
Non-spontaneous in the forward direction at Const. Temp. $\rightarrow T_1 = T_2$

then,

$$\Delta G_f = \Delta H - T \Delta S$$

We know that

ΔG_f	ΔH	ΔS	T
-ve	+	+	high
-ve	-	+	
+ve	+	=	low
-ve	-	-	

$$\Delta H = \Delta E + P\Delta V \quad (\text{at Const P})$$

$$\therefore \Delta G_f = \Delta E + P\Delta V - T\Delta S \quad (\text{at Const T})$$

$$\Delta G_f = \Delta E + RT \ln K \Rightarrow \Delta G_f^\circ = -RT \ln K$$

5. Helmholtz Free Energy (A) Constant V (Maximum work)

It is also known that, "a part of internal energy of a system to do some useful work at const temp. This part of internal energy (E) which is iso thermally available is called "work function" (A) of the system.

It is mathematically defined as

$$A = E - TS \quad \text{--- (1)}$$

Extensive Property / State function

$$\Delta A = \Delta E - T\Delta S \quad \text{--- (2)}$$

But the entropy change is given as

$$\Delta S = \frac{\nabla_{\text{rev}}}{T} \quad \text{--- (3)}$$

$$\text{or } T\Delta S = \nabla_{\text{rev}} \quad \text{--- (4)}$$

Substituting (4) in (2),

$$\Delta A = \Delta E - \nabla_{\text{rev}} \quad \text{--- (5)}$$

But according to first law of thermodynamics

$$\Delta E = \nabla V - w$$

$$\Delta E - q_v = -w \quad \text{--- (6)}$$

sub (6) in (5),

$$\Delta A = -w \quad (\text{or})$$

$$\Delta A = -w_{\text{max}}$$

↓ Work done by the System

(w_{max} - maximum work)

6. Gibbs-Helmholtz Equation:

$$G_f = H - TS \quad \text{--- (1)}$$

$$\text{and } H = E + PV \quad \text{--- (2)}$$

Substituting (2) in (1)

$$G_f = E + PV - TS$$

Upon differentiating,

$$dG_f = dE + PDV + VDP - TdS - SdT \quad \text{--- (3)}$$

also,

$$dE = dq_v - PdV \quad (\text{First Law}) \quad \text{--- (4)}$$

$$dq_v = TdS \quad (\text{Second Law}) \quad \text{--- (5)}$$

Substituting the values of (4) and (5) in (3),

$$dG_f = dq_v - PdV + PDV + VDP - TdS - SdT$$

$$\therefore TdS + VDP - TdS - SdT$$

$$dG_f = VDP - SdT$$

at Const Pressure,

$$dG_f = -SdT$$

$$\delta G = -S\delta T$$

For any two States of the System,

$$\delta G_1 = -S_1 \delta T$$

$$\delta G_2 = -S_2 \delta T$$

$$\delta G_2 - \delta G_1 = -S_2 \delta T - (-S_1 \delta T)$$

$$\delta G = -S_2 \delta T + S_1 \delta T$$

$$\delta G = -(S_2 - S_1) \delta T$$

$$\frac{\delta G}{\delta T} = -\Delta S \quad \text{--- (6)}$$

But according to the definition of free energy,

$$\Delta G = \Delta H - T\Delta S$$

$$-\Delta S = \frac{\Delta G - \Delta H}{T} \quad \text{--- (7)}$$

Substituting (7) in (6),

$$\frac{\Delta G - \Delta H}{T} = \left[\frac{\delta \Delta G}{\delta T} \right]_P \quad (\text{or})$$

$$\Delta G - \Delta H = T \left[\frac{\delta \Delta G}{\delta T} \right]_P$$

$$\boxed{\Delta G = \Delta H + T \left[\frac{\delta \Delta G}{\delta T} \right]_P}$$

This equation is Called Gibbs-Helmholtz equation in terms of free energy and enthalpy changes at const. pressure.

Application of Gibbs-Helmholtz Equation:

1. The calculation of enthalpy change of the reaction in galvanic cell,

If a cell yields nF coulombs of electricity in a reversible manner, it must be equal to the decrease in free energy, then,

$$-\Delta G = nFE^\circ \quad \text{--- (1)}$$

Hence, Gibbs-Helmholtz eqns. is written as

$$-nFE^\circ = \Delta H + T \left[\frac{\delta (nFE^\circ)}{\delta T} \right]_P$$

$$(\text{or}) \quad -nFE^\circ = \Delta H - nFT \left[\frac{\delta E^\circ}{\delta T} \right]_P$$

$$(\text{or}) \quad \Delta H = -nF \left[E^\circ - T \left[\frac{\delta E^\circ}{\delta T} \right]_P \right]$$

Knowing the value of E° and the temp. coefficient $\left(\frac{\delta E^\circ}{\delta T} \right)$ of the cell reaction, it is possible to evaluate the enthalpy change (ΔH) of the reaction.

2. Calculation of Entropy change:

ΔH and ΔS are related by the equation

$$\Delta G = \Delta H - T\Delta S$$

We know that $\Delta G = -nFE^\circ$, and ΔH can be calculated by the eqns,

$$\Delta H = -nF \left[E^\circ - T \left[\frac{\delta E^\circ}{\delta T} \right]_P \right]$$

Hence ΔS can be calculated easily from the above equation.

3. Calculation of EMF of the Cell:

$$\Delta H = -nF \left[E^\circ - T \left[\frac{\delta E^\circ}{\delta T} \right]_P \right]$$

(or)

$$E^\circ = \left[-\frac{\Delta H}{nF} \right] + T \left[\frac{\delta E^\circ}{\delta T} \right]_P$$

Electrochemical Cells:

An electrochemical cell is a device, used to convert chemical energy into an electrical energy. It consists of two electrodes namely anode, cathode and an electrolyte. In this cell, electrons transferred in the redox reaction is utilized as a source of producing electrical energy.

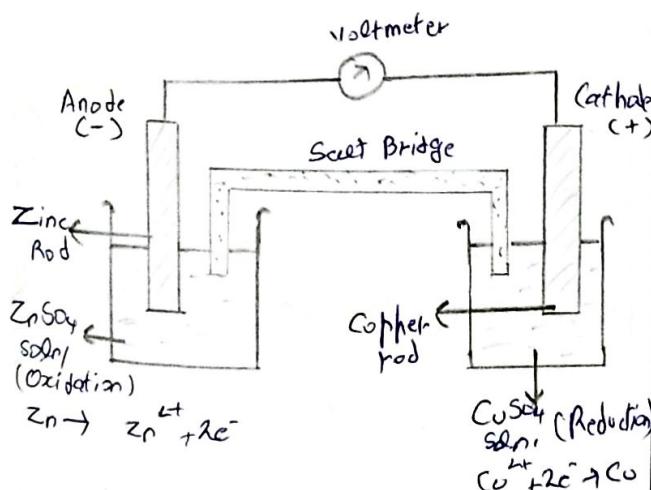
Galvanic Cell:

In a galvanic cell, a Zinc rod is partially immersed in 1M $ZnSO_4$ solution and a Copper rod is partially immersed in 1M $CuSO_4$ solution. The two solutions are interconnected by a salt-bridge. The salt bridge is a U-tube containing saturated KCl or NH_4NO_3 in agar-agar gel. The salt bridge provides electrical contact between two compartments, without allowing them to mix with each other.

Anode - Oxidation occurs;

Cathode - Reduction occurs.

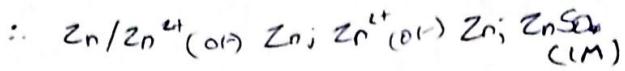
Each electrode is regarded as a half cell.



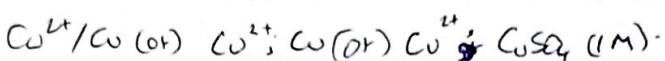
Cell Representation:

1. Anode is written on the left hand side while cathode is written on the right hand side.
2. Anode is written by writing the metal first and then electrolyte. The two are separated by a vertical line or a semi-colon. The electrolyte may be represented by the formula of the whole compound or by

ionic species. Additional information regarding concentration may also be mentioned in bracket.

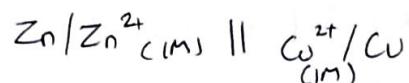


3. The Cathode of the cell is written on the right hand side. In this case, the electrolyte is represented first and the metal thereafter. The two are separated by a vertical line or a semi-colon.



4. A salt bridge is indicated by two vertical lines separating the two half-cells.

In Daniel cell, we may represent it as



The practical application of galvanic cell is Daniel cell.

Relationship between Cell Potential and Free energy:

Let us consider the electrochemical cell in which n equivalent (no. of moles) of reactants are converted into products. Then, the quantity of electricity that flows through the cell is nF .

Where F = Faraday Constant = 96485 C/equ.

When this amount of electricity is transported through the cell of emf E volt, then the amount of electrical work done by the cell = NEF .

The work done by the cell is at the expense of free energy decrease resulting from the cell reaction.

\therefore Decrease in Gibbs free energy = Electrical work obtainable from the cell.

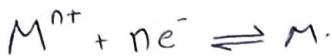
$$\text{i.e., } (\Delta G)_T, p = NEF$$

Single Electrode Potential:

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called SEP.

Derivation of Nernst Equation:

Consider the following redox reaction



For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium constant (k) are interrelated as

$$\begin{aligned}\Delta G &= -RT \ln k + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ &= \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} - \textcircled{1}\end{aligned}$$

Where ΔG° = Standard free energy change.
The above equation is known as Van't Hoff isotherm.

The decrease in free energy ($-\Delta G$) in the reaction will produce electrical energy.
In the cell, if the reaction involves transfer of $n e^-$ s, then Faraday 'F' of electricity will flow. If E is the emf of the cell, then the total electrical energy (nFE) produced in the cell is

$$\begin{aligned}-\Delta G &= nFE \quad \text{(or)} \\ -\Delta G^\circ &= nFE^\circ \quad \textcircled{2}\end{aligned}$$

- ΔG - decrease in free energy change.
- ΔG° - decrease in standard free energy change.

Comparing eqs ① and ② it becomes:

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]} - \textcircled{3}$$

Dividing above eqs-③ by $-nF$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

[the activity of solid metal $[M] = 1$]

In general

$$(E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]})$$

(or)

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^\circ + \frac{2.303 RT}{nF} \log [M^{n+}] \quad \textcircled{4}$$

When $R = 8.314 \text{ J/K/mol}$,

$F = 96500 \text{ Coulombs}$

$T = 298 \text{ K } (28^\circ \text{C})$,

the above equation becomes

$$E = E^\circ_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \quad \textcircled{5}$$

Similarly for oxidation potential

$$E = E^\circ_{\text{oxi}} - \frac{0.0591}{n} \log [M^{n+}] \quad \textcircled{6}$$

The eqs ⑤ and ⑥ are known as Nernst eqs for single electrode potential.

• Applications:

1. The emf of the acid-base reaction is calculated with the help of Nernst eqs.

$$\begin{aligned} p^{H^+} &= -\log [H^+] \\ p^{OH^-} &= -\log [OH^-] \\ p^H + p^{OH^-} &= 14 \end{aligned}$$

$$\begin{aligned} E_{\text{cell}} &= E_R - E_L \\ &= 0.2422 - \frac{0.0591}{n} \log [H^+] \end{aligned}$$

(or)

$$\text{EMF of the cell} = 0.2422 + \frac{0.0591}{n} p^H$$

2. Predicting Spontaneity (or) feasibility of Redox reactions.

Spontaneity of the redox reaction can be predicted from the emf (E°) value of the complete cell reaction.

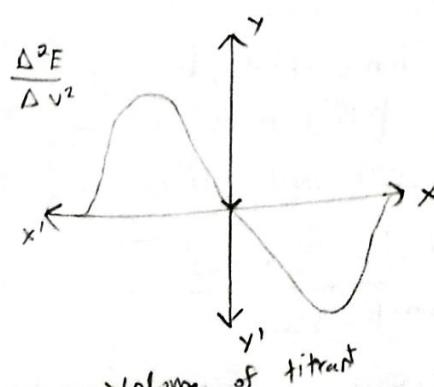
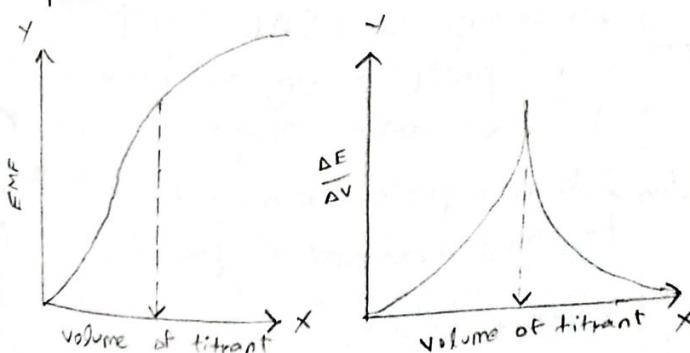
$$(\Delta G = -nFE^\circ)$$

- i) If E° of the cell is positive, $\Delta G = -ve$ i.e., the reaction is feasible.
- ii) If E° of the cell is negative, the reaction is not feasible as $\Delta G = +ve$.

EMF of the cell for Redox reaction

$$= \frac{E_1 + E_2}{2}$$

Graphs:



• Solubility Equilibria:

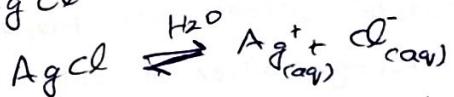
It is a type of dynamic equilibrium that exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound.

K_{sp} is the solubility product constant. It is the equilibrium constant which exists in between a solid and its respective ions in a solution. The value of the constant identifies the degree of which the compound can dissociate in water.

For ex, the higher the K_{sp} , the more soluble the compound is.

• Expression of Solubility Product:

Let us consider the solubility of AgCl .



(usually solubility product is calculated only for insoluble salts. because soluble salts will completely dissolve in solvents and there is no solubility product.)

If we dissolve 1g of AgCl , in 1 lit of water, only 0.001 mol of AgCl will be dissociated into its ions.

$$\therefore K_{sp} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{H}_2\text{O}]}$$

$[\text{AgCl}]$ can not be written, as it is a solid. K_{sp} can be written only for ions. The amount (or) concentration of H_2O is also a constant because it is not taking part in the reaction.

$$K_{sp} [\text{H}_2\text{O}] = [\text{Ag}^+][\text{Cl}^-]$$

$$(or) \quad K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

• Hard-Soft-Acid-Base (HSAB) Principle:

It is a qualitative concept introduced by Pearson to explain the stability of metal complexes and the mechanisms of their reactions.

According to Lewis concept,

An acid is an electron pair acceptor.
An base is an electron pair donor.

This can be further divided into Hard or Soft - acids and bases.

According to HSAB Concept, hard acids prefer binding to the hard bases to give ionic complexes, whereas the soft acids prefer binding to soft bases to give covalent complexes.

- The large electronegativity differences between hard acids and hard bases give rise to strong ionic interactions.
- The electronegativities of soft acids and soft bases are almost same and hence have less ionic interactions. i.e., the interactions between them are more covalent. *Covalent Compounds*
- The interactions between hard-acid-soft-base or soft-acid-hard-base are unstable. Lead to polar Covalent Compounds

• Corrosion:

Any process of destruction or disintegration and consequent loss of solid metallic material through an unwanted chemical or electrochemical attack by its environment starting at its surface is called corrosion. Thus, corrosion is a process of "reverse extraction of metals".

Ex: 1) Rusting of Fe, when exposed to atmosphere.

2) Formation of green film of basic carbonate ($\text{CuCO}_3 + \text{Cu(OH)}_2$) on the surface of Cu, when exposed to moist air containing CO_2 .

• HSAB Theory:

According to this theory, Lewis acids and bases can be further divided into hard (or) soft acids and bases.

Hard Lewis Acid:

Characteristics:

(Large radius)
Small size, highly charged Cations, high positive charge, empty orbitals in their valence shells, low electronegativity and low electron affinity.

Ex: H^+ , Li^+ , K^+ , Ca^{2+} , Al^{3+} , BF_3 , AlCl_3 , CO_2 , SO_3 etc.

Soft Lewis Acids:

Characteristics:

Large ionic radii, low positive charge, completely filled atomic orbitals, readily polarizable. *Intermediate Salts*
Ex: Cu^{2+} , Ag^+ , Hg^+ , Pt^{2+} , BH_3 , Br_2 , I_2 etc.

• HSAB Principle

According to HSAB Concept, hard acids prefer binding to hard bases to give ionic complexes whereas soft acids prefer binding to soft bases to give covalent compounds

Hard Lewis Bases:

Characteristics:

Small ionic radii, highly electronegative, weakly polarizable, strongly solvated
Ex: F^- , OH^- , NH_3 , H_2O , SO_4^{2-} , PO_4^{3-} , etc.

Soft Lewis Bases:

Characteristics:

Large ionic radii, intermediate electronegativity, highly polarizable.
Ex: H^- , R^- , CO , SCN^- , $\text{C}_6\text{H}_5\text{C}_6$, RNC .

→ HSAB Principle:

→ The large electronegativity differences between hard acid and hard base give rise to strong ionic interactions.

The electronegativities of soft acids and soft bases are almost same and hence have less ionic interactions. i.e. the interactions between them are more covalent.

The interaction between H-A - S-B (or) S-A - H-B are mostly less stable.

• Corrosion:

→ Classification:

Based on the mechanism followed, corrosion may be classified into two types:

- 1) Dry or Chemical Corrosion or Direct chemical attack.
- 2) Wet or Electrochemical Corrosion.

1) Dry or Chemical Corrosion:

This type of corrosion is mainly caused due to the direct reaction of metal surfaces with the atmosphere gases like O₂, CO₂, H₂S, SO₂, N₂ Cl₂ etc. There are 3 main types of chemical corrosion.

a) Oxidation Corrosion.

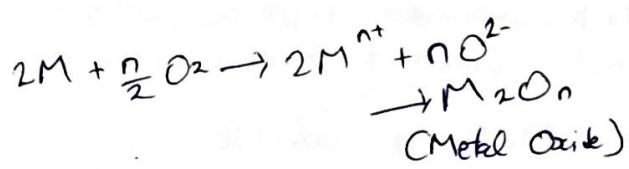
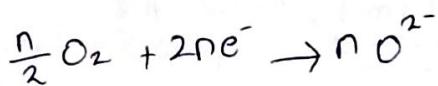
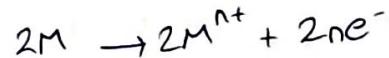
b) Corrosion by other gases.

c) Liquid-metal Corrosion.

a) Oxidation Corrosion:

This is brought about by the action of clean metal surface with O₂ at low & high temp/ in the absence of moisture. Alkali and alkaline earth metals are quickly oxidised even at low temp. All the other metals are oxidised at high temperature.

The reactions are



Mechanism:

Oxidation occurs first at the surface of the metal and the resulting metal oxide scale forms a barrier which tends to restrict further corrosion. For oxidation to continue, either the metal must diffuse outward or the oxygen must diffuse inward through the scale to the underlying metal. Both transfers occur, but the outward diffusion is more rapid than the inward diffusion due to smaller size and higher mobility of the metal ion.

Nature of the oxide film formed plays an important role. If the film is,

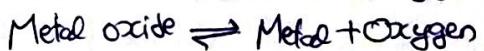
1. Stable

It means formation of an impermeable coating on the metal surface, which restrict further penetration of oxygen inside the metal. This film acts as a protective coating thereby shielding the metal surface.

Ex: Al, Sn, Pb, Cu, Pt etc are stable oxides.

2. Unstable:

i.e. the oxide layer formed decomposes back into the metal and oxygen.



∴ Oxidation Corrosion is not possible in this case

Ex: Au, Ag, Pt do not undergo oxidation.

3. Volatile:

The oxide layer evaporates as soon as it is formed, leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion.

Ex: MoO_3 is volatile.

4. Porous:

The oxide layer formed has pores or cracks through which atmospheric oxygen can penetrate through the surface of the metal and corrosion continues till the whole metal is converted into metal oxide.

→ Pilling-Bedworth Rule:

According to Pilling-Bedworth rule, "an oxide is protective or non-porous, if the volume of the oxide is greater than the volume of the metal from which it is formed".

On the other hand, "if the volume of the oxide is less than the volume of the metal, the oxide layer is porous and hence non-protective."

1. Protective and non-porous:

Al_2O_3 whose volume is greater than the volume of the metal Al. ∵ an extremely strong non-porous layer is formed thereby decreasing the rate of corrosion.

2. Non-Protective and Porous:

Alkali and alkaline earth metals form oxides of volume less than the volume of the metals. ∴ this layer is affected by stress and strain thereby developing cracks and pores in its structure. Thus corrosion continues non-stop.

b) Corrosion by Other gases:

Gases like CO_2 , Cl_2 , F_2 , H_2S , SO_2 etc will also attack the surface of the metals leading to corrosion.

In these cases the effect of corrosion mainly depends on the chemical affinity between the metal and the gas involved.

1) If the film formed is protective and non-porous, the extent of attack decreases, because the film formed protects the metal from further attack.

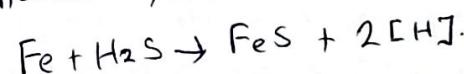
Ex: AgCl film.

2) If the film formed is non-protective or porous, the extent of attack increases and the surface of the whole metal is destroyed.

Ex: D₂y Cl_2 gas attacks Sn forming volatile SnCl_4 .

→ Corrosion by Hydrogen Gas:

It is a kind of corrosion due to hydrogen gas. When metal is exposed to hydrogen environment like H_2S , this causes the evolution of H_2 at the metallic surface.

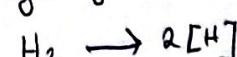


This atomic hydrogen diffuses inside the metal easily and gets collected in the voids present inside the metal where it recombines to produce H_2 molecule.

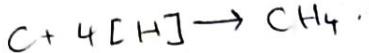
This H_2 gas leads to cracking or blistering of the metal at high pressure which reduces the strength and activity of metal.

→ Decarburisation:

Presence of C in steel give sufficient strength to it. When steel is exposed to H_2 environment at high temperature atomic hydrogen is formed.



This reacts with C on Steel and produces methane gas.



Hence, the Carbon content of steel is decreased. Collection of this gas inside the steel leads to cracking. In this way steel loses its strength and is termed as decarburization.

c) Liquid-Metal Corrosion:

It is due to the chemical action of flowing liquid metal at high temp. on solid metal or alloy.

This type of corrosion occurs in nuclear power reactors.

This corrosion involves either

- 1) dissolution of solid metal by a liquid metal (or)
- 2) Internal penetration of the liquid metal into the solid metal.

Both these modes will lead to the weakening of the metal.

2) Wet (or) Electrochemical Corrosion:

This type of corrosion occurs,

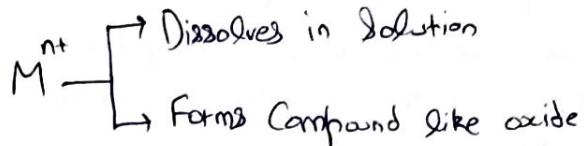
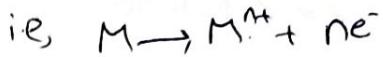
- a) When a metal is exposed to an electrolyte with varying amount of oxygen.
- b) When two dissimilar metals or alloys are in contact with each other in presence of an aqueous solution or moisture.

Mechanism:

Corrosion occurs due to the existence of separate anodic and cathodic areas between which current flows through the conducting solution.

At anodic area,

Oxidation takes place by the liberation of free e^- 's and the metal ion is destroyed either by dissolving or to the combined state.



Hence, corrosion always occurs at anodic areas.

At Cathodic area,

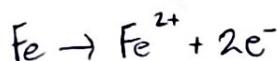
Reduction reaction takes place by the gain of e^- 's either by

- a) Evolution of Hydrogen or
- b) Absorption of Oxygen, depending upon the nature of the corrosive environment.

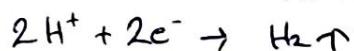
Hence the metallic ions (at anodic part) and non-metallic ions (OH^- or O^{2-}) (at cathodic part) will diffuse towards each other through the medium and form a corrosive product somewhere between anode and cathode.

a) Evolution of Hydrogen:

It occurs usually in acidic environments. Considering Fe, the anode reaction is dissolution of Fe as Fe^{2+} ions with the liberation of e^- 's.



These e^- 's flow through the metal, from anode to cathode, where H^+ ions are eliminated as hydrogen gas.

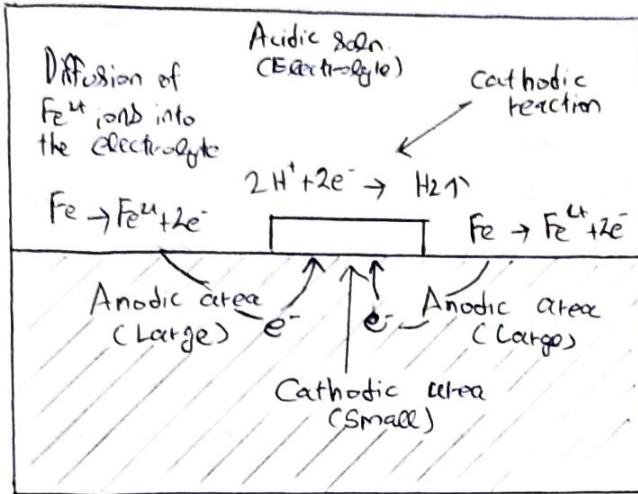


The overall reaction is,



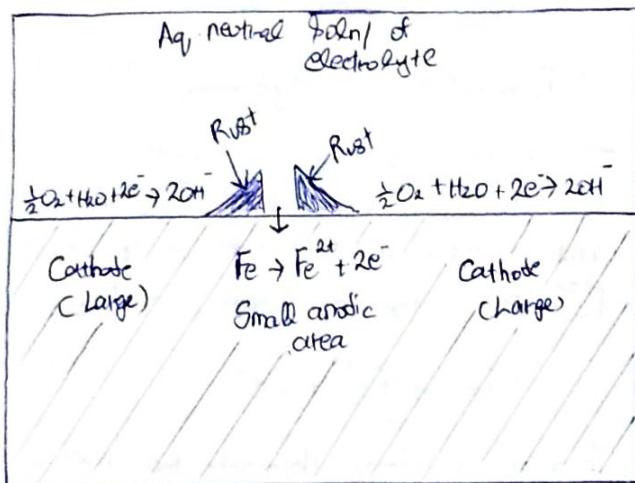
This type of corrosion causes,

"displacement of H^+ ions from acidic solution by metal ions". Consequently all metals above hydrogen in the emf series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen. In hydrogen evolution type corrosion usually the anodes are very large areas and the cathodes are small areas.



b) Absorption of Oxygen:

This type of corrosion takes place on the metal surfaces in neutral parts or weakly alkaline environment with oxygen.

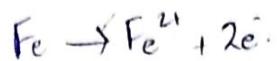


The formation of anodic area on the metal surface is due to various factors like:

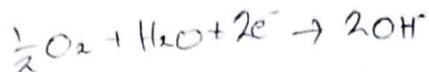
1. Partial roughness of metal surface
2. Minute cracks on the surface
3. Presence of impurities.

When Fe is exposed to neutral or alkaline environment the following reaction takes place,

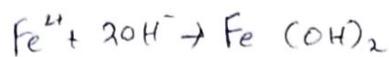
At anode: Liberation of e^- 's takes place



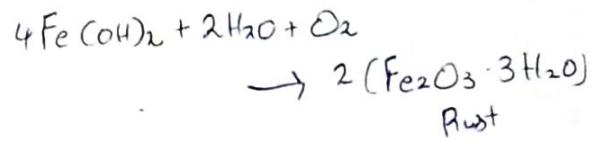
At cathode e^- 's are absorbed as follows:



Fe^{2+} and OH^- ions are attracted to the metal surface to form the product ferrous hydroxide



Finally with more oxygen and moisture ferrous oxide is easily oxidized to $Fe(OH)_3$.



Hence excess of oxygen and moisture greatly accelerates corrosion.

• Types of wet or electrochemical corrosion:

→ Continued on the back, flip the book

• Free Energy of a Corrosion Reaction:

$$\Delta G_f = -nFE$$

If $\Delta G < 0$ It is spontaneous and

• Corrosion will occur.

If $\Delta G > 0$ it is not spontaneous and corrosion will not occur.

Types of wet or Electrochemical Corrosion:

1. Galvanic Corrosion.

2. Differential Aeration Corrosion.

Galvanic Corrosion:

It is also known as Bimetallic Corrosion. It occurs when two dissimilar metals are connected and exposed to corrosive environment. The less noble metal undergoes corrosion and more noble metal is cathodically protected by the galvanic current.

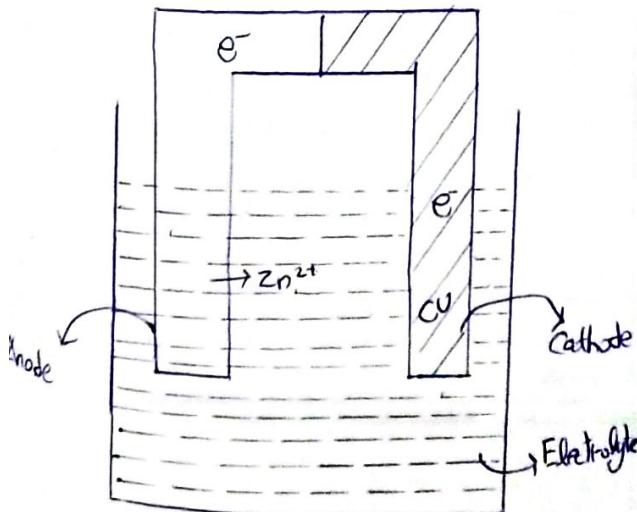
In case of Zn and Cu, Zn will act as anode (higher in electrochemical series) and undergoes corrosion whereas as Cu (lower in emf series) acts as a cathode and is not effected.

Current flows from anode to cathode, corrosion takes place at anode while cathodic metal is not affected.

Prevention

It can be prevented by,

- 1) Selecting the metals, which are very close in their electrode potential.
- 2) Providing an insulating material to the two metals.

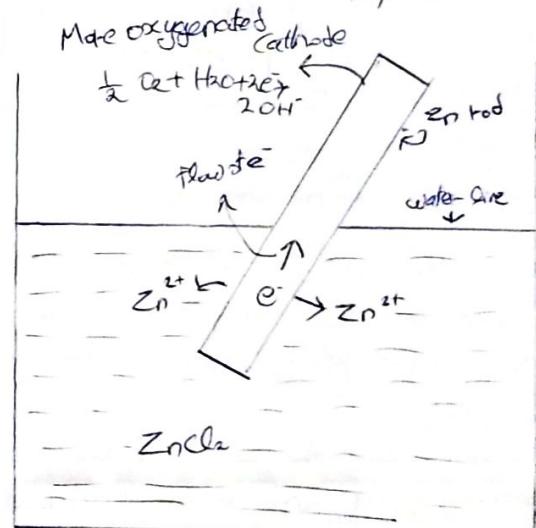
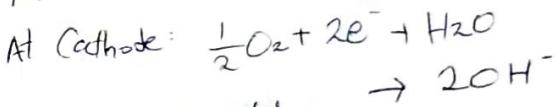
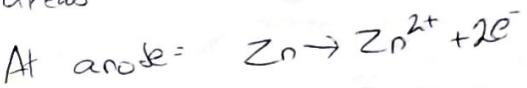


2. Differential Aeration Corrosion:

This occurs when different parts of the metal are exposed to different air concentrations.

If a metal is partially immersed in a dilute solution of NaCl, the parts above are closely adjacent to the water-line are more exposed to oxygen and hence become cathodic. On the other hand parts are immersed to greater depth have exposed to less oxygen concentration become anodic.

Zinc dissolves at the anodic areas.



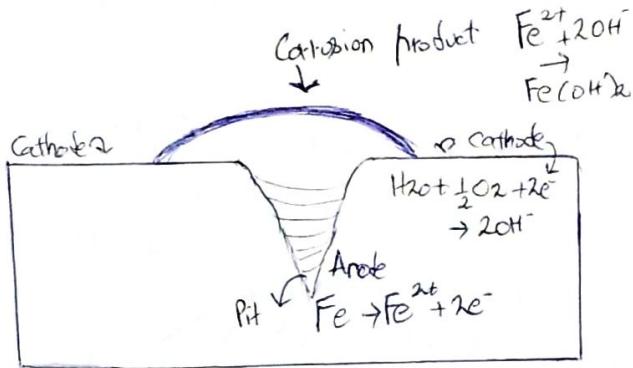
• Examples of Differential Aeration Corrosion:

1. Pitting Corrosion.
2. Water-line Corrosion.
3. Stress Corrosion.

Pitting Corrosion:

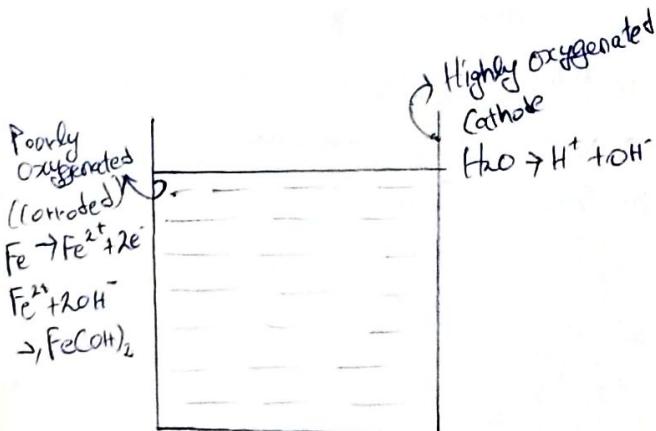
It is a localised accelerated attack resulting in the formation of cavities around which the metal is relatively unattacked. This results in the formation of holes or cavities in the metal.

Let us consider a water drop resting on the metal surface. The area covered by water drop acts as anode due to less oxygen concentration and suffers corrosion. The uncovered area acts as cathode due to high oxygen concentration.



2. Water Line Corrosion:

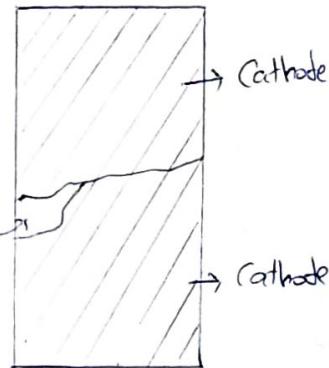
When water is stored in a steel tank, it is seen that the maximum amount of corrosion takes place along a line just below the level of water meniscus. The area above the water line is highly oxygenated and acts as a cathode and is completely unaffected.



3. Stress Corrosion:

This type of corrosion is seen in fabricated articles of certain alloys (like Zn brass and Ni brasses) due to the presence of stress caused by heavy working.

These pure metals are relatively immune to corrosion. Stress results in the formation of cracks which grows and propagates till failure occurs.



Ex:

Caustic embrittlement, occurring in mild steel when exposed to alkaline solutions at high temperature and stresses.

Boiler water usually contains certain proportion of Na_2CO_3 , added for water softening purposes. In high temp pressure boilers, this breaks up to give NaOH and CO_2 and makes boiler water alkaline.

Factors Influencing Corrosion:

Corrosion takes place in the metal due to the influence of its environment.

Corrosion mainly depends on,

i) Nature of the metal.

ii) Nature of the environment.

i) Nature of the metal:

a) Position in Galvanic Series

b) Over Voltage.

c) Relative areas of anode and Cathode.

d) Purity of Metals.

e) Physical State of metals.

f) Nature of the Surface Film.

g) Nature of Corrosion product.

a) Position in Galvanic Series:

Metals with negative electrode potential (compared to hydrogen) in electrochemical series and in galvanic series are more prone to Corrosion.

These metals are highly reactive in nature and they behave as anodes.

On the other hand metals with positive electropotential are less prone to Corrosion. They behave as cathode and are less reactive.

b) Over Voltage:

When Zn metal is placed in H_2SO_4 solution, it undergoes corrosion forming a film evolving hydrogen gas. The initial evolution is slow because of high overvoltage of $\text{Zn}(\text{0.70V})$ metal.

If few drops of CuSO_4 are added, the corrosion rate (i.e. dissolution of Zn metal to the electrolyte) is accelerated because some Cu gets deposited on the Zn metal forming minute cathodes where the overvoltage is 0.33V. Thus, reduction in overvoltage of the corroding metal accelerated

the corrosion rate. Cu will get thereby reducing the concentration of e^- . Hence voltage will decrease

$$\text{Corrosion Rate} \propto \frac{1}{\text{Over Voltage}}$$

c) Relative areas of anode and Cathode:

When two dissimilar metals are in contact, corrosion in anodic area will be directly proportional to the ratio of areas of cathodic parts and anodic parts.

$$\text{Corrosion area} \propto \frac{\text{Area of Cathode}}{\text{Area of anode}}$$

Corrosion will be severe if the anodic area is smaller and cathodic area is larger. The larger the cathodic area will create a great demand for e^- which can be satisfied by smaller anodic area by undergoing further corrosion.

d) Purity of Metals:

Impurities in a metal generally causes 'heterogeneity' and thus tiny electrochemical cells are formed and the anodic part gets corroded.

Ex:

Zn metal containing impurities such as Pb or Fe undergoes corrosion due to formation of local electrochemical cells.

E) Physical State of the Metal

The rate of corrosion is influenced by physical state of the metal like grain size orientation of crystals, stress etc.

The smaller the grain size of the metal, the greater will be its solubility and hence greater will be its corrosion.

Also, areas under stress, even in a pure metal tend to be anodic and corrosion takes place at these areas.

F) Nature of the Surface Film

In aerated atmosphere, normally all metals get covered with a thin surface film of metal oxide. Metals like Mg, Fe etc form oxides whose specific volume is less than the volume of the metal. Hence, the oxide film formed will be porous and more oxygen diffuses inwards leading to more corrosion.

Metals like, Cr, Al, Ni etc form oxides whose specific volume is greater than that of the metal atom. This oxide film is compact and impervious and corrosion will be prevented.

g) Nature of Corrosion Product

In electrochemical corrosion, if corrosion product is soluble in the corroding medium, corrosion proceeds at a faster rate. On the other hand if the product is insoluble or if it interacts with the medium to form another insoluble product which will act as a barrier thereby suppressing further corrosion.

2. Nature of the Environment

a) Temperature

b) Humidity

c) Presence of Corrosive gases

d) Presence of Solid suspended particles

e) Effect of P^H

f) Nature of ions present

a) Temperature

Increase in temperature increases the reaction rate as well as the diffusion rate and hence the rate of corrosion is increased.

Temperature \propto Corrosion Rate

b) Humidity:

Humidity is directly proportional to corrosion rate. It is the deciding factor of atmospheric corrosion. The basic requirement for enhancement of corrosion in humid conditions is that the atmospheric gases like CO_2 , O_2 etc dissolve in water to produce the electrolyte which is essential for electrochemical corrosion.

Humidity \propto Corrosion

c) Presence of Corrosive gases:

In the industrial area, the atmosphere is polluted with CO_2 , SO_2 , H_2S etc and fumes of HCl , H_2SO_4 etc.

These gases produce electrolytes which are acidic thereby increasing atmospheric corrosion.

Similarly marine air atmosphere contains more Cl^- ions which also increases the corrosion rates.

d) Presence of Solid suspended particles:

If the suspended particles are chemically active like $NaCl$, $(NH_4)_2SO_4$ etc they absorb moisture and act as strong

electrolytes, thereby increasing corrosion rate

If the suspended particles are chemically inactive like charcoal, they absorb both gases and moisture which also slowly increases the corrosion rate.

Effect of pH

Generally acidic medium is more corrosive than alkaline medium.

The corrosion rate of Fe in oxygen free water is slow at $pH < 5$. But the corrosion rate is much higher in presence of oxygen.

Consequently corrosion of metals can be reduced by increasing the pH of the attacking environment.

Ex: Zn is readily corroded in acidic solution, suffers very less corrosion in alkaline medium ($pH = 11$)

f) Nature of ions present:

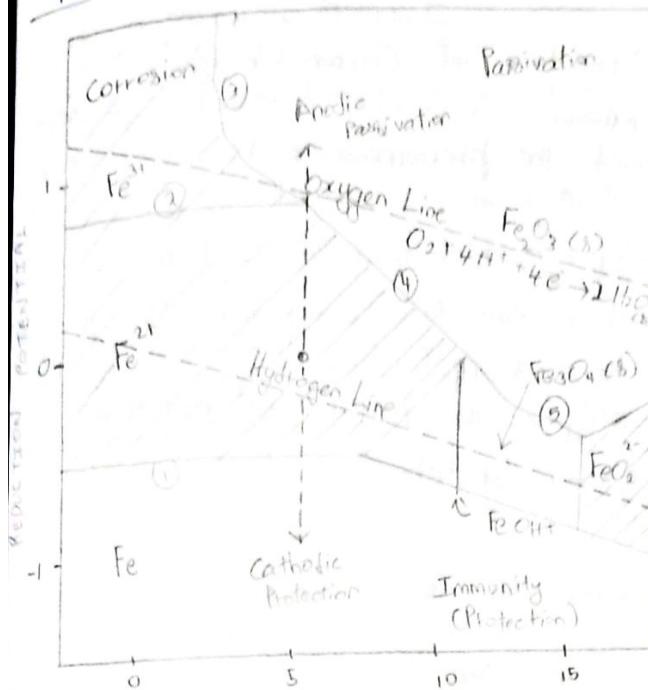
Anions like Silicates when present in the medium lead to the formation of insoluble reaction products, which stop further corrosion. Whereas the Cl^- ions in the medium destroy the oxide film and expose the metal for further corrosion.

• Corrosion Control:

Prevention of corrosion is very important as it is very harmful for metals causing huge losses to industries. This can be controlled in several ways:

- 1 Proper Designing.
- 2 Use of Pure metals.
- 3 Use of metal alloys.
- 4 Change of Corrosive environment.
- 5 Use of Corrosion Inhibitors.
- 6 Surface Treatment for metal Coating.
- 7 Electroplating.
- 8 Electroless plating.
- 9 Surface or Chemical Conversion Coating.

Pourbaix Diagram (for Fe)



1. It represents the stability as a function of potential and pH.
2. At a particular combination of pH and potential, a stable phase can be determined from the Pourbaix diagram.
3. The diagram is plotted by taking redox potential of the corroding system in Y-axis and pH on the X-axis.
4. These diagrams are constructed from the calculations based on Nernst equation and solubility data for metal and its species.
5. For example Fe - Pourbaix diagram, the species are Fe, Fe₂O₃, Fe(OH)₂, Fe₃O₄ etc in equilibrium.
6. These diagrams are useful to control corrosion of pure metals in aqueous environment.

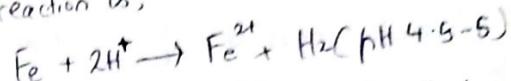
Depending on the potential in the given medium and the corrosion behaviour of the metal, three states are possible:

- a) Corrosion (Active state)
- b) Passivity (Forming passive layers inhibiting the corrosion process on the surface of the metal)
- c) Immunity (Thermodynamic stability)

a) Corrosion: (Active State)

The corrosion of iron is indeed rapid in parts of the Pourbaix diagram where the element is oxidized to a soluble, ionic product.

At slightly acidic pH, the corrosion reaction is,



This is possible for water containing relatively little oxygen i.e., in solutions where the potential is near to the hydrogen line.

b) Passivity:

Saturating water with air or oxygen moves the system closer to oxygen line where the most stable species Fe₂O₃ is formed. This acts as the protective coating on the metal surface that greatly reduces the corrosion reaction. This phenomenon is called passivation.

c) Immunity or Cathodic Protection:

This is most frequently carried out by connecting a more active metal such as Mg or Zn to the iron object (ex: ship hull or underground pipe line) that is being protected. The active metal (higher oxidation potential than Fe in electrochemical series) slowly corrodes, which must be eventually replaced.

Oxidizing conditions are described by the top part of the diagram (high +ve electrode potential).

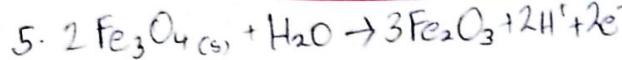
Reducing conditions are described by the bottom part of the diagram (high -ve E.P.)

Acidic Solutions are represented in the left side ($\text{pH} < 6$)

Alkaline Solutions are represented in the right side ($\text{pH} > 6$)

Reactions:

1. $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$
2. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$
3. $2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+$
4. $2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 6\text{e}^-$



15-10-20

ORGANIC CHEMISTRY:

Introduction to Stereo Chemistry:

The compounds having same molecular formula but different physical and chemical properties are known as isomers.

And the phenomenon is known as isomerism. This difference in properties is due to the difference in arrangement of atoms within the molecules of the isomers.

Based on this, there are two types of isomerism.

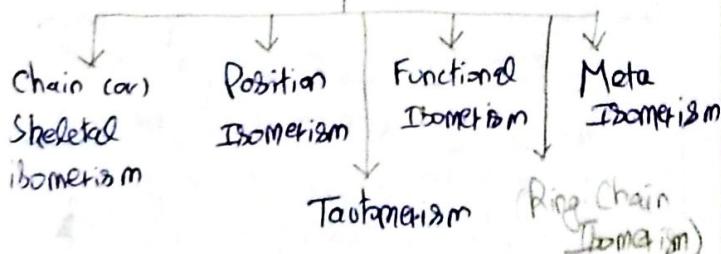
1. Structural Isomerism:

This type of isomerism arises from the difference in the arrangement of atoms within the molecule resulting in two or more different structural formulae and the isomers are known as structural isomers. Thus, the structural isomers have same molecular formula but different structures.

2. Stereo Isomerism:

When the isomers have the same structural formulae but they differ in relative arrangement of atoms or groups in space, the phenomenon is termed as Stereo Isomerism and the isomers are known as Stereoisomers. The spatial arrangement of atoms or groups is also referred to as 'Configuration' of the molecule.

Structural Isomerism



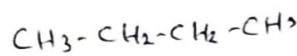
1. Skeletal (or) Chain Isomerism:

Isomers differing in the structure of carbon chains are known as skeletal or chain isomers, and the phenomenon is known as chain isomerism.

→ Ex-1 Mol formula C₄H₁₀

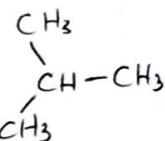
There are two compounds corresponding to this mol formula which differ only in the nature of ~~isomerism~~.

Carbon Skeleton-



n-butane

(Straight chain)



Iso-butane

(Branched chain)

→ Ex-2 Mol formula C₃H₈

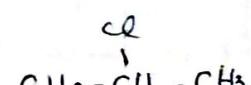
2. Position Isomerism:

Compounds with same molecular formula but different in the position of the functional group in a chain gives rise to position isomerism.

→ Ex-1 Mol Formula C₃H₇Cl



1-chloropropane



2-chloropropane

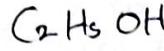
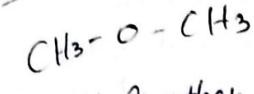
They have same chemical properties but differ in physical properties.

3. Functional Isomerism:

Isomerism exhibited by compounds differing in functional groups is known as functional isomerism.

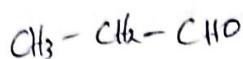
As the functional groups largely determine the properties of a compound, such compounds differ in their physical and chemical properties.

Ex 1 Mol. Formula C_2H_6O

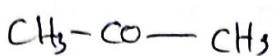


Ethyl alcohol.

Ex 2 Mol. Formula C_3H_6O



Propanaldehyde



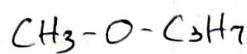
Acetone

4. Metamerism:

Compounds of the same homologous series show this type of isomerism because unequal distribution of carbon atoms on either side of the functional group in the molecule.

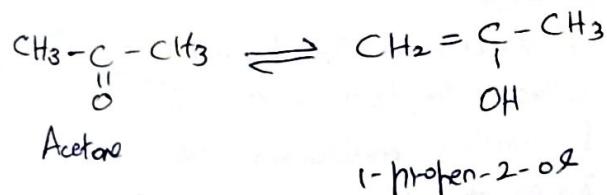
Ex 3 Mol formula C_4H_10O

Diethyl ether and methyl propyl ether.



5. Tautomerism:

It is the type of isomerism in which two functional isomers exist together in equilibrium. The two forms existing in equilibrium are called as tautomers.



Stereo Isomerism:

It is of two types:

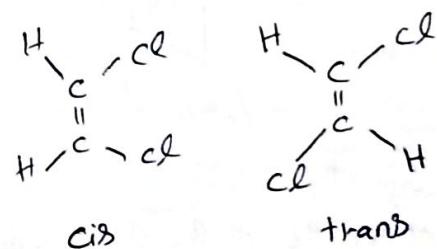
- Geometrical (or) Cis-trans isomerism
- Optical Isomerism.

1. Geometrical Isomerism:

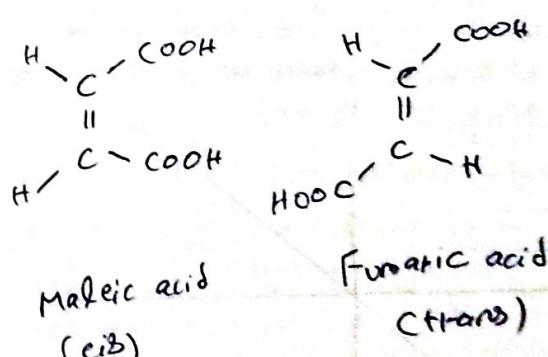
Isomers, which possess the same structural formula but differ in spatial arrangement of the groups around the double bond, are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

The isomer which has similar groups on the same side of the double bond is called 'Cis' and the other which has similar groups on the opposite side of the double bond is known as 'trans'. This type of isomerism is also known as Cis-trans isomerism.

Ex 1, 2-dichloro ~~ethane~~ ^{ethane}



Ex Maleic & fumaric acid



• Optical Isomerism

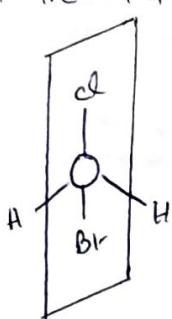
The compounds having same chemical and physical property but they show a pronounced difference in their behaviour towards plane polarised light.

The property by which the substances rotate the plane of the plane polarized light is referred to as its optical activity.

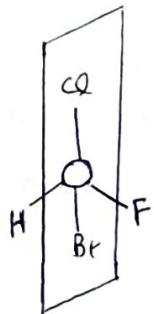
An object or a molecule is considered as symmetric, if it possesses a plane of symmetry, a centre of symmetry or an alternating axis of symmetry.

→ Plane of Symmetry

A molecule has a plane of symmetry, if on passing a plane through it, one half of the molecule is the mirror image of the other half.



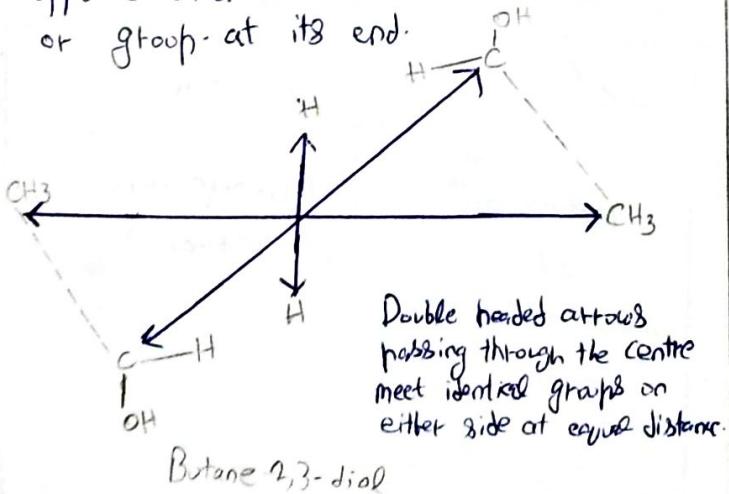
Symmetric



Asymmetric

→ Centre of Symmetry

It is a point in the molecule passing through which, if a line is drawn, from any atom or group and then extended to equal distance in the opposite direction meets an identical atom or group at its end.

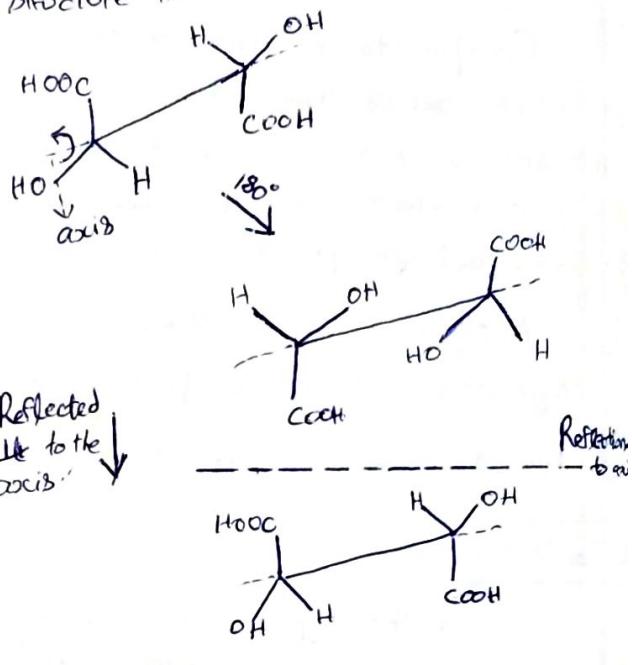


→ Axis of Symmetry:

It is an axis through which rotation of the molecule by certain angle will result in an arrangement, identical (or) indistinguishable with initial mol.

→ Alternating axis of Symmetry:

It is an axis through which if the molecule is rotated by a certain angle and reflected across a plane at right angles to the axis, another identical structure is obtained.



19.10.2020

→ Asymmetric (or) Disymmetric Molecules:

1. A molecule with no element of symmetry.
2. A tetrahedral sp^3 hybridized carbon attached to four different groups.
3. Disymmetric molecules are not superimposable with mirror image.

→ Non-disymmetric (or) Symmetric:

1. These are superimposable on their mirror image.
2. The molecule will possess a plane of symmetry, a centre of symmetry or an alternating axis of symmetry.

Enantiomorphs (or) Enantiomers (^{Not} Interimposable)

A pair of molecules which are related to each other as an object to its mirror image.

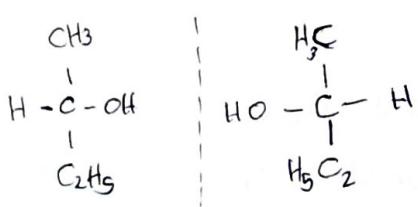
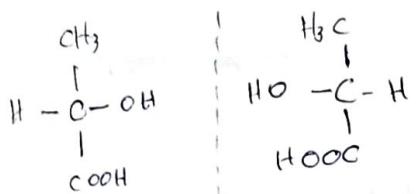
Chiral: A Chiral molecule is not superimposable on its mirror image.

i.e An asymmetric carbon attached to four different groups.

Achiral: An achiral molecule is superimposable on its mirror image.

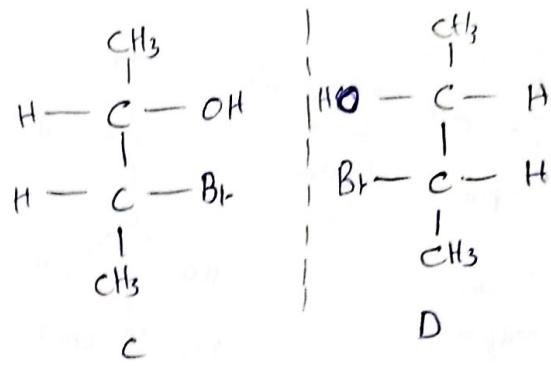
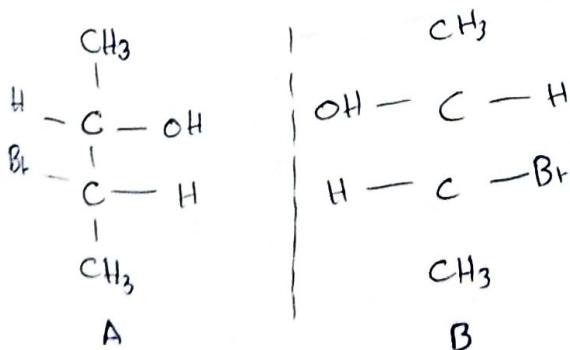
Chirality: Molecule should be non-superimposable on its mirror image.

Thus a molecule will not be chiral if it possesses a plane of symmetry.



Diestereomers:

Isomers that are not related to each other as object and mirror image are known as diastereomers and the phenomenon is known as diastereomerism.



A is the mirror image of B
C is the mirror image of D.

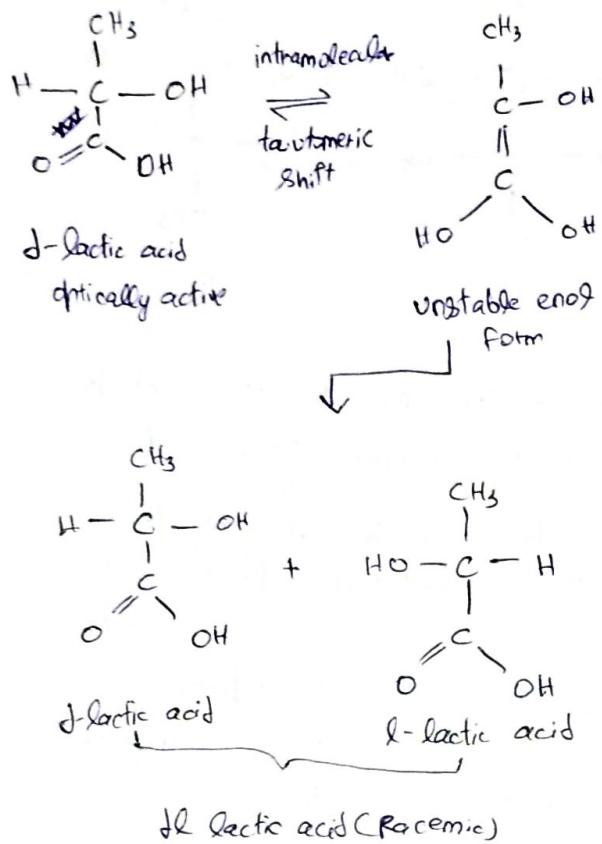
Thus the four isomers are two pairs of enantiomers. Now compare A with C and D, B with C and D. They are neither superimposable nor they are mirror images. They are called diastereomers.

Racemization:

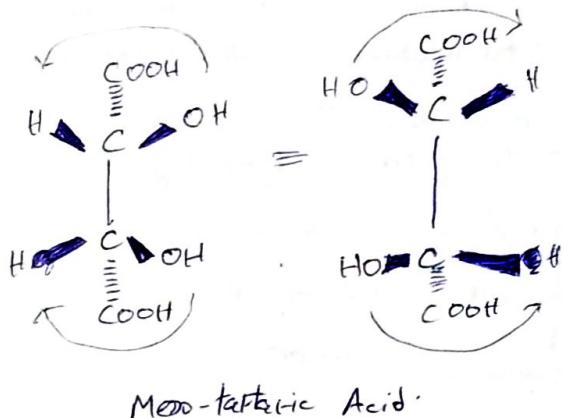
Walden observed that many optically active substances when kept for long time tend to become racemic mixtures. That is application of heat, light etc to the optically active compounds, may result in the loss of their optical activity. This conversion of dextro or laevo compounds to their racemic forms (dl or + -) is known as Racemization.

Racemization occurs through some intramolecular rearrangement caused by light, heat or catalysts. Because of this rearrangement, the optically active compound exists temporarily in equilibrium with this rearrangement product. The latter does not have asymmetric centre so that when it again forms the asymmetric centre, both d and l forms are obtained in equal amounts. For example - Racemisation of Lactic acid:

2-Meso form (Internal Compensation)



This optical inactivity arises in the molecule because of equal and opposite rotation by two similar asymmetric carbon atom of the same molecule i.e. D rotation of one-half of the molecule is compensated by L rotation of the other half. Since, this compensation comes from within the molecule itself, the molecule is said to be inactive due to internal compensation.



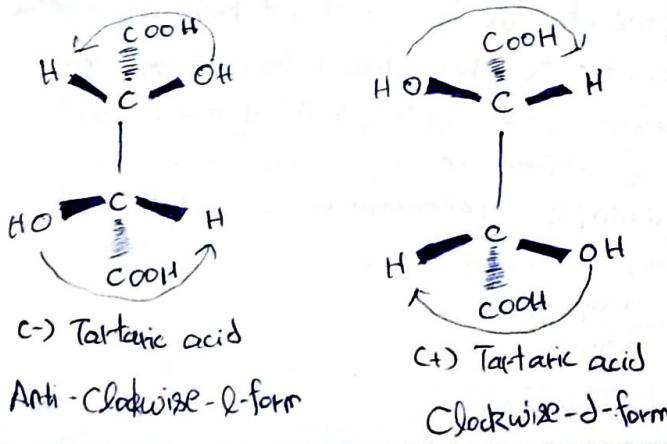
I. Compounds having Carbonyl group adjacent to asymmetric Carbon atom carrying a hydrogen are most easily racemized.

Tartaric acid:

I. External Compensation:

DL form (or) Racemic form :

The optical inactivity arising due to the presence of equal amounts of the D and L forms by equal and opposite optical activity of each isomer and therefore is regarded as arising from external compensation (\pm) form.



Cahn, Ingold, Prelog (or)

Rectus- Sinister (or) R-S System:

Interconversion of Fischer, Sawhorse and Newmann Projection formulae:

Sawhorse and Newmann Projection formulae:

(Turn Back - Pg 6)

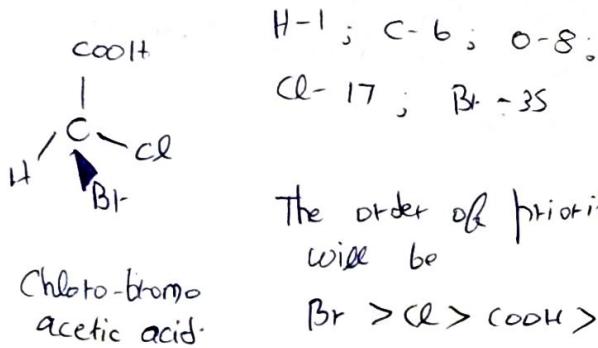
Cahn, Ingold, Prelog (or)

Rectus- Sinister (or) R-S System:

Sequence Rules:

Used to name the enantiomers of a chiral compound. In this R-S system, the atoms joined to the asymmetric carbon atoms directly are arranged in a sequence.

- The order of priority (or) sequence is determined on the basis of atomic numbers of the atoms joined directly to asymmetric carbon, the greater the atomic number the higher the order.

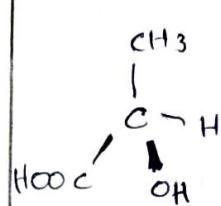


- If two or more atoms attached to a symmetric Carbon atom are same, then the atoms next to those similar atoms are taken into consideration for determination of the priority order.

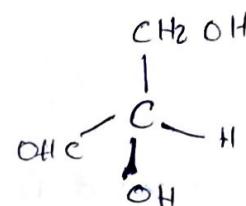
If these are also the same, then the third atoms are taken into consideration and so on.

Thus for $-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_3$, the order of priority will be $-\text{CH}_2-\text{CH}_3 > -\text{CH}_3$ because methyl C is joined to H, H and H whereas ethyl, it is joined to C, H and H.

3. For determining the priority, multiple bonds are treated as separate single bonds. Thus $\text{H}-\text{C}=\text{O}$ is regarded as carbon linked to 2 oxygen and 1 hydrogen.

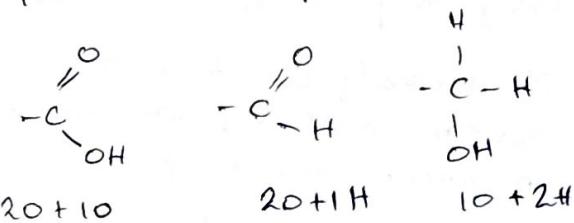


Lactic acid



Glyceraldehyde

The order of priority of



will be,

∴ in lactic acid, the order of priority will be,
 $\text{OH} > \text{COOH} > \text{CH}_3 > \text{H}$

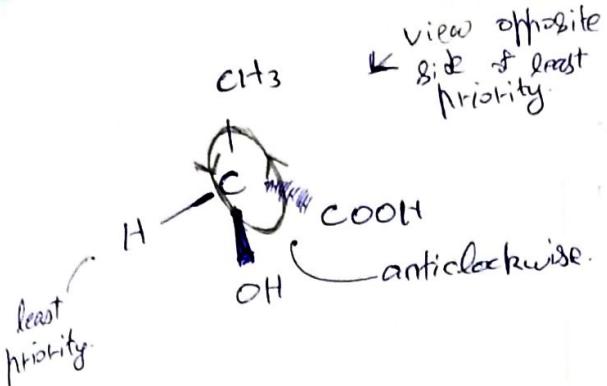
in glyceraldehyde,

$\text{OH} > \text{CHO} > \text{CH}_2\text{OH} > \text{H}$

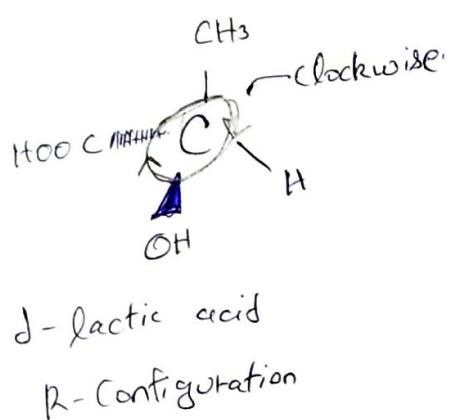
After fixing the priority order of groups, joining the asymmetric carbon, the tetrahedral structure of the isomer is viewed from the side opposite to the group of lowest priority, and the arrangement of rest of the groups is observed.

If the arrangement of groups is going from top priority to the least in clockwise direction, the Configuration is considered as "Rectus (or) R"

If this arrangement is in anti-clockwise direction, the Configuration is termed as "Sinister (or) S" Configuration



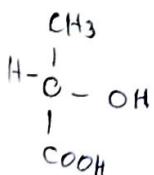
L-lactic acid
S- Configuration.



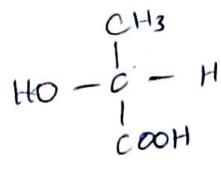
The racemic modification is termed as RS compound. This system is thus very convenient for writing the absolute configuration of the compounds.

Usually, the optical isomer must be represented by a tetrahedral perspective (or) projection formula as the planar representation will not give a correct idea of the molecule.

However, for the sake of convenience, planar formulae are still extensively used for writing the configurations of optical isomers. But they remain as non-superimposable. Thus, the lactic acid may be conveniently represented as:



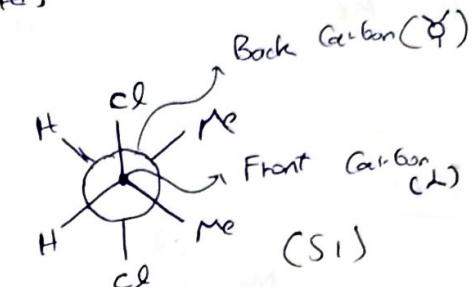
D-lactic acid



L-lactic acid

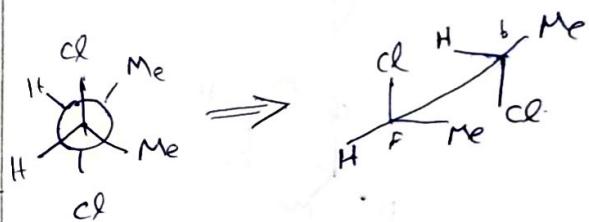
• Interconversion of Fischer Sawhorse and Newmann projection formulae

Let us consider the following structure,



Newmann Projection Formula

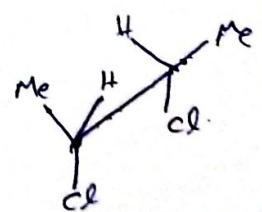
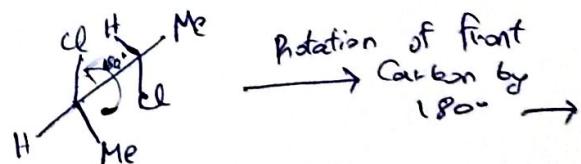
First, Convert Structure (S1) into Sawhorse projection formula



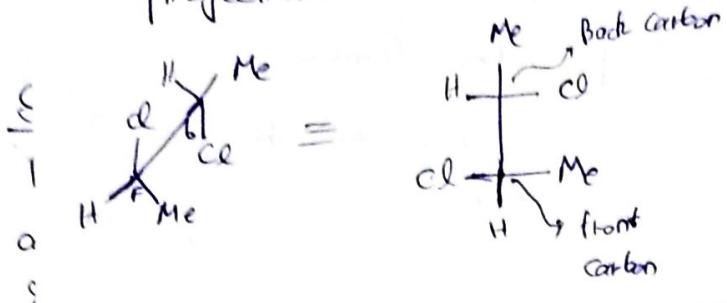
In the back Carbon we have a Y and in the front Carbon we have a J like this.

In the back Carbon, in the left hand side we have H and in right hand side we have -Me and Cl. In the front Carbon, we have left side -H and right side Me and upward Cl.

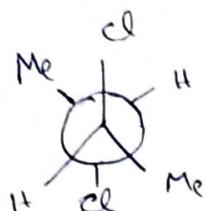
In the front Carbon, we have left side -H and right side Me and upward Cl.



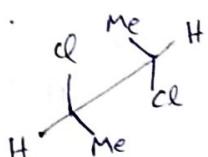
iii) Sawhorse projection to Fischer projection



Ex:



Newmann projection



Sawhorse projection



Fischer projection