

CHEMICAL THERMODYNAMICS

INTRODUCTION

Thermodynamics means flow of heat. It deals with the quantitative relation between heat and other forms of energy in all types of physical and chemical processes.

Scope of Thermodynamics.

(i) Many important laws of physical chemistry can be derived from the laws of thermodynamics.

(ii) It can predict whether a given process will occur spontaneously or not under given set of conditions of temperature, pressure and concentration.

Thermodynamic terms

System

The part of the universe which is selected for theoretical and experimental investigation is called system. A system usually has a definite amount of a specific substance.

Homogeneous System

When a system is uniform throughout, it is called a homogeneous system. It is made up of only one phase.

Ex: Single solid, mixture of gases.

Heterogeneous System

When a system is not uniform throughout, it is called a heterogeneous system. It is made up of two or more phases.

Ex: Ice in contact with water

Surroundings

A System has a definite amount of specific substance. It is separated from the rest of the universe called surroundings by a definite boundary.

Boundary

The real or imaginary surface separating the system and surroundings is called the boundary.

Types of Thermodynamic Systems

Isolated system

A system which can exchange neither energy nor matter with its surroundings is called an isolated system. The boundary is both sealed and insulated.

Ex:- Thermos flask containing boiled water.

Closed system

A system which can exchange energy but not matter with its surroundings is called a closed system. The boundary is sealed but not insulated.

Ex:- A gas contained in a cylinder fitted with a piston.

Open system

A system which can exchange matter as well as energy with its surroundings is called an open system. The boundary is open and un-insulated.

Ex:- Hot water contained in a beaker.

Properties of a System

Intensive Property

A property which does not depend on the quantity of matter present in the system is known as intensive property.

Ex: Pressure, Temperature, density and concentration

Extensive Property

A property that depends on the quantity of matter present in the system, is called an extensive property.

Ex: Volume, number of moles, enthalpy, entropy and free energy.

State function

The value of a particular property of a system depends only on the state of the system and does not depend on the path by which it is carried out, then this property is called state function.

Ex: Internal Energy, enthalpy, entropy, free energy.

Path function

The value of a property of a system depends on the state and path, the property is known as path function.

Ex: Heat, work, etc.,

Thermodynamic Processes

When a thermodynamic system changes from one state to another, the operation is called a process. These processes involve the change of conditions of pressure, temperature and volume.

Isothermal Process

A process that is carried out under constant temperature is called isothermal process.

$$\text{i.e., } dT = 0$$

Adiabatic Process

A process in which there is no exchange of heat between the system and the surroundings is known as an adiabatic process.

$$\text{i.e.,} \text{ Thermally insulated } dq = 0$$

Isobaric Process

A process which takes place at constant pressure is known as isobaric process.

$$\text{i.e., } dp = 0$$

Isochoric process

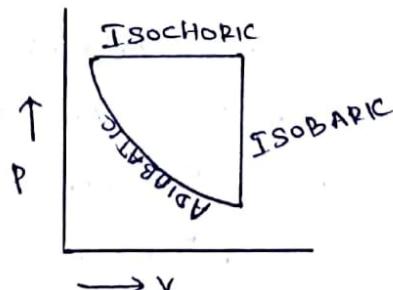
A process in which the volume remains constant is known as isochoric process.

$$\text{i.e., } dv = 0$$

Cyclic Process

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cyclic process.

$$\text{i.e., } dE = 0$$



Reversible Process

A process is said to be reversible, if at any instant during the transformation, the system does not deviate from equilibrium by more than an infinitesimal amount.

Ex: Daniel cell.

Irreversible Process

A process that occurs rapidly or spontaneously such that it does not remain in equilibrium during the transformation is called an irreversible process.

Ex: Consider a gas contained in a cylinder.

Differences between Reversible and Irreversible processes

S.No	Reversible Process	Irreversible process.
1.	It is an imaginary process	It is a real process
2.	It takes place in infinite time	It takes place in finite time
3.	All the stages of operation are in equilibrium state	Only the initial and final states of the operation are in equilibrium state.
4.	It is a slow process	It proceeds at a measurable speed.
5.	Workdone is greater	Workdone is smaller.
b.	non-spontaneous process	Spontaneous process.

Internal Energy (E) or (U)

The total of all the possible kinds of energy of a system such as rotational, vibrational, translational, Electronic and potential energy is called as internal energy.

$$E = E_r + E_v + E_t + E_e + E_p$$

It is impossible to determine the absolute value of the internal energy of a system. But, the change in Internal energy (ΔE) can be easily measured.

Internal energy is a state function and the value of it depends on the mass of the matter contained in a system. Therefore internal energy is an extensive property.

The internal energy of a system represented by the symbol E and the change in internal energy from initial state to final state is given by ΔE .

$$\Delta E = E_2 - E_1$$

E_2 - Internal Energy in final state

E_1 - Internal Energy in initial state.

$$\Delta H = +ve ; E_2 > E_1$$

$$\Delta H = -ve ; E_2 < E_1$$

The SI Unit of internal energy is Joule (J). Calorie (1 cal = 4.184 J) can also be used.

ENTHALPY (or) Heat Content of the System

Enthalpy is defined as "the total heat content of a system at constant pressure is equivalent to the sum of internal energy E and PV".

$$H = E + PV.$$

The enthalpy change is denoted by ΔH . It is the enthalpy difference of a system in the final state (H_2) and the initial state (H_1).

$$\Delta H = H_2 - H_1$$

For a system having energy E_1 and E_2 & P_1V_1 and P_2V_2 the change in enthalpy is given by,

$$\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

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

$$\therefore \Delta H = \Delta E + P\Delta V \quad \because P\Delta V = W$$

$$\therefore \Delta H = \Delta E + W$$

At constant volume, $\Delta V = 0$

$$\therefore \Delta H = \Delta E$$

Zeroth law of Thermodynamics

It deals with thermal equilibrium among the systems which are in contact with each other.

When two systems at two temperatures are brought into contact with each other, after sometimes they attain equal temperature and thermal equilibrium exists.

First law of Thermodynamics.

First law states that "Energy can neither be created, nor be destroyed. It can only be transformed from one form to another.

$$\Delta E = q_f - w$$

where,

q_f - the amount of heat

w - work done by the system

The above equation provides relationship between Change in, internal energy (ΔE) of the system, heat supplied to the system (q_f) and work done by the system.

Limitations.

- (i) The first law gives relation between heat absorbed and the work performed by a system. But it does not give any restriction on the direction of flow of heat.
- (ii) The first law does not tell that heat energy cannot be completely converted into an equivalent amount of work.
- (iii) It does not tell whether a specified change or a process including a chemical reaction can occur spontaneously.

Second law of Thermodynamics

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- (i) Second law of Thermodynamics helps us to determine the direction in which energy can be transformed.
- (ii) It also helps to predict whether a given process can occur spontaneously.
- (iii) It also helps to know about the equilibrium conditions.

It states that, "whenever a spontaneous process takes place, it's accompanied by an increase in the total energy of the universe."

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$\Delta S_{\text{univ}} > 0$, for a irreversible process

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

- (i) Clausius statement: It is impossible to construct a machine which can transfer heat from a cold body to a hot body, unless some external work is done to the machine.
- (ii) Kelvin-Planck statement: It is impossible to convert the heat completely into an equivalent amount of work, without producing some other changes in some parts of the system.
- (iii) Entropy statement: A spontaneous process is always accompanied by an increase in entropy of the universe.
(i.e.) System and surroundings.

Entropy

Entropy is a thermodynamic state quantity. It is a measure of randomness or disorder of the molecules of the system. It is a state function and depends only on the initial and final states of the system.

The symbol of entropy is S .

Ex:-

When ice is melted, entropy increases

when a gas is liquefied, entropy decreases

The change in entropy, ΔS is given by,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \text{ cal/deg} \text{ or } \text{JK}^{-1} \text{ mol}^{-1}$$

Significance of Entropy

1. Entropy and Unavailable energy.

When ~~as~~ heat is supplied to the system, only small portion of heat is used to do some work and the remaining portion of heat is called unavailable energy. Since, entropy is a measure of unavailable energy.

It can be explained as an unavailable energy per unit temperature.

$$\text{Entropy} = \frac{\text{Unavailable Energy}}{\text{Temperature}}$$

2. Entropy and disorder.

Entropy is a measure of disorder (or) randomness of a system.

Ex: All Natural process.

3. Entropy and probability

An irreversible process tend to proceed from less probable state to more probable state. Since entropy increases in a spontaneous process entropy may be defined as a "function of probability of the thermodynamic state".

Entropy Change in a Reversible Process.

For a reversible isothermal process, if the system absorbs q amount of heat from the surroundings at temperature T , then the resultant increase in entropy of the system is given by,

$$\Delta S_{\text{system}} = + \frac{q}{T}$$

At the same time, the entropy of the surroundings decreases,

$$\Delta S_{\text{surroundings}} = - \frac{q}{T}$$

Hence, the net change in the entropy is given by,

$$\begin{aligned}\Delta S_{\text{Total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= \frac{q}{T} + [-\frac{q}{T}]\\ &\therefore \Delta S_{\text{Total}} = 0\end{aligned}$$

Thus, for a reversible isothermal process, there is no net change in entropy.

Entropy change in an Irreversible process

consider a system at higher temperature T_1 and its surroundings at lower temperature T_2 . Let a quantity of heat q is absorbed irreversibly from the system to surroundings.

$$\text{Decrease in entropy of System } \Delta S_{\text{System}} = -\frac{q}{T_1}$$

$$\text{Increase in entropy of Surroundings } \Delta S_{\text{Surroundings}} = +\frac{q}{T_2}$$

∴ Net entropy change in the process is given by,

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$$

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

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

$$\Delta S = q \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

Since $T_1 > T_2$, $T_1 - T_2 = +ve$

$$\therefore \Delta S = +ve$$

(as)

$$\Delta S_{\text{Total}} > 0$$

In an irreversible process the entropy of the system increases.

Entropy change of an Ideal gas At constant temperature

According to first law of thermodynamics,

$$dE = q - PdV$$

$$(as) \quad dE = q - w \longrightarrow ①$$

For a reversible isothermal expansion, there is no change in Internal Energy i.e., $dE = 0$.

∴ Equation (1) becomes $q_{rev} - w = 0$

$$q_{rev} = w \rightarrow (2)$$

The 'work done' in the expansion of n moles of a gas from volume V_1 to V_2 at constant temperature T is given by,

$$w = nRT \ln \frac{V_2}{V_1} \rightarrow (3)$$

Combining equation (2) and (3), we get

$$q_{rev} = nRT \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S = \frac{q_{rev}}{T}$$

$$T\Delta S = nRT \ln \frac{V_2}{V_1}$$

$$T\Delta S = q_{rev}$$

$$\div T \quad \Delta S = nR \ln \frac{V_2}{V_1}$$

(or)

$$\Delta S = 2.303 nR \log \frac{V_2}{V_1} \rightarrow (4)$$

$$\Delta S = 2.303 nR \log \frac{P_2}{P_1} \times \frac{P_1}{RT}$$

$$\therefore P_1 V_1 = RT; V_1 = \frac{RT}{P_1}$$

$$P_2 V_2 = RT; V_2 = \frac{RT}{P_2}$$

$$\therefore \Delta S = 2.303 nR \log \frac{P_1}{P_2}$$

Energy change of phase Transition.

1. Transition from solid to liquid phase.

It is the change in entropy when a solid changes into liquid at its fusion point. Consider 1 mole of a solid substance melts reversibly at

fusion point (T_f) at constant pressure. Let molar heat of fusion be ΔH_f . Then the entropy change of the phase transition process (ΔS_f) is given by,

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

2. Transition from liquid to vapour phase.

Let us consider 1 mole of a liquid substance vapourise reversibly at its boiling point (T_b) at constant pressure. Let molar heat of vapourisation be (ΔH_v). Then, the entropy change of the phase transition process (ΔS_v) is given by,

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

The processes of both fusion and vapourisation are accompanied by increase in entropy, since ΔH_f and ΔH_v both are positive.

PROBLEMS BASED ON ENTROPY.

1) Calculate the entropy change when 10g of ice is converted into liquid water at 0°C . Molar heat of fusion of ice is 80 cal g^{-1} .

$$\text{Given: } T = 0^\circ\text{C} + 273 = 273 \text{ K}$$

$$\left. \begin{array}{l} \text{Molar heat of fusion of ice} \\ \Delta H_f \end{array} \right\} = 80 \text{ cal g}^{-1}$$

$$\therefore \text{Entropy change of fusion } \Delta S_f = \frac{\Delta H_f}{T_f} = \frac{80}{273}$$

$$\Delta S_f = 0.293 \text{ cal K}^{-1} \text{ g}^{-1}$$

2) Calculate the change in entropy accompanying the ¹⁵ isothermal expansion of 5 moles of an ideal gas at 330K until its volume has increased six times.

Given: $V_1 = 1$, $V_2 = 6$ No. of moles (n) = 5; Gas Constant (R) = 1.987 cal

$$\left. \begin{array}{l} \text{Entropy change in an isothermal} \\ \text{expansion of an ideal gas } (\Delta S) \end{array} \right\} = 2.303 nR \log \frac{V_2}{V_1}$$

$$= 2.303 \times 5 \times 1.987 \times \log \frac{6}{1}$$

$$= 2.303 \times 5 \times 1.987 \times 0.778$$

$$\Delta S = 17.8 \text{ cal K}^{-1}$$

HELMHOLTZ FREE ENERGY.

A part of internal energy of a system can be used at constant temperature to do some useful work. This part of internal energy (E), which is isothermally available is called "work function" (A) of the system. It is mathematically defined as,

$$A = E - TS \longrightarrow (1)$$

For a change from state 1 to 2 at constant temperature,

$$\Delta A = \Delta E - T \Delta S \longrightarrow (2)$$

The entropy change (ΔS) is given by

$$\Delta S = \frac{q_{rev}}{T} \quad (\text{or}) \quad T \Delta S = q_{rev} \longrightarrow (3)$$

Substituting equation (3) in (2),

$$\Delta A = \Delta E - q_{rev} \longrightarrow (4)$$

According to I law of Thermodynamics,

$$\Delta E = q - w$$

$$\Delta E = q - W$$

$$-W = \Delta E - q \longrightarrow (5)$$

Comparing eqn (4) & (5),

$$\Delta A = -W$$

$$-\Delta A = W_{\max}$$

Thus, decrease of work function ($-\Delta A$) of a process at constant temperature gives a maximum work obtained from the system.

FREE ENERGY (G) GIBBS FREE ENERGY

The isothermally available energy present in a system is called Free Energy (G). It is mathematically defined as,

$$\left. \begin{array}{l} \text{Available} \\ \text{Energy} \\ (G) \end{array} \right\} = \text{Total Energy (H)} - \text{Unavailable Energy} \\ (\text{TS})$$

$$\therefore G = H - TS$$

significance:

Free energy (G) is the total available energy present in a reversible system at constant temperature & pressure as useful work.

$$G = H - TS \longrightarrow (1)$$

For a change from state 1 to 2 at constant T,

$$\Delta G = \Delta H - T \Delta S \longrightarrow (2)$$

We know,

$$\Delta H = \Delta E + P \Delta V \longrightarrow (3)$$

Substituting eqn ③ in ②.

$$\Delta G = \Delta E + P\Delta V - T\Delta S \longrightarrow (4)$$

Eqn (4) may be written as,

$$\therefore \Delta A = \Delta E - T\Delta S$$

$$\Delta G = \Delta A + P\Delta V \longrightarrow (5)$$

$$\Delta G = -W_{max} + P\Delta V$$

$$-\Delta G = W_{max} - P\Delta V$$

Thus, the decrease of free energy ($-\Delta G$) of a process at constant T & P is equal to the useful work obtainable from the system.

Standard Free Energy Change (ΔG°)

It is defined as "The free energy change for a process at 298 K in which the reactants are converted into products in their standard states".

$$\Delta G^\circ = \sum G^\circ_{(products)} - \sum G^\circ_{(reactants)}$$

The value of ΔG° can be derived from standard free energies of formation. (ΔG_f°).
Spontaneous process.

A process which proceeds on its own without any external assistance is termed as spontaneous (o) Natural process.

The tendency of a process to occur naturally is called Spontaneity.

Criteria for the spontaneous process.

According to II law of thermodynamics a process is said to be spontaneous only when ΔS_{total} is positive.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \longrightarrow (1)$$

If the reaction is carried out at constant T & P,
The amount of heat transferred from
the system to surroundings (ΔS_{system}) } $= (-q_p)_{\text{system}}$

$$\therefore (q_p)_{\text{surroundings}} = -(-q_p)_{\text{system}} = -\Delta H_{\text{system}}$$

Since the surrounding is a large area, at constant T

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T} \longrightarrow (2)$$

On substituting eqn (2) in (1),

$$\Delta S_{\text{Total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

Multiplying both sides by T,

$$T\Delta S_{\text{Total}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}} \longrightarrow (3)$$

$$\therefore T\Delta S_{\text{Total}} = \Delta H_{\text{system}} - \Delta G - \Delta H_{\text{system}} \quad \because \Delta G = \Delta H - T\Delta S$$

$$T\Delta S_{\text{Total}} = -\Delta G$$

$$-T\Delta S_{\text{Total}} = \Delta G \longrightarrow (4)$$

The eqn (4) is the criterion for spontaneity in terms of free energy (G) of the system. Thus,

If $\Delta G = -\text{Ve}$ ($\Delta G < 0$), the process is spontaneous.

If $\Delta G = 0$, the process is in equilibrium.

If $\Delta G = +\text{Ve}$, ($\Delta G > 0$), the process is non-spontaneous.

Gibbs-Helmholtz Equation.

Consider the following relations,

$$G = H - TS \longrightarrow (1) \text{ Gibbs free energy}$$

$$H = E + PV \longrightarrow (2) \text{ Enthalpy.}$$

Substituting Eqn (2) in (1),

$$G = E + PV - TS \longrightarrow (3)$$

For infinitesimal change,

$$dG = dE + pdV + Vdp - Tds - sdT \longrightarrow (4)$$

According to I & II law of thermodynamics,

$$dE = dq - pdv \quad (\text{I Law})$$

$$dq = TdS \quad (\text{II Law})$$

$$\therefore dE = Tds - pdv \longrightarrow (5)$$

Substituting eqn (5) in (4),

$$dG = Tds - pdv + pdV + Vdp - Tds - sdT$$

$$\therefore dG = Vdp - sdT \longrightarrow (6)$$

At constant (P) $dP=0$, then Eqn (6) becomes,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \rightarrow (7)$$

Substituting Eqn (7) in Eqn (1),

$$G = H + TS$$

$$(a) \quad G = H + T\left(\frac{\partial G}{\partial T}\right)_P.$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P.$$

For a change from state 1 to 2, variables such as Free energy (G) and Enthalpy (H) undergoes changes, then the above eqn can be written as,

$$\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_P$$

$$(a) \quad \Delta H = \Delta G - T \left[\frac{\partial (\Delta G)}{\partial T} \right]_P$$

Similarly,

$$\Delta A = \Delta E + T \left[\frac{\partial (\Delta A)}{\partial T} \right]_P, \text{ may be derived.}$$

Significance.

- (i) It relates the free energy change (ΔG) to enthalpy change (ΔH) and the rate of change of free energy with temperature at constant P.

(ii) If $\Delta G = -ve$, the process is spontaneous.

Applications of Gibbs-Helmholtz Equation.

(i) Calculation of Entropy change (ΔS),

ΔH & ΔS are related by the equation,

$$\Delta G = \Delta H - T\Delta S \longrightarrow (1)$$

We know that,

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

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

(ii) Calculation of free energy change,

The free energy change (ΔG) for an ideal gas expanding reversibly and isothermally is calculated by the following relations,

$$\Delta G = nRT \ln \frac{P_2}{P_1} \quad P_1V_1 = P_2V_2$$

(or)

$$\Delta G = nRT \ln \frac{V_1}{V_2} = 2.303 nRT \log \frac{V_1}{V_2}$$

(iii) It is applicable for a process occurring at constant pressure. It is used to calculate ΔH from the values of free energy change at two different temperature.

(iv) For a process, at constant (V) the equation can be modified as,

$$\Delta A = \Delta E + T \left(\frac{\partial (\Delta A)}{\partial T} \right)_V$$

5. CORROSION

5.1 INTRODUCTION

Most of the metals in nature exist as ores in the form of metallic oxides, carbonates, hydroxy carbonates, oxides, sulphides, chlorides and silicates. During extraction process, they are reduced to their metallic states. For the extraction process, considerable amount of energy is needed. A pure metal will be having higher energy. Therefore, it has a natural tendency to come back to its combined form (ore) which will have low energy.

The process by which a pure metal goes to its combined form is called corrosion.

Hence, corrosion process is the reverse of extraction of metals.

Definition

Corrosion is defined as the spontaneous process of degradation or deterioration of metallic constructions in the course of their chemical, bio-chemical or electrochemical interaction with the environment.

Examples:

Rusting of iron

When a piece of iron is exposed to atmospheric conditions, a layer of reddish scale and powder of oxide (Fe_3O_4) is formed on the surface.

Formation of green film on copper surface

When copper is exposed to moist-air containing CO₂, a green film of basic carbonate [CuCO₃ + Cu(OH)₂] is formed on the surface of copper.

5.2 CLASSIFICATION OF CORROSION

Based on the mechanism of corrosion, it is broadly classified into two types. They are

- 1) Dry Corrosion (or) Chemical Corrosion
- 2) Wet Corrosion (or) Electrochemical Corrosion.

5.2.1 Dry Corrosion (or) Chemical Corrosion

Dry (or) chemical corrosion takes place due to the direct chemical action of atmospheric gases, such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen (or) anhydrous inorganic liquid with metal surfaces.

Types of Dry Corrosion

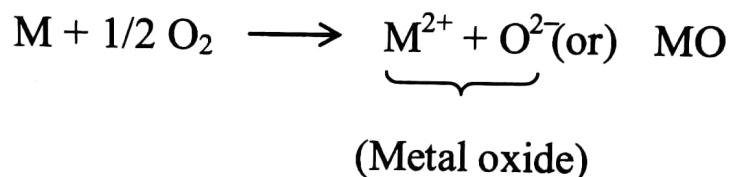
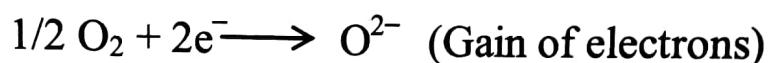
Dry corrosion is further classified into

- a) Oxidation corrosion
- b) Corrosion by other gases
- c) Liquid metal corrosion

a) Oxidation corrosion

When oxygen directly attacks the metal surfaces at low (or) at high temperatures, oxidation corrosion takes place. This type of corrosion usually occurs in the absence of moisture.

The following reactions take place during oxidation corrosion:



Mechanism

- Oxygen attacks the surface of the metal and oxidation takes place. This results in the formation of metal oxide scale.
- The metal oxide scale formed on the metal surface acts as a barrier and prevents further oxidation.
- If oxidation has to continue, either the metal ions must diffuse outward through metal oxide barrier or the oxide ions must diffuse inward through the barrier.
- Though both transfers occur, the outward diffusion of the metal ions is more rapid than the inward diffusion of oxide ions.

- This may be accounted for by the higher mobility and smaller size of metal ions when compared to oxide ions.

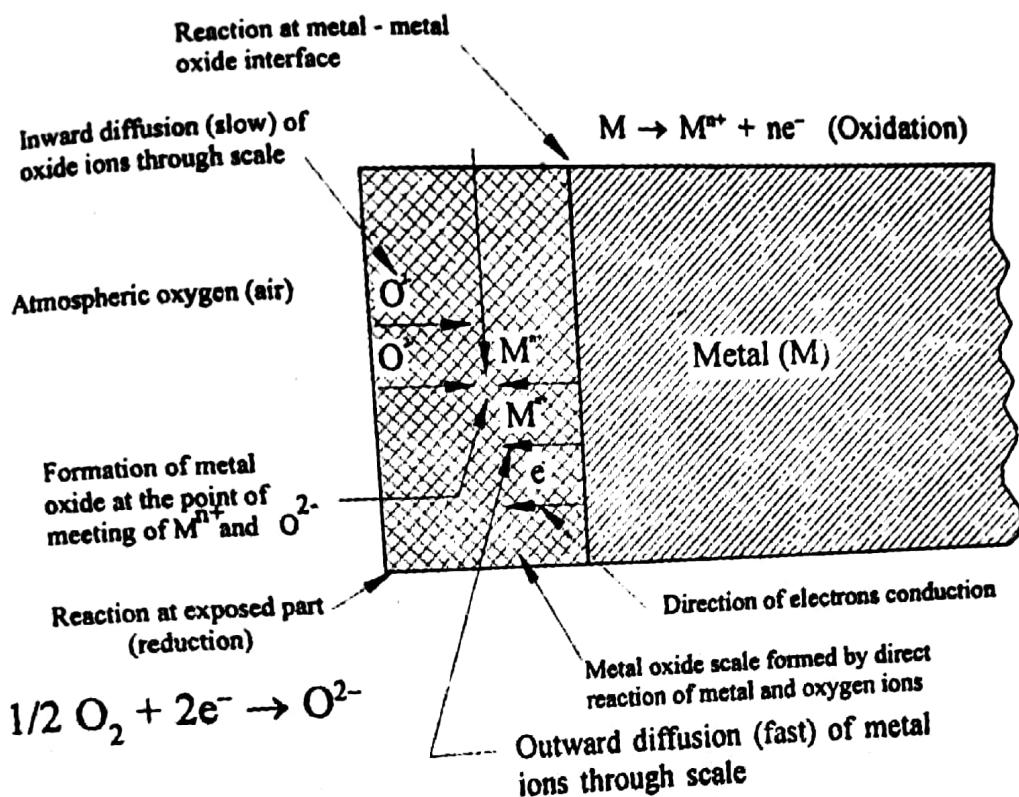


Fig.5.1 Oxidation mechanism of metals

Nature of the metal oxide

The nature of the metal oxide formed is the deciding factor for further oxidation.

i) Stable

If the metal oxide layer formed is stable, fine-grained, tightly adhering and impervious in nature, further oxidation corrosion is prevented.

Eg: Oxide films on Al, Sn, Pb, Cu, Pt, etc.

ii) Unstable

The oxide film formed decomposes back into metal and oxygen and hence corrosion is not possible in such a case.

Eg : Silver, Gold, Platinum.

iii) Volatile

If the metal oxide layer formed is volatile in nature, it volatilizes rapidly as soon as it is formed. Therefore, corrosion occurs rapidly and continuously leading to excessive destruction.

Eg : Molybdenum oxide (MoO_3)

iv) Porous

If the metal oxide layer formed is having pores or cracks, the atmospheric oxygen will attack the underlying surface of the metal through the pores or cracks. In such cases, corrosion will continue till the entire metal is converted into its oxide.

Eg : Oxides of alkali and alkaline earth metals

Pilling - Bedworth Rule

According to this rule, "an oxide is protective (and) non-porous, if the volume of the oxide is greater than the volume of the metal from which it is formed."

Eg : If the Aluminium oxide layer volume is greater than the volume of Al, corrosion will not take place.

On the other hand, the metal oxide film is non -protective and highly porous, if the volume of the metal oxide is lower than the volume of the metal.

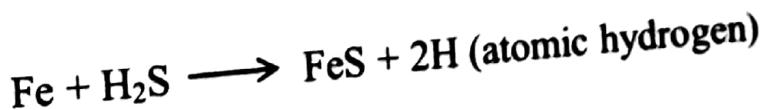
Eg: Volume of oxide layer of alkaline and alkali earth metals is less than the volume of the metals. Hence corrosion takes place.

b) Corrosion by other gases

Besides oxygen, gases like H₂, SO₂, Cl₂, H₂S, CO₂, F₂ etc do cause corrosion. The extent of corrosion mainly depends on the chemical affinity between the metal and the gas involved. These gases react with the metal surface and form either the protective layer (or) non -protective layer.

Corrosion by hydrogen

Hydrogen gas attacks the metal surface and causes corrosion. When an iron piece is exposed to an aqueous solution of H₂S, evolution of atomic hydrogen takes place on the iron surface.



At high temperature, atomic hydrogen is formed by the thermal dissociation of molecular hydrogen.



This atomic hydrogen diffuses into the metal and collects in the voids. There it recombines to form molecular hydrogen.



The formation of hydrogen results in increase in the pressure of hydrogen inside the voids and causes blisters and fissures. This process is termed as "**hydrogen embrittlement**".

At high temperature also hydrogen corrosion is possible. Here atomic hydrogen is formed by thermal dissociation of hydrogen molecule.



When steel is exposed to this environment, the atomic hydrogen readily combines with carbon of steel and produces methane gas.



Collection of these gases in the voids develop very high pressure which causes crack. Thus the process of decrease in carbon content in steel is called as **decarburization** of steel.

The atomic hydrogen produced can also combine with other atoms such as O, N and S present in the metals.

- (i) Cl₂ gas attacks Ag surface to form silver chloride film. The AgCl film protects the metal from further attack.

(ii) Sn attacked by dry Cl_2 gas form volatile SnCl_4 film. Since the film formed is volatile and non -protective, corrosion will continue.

(iii) Fe attacked by H_2S form FeS layer.

c) **Corrosion by liquid metal**

This type of corrosion is due to the action of flowing liquid metal at high temperatures on solid metal. Such corrosion is found to occur in devices used for nuclear power. The corrosion reaction may involve either the dissolution of solid metal by a liquid metal (or) the internal penetration of liquid metal into the solid metal.

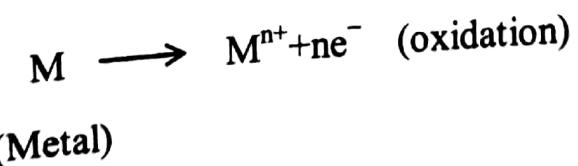
5.2.2 Wet or Electrochemical Corrosion

This type of corrosion takes place

i) When a conducting liquid is in contact with a metal (or)

ii) When two dissimilar metals are either immersed (or) partially dipped in a solution.

iii) When a metal is exposed to varying concentration of oxygen or electrolyte.



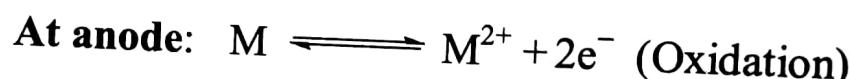
Separate anodic and cathodic regions are set up and current flows between them through the solution. Oxidation takes place at anode and

reduction takes place at cathode. Corrosion always occurs at anode and cathodic area remains unaffected.

The metallic ions formed at anode and non - metallic ions formed at cathode diffuse through the conducting medium and form a corrosion product.

Mechanism of Wet or Electrochemical corrosion

In an electrochemical corrosion, electron - current flows between the anodic and cathodic regions. At the anode, the dissolution of metal into corresponding metallic ions takes place. The electrons liberated during this process is consumed at the cathode.



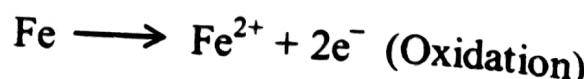
The consumption of electrons by cathodic region may take place by either of the following types:

- a) Evolution of hydrogen
- b) Absorption of oxygen

a) Evolution of hydrogen

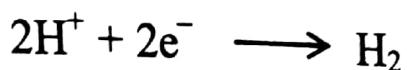
This type of corrosion occurs in acidic environments. Consider the corrosion process in an iron metal. At anodic region, the iron is dissolved into ferrous ions, where electrons are liberated.

At anode :



These liberated electrons flow from anode to cathode. At cathode, H^+ ions are liberated as hydrogen gas.

At cathode :



The overall reaction is



This type of corrosion takes place in all metals above hydrogen in the electro chemical series.

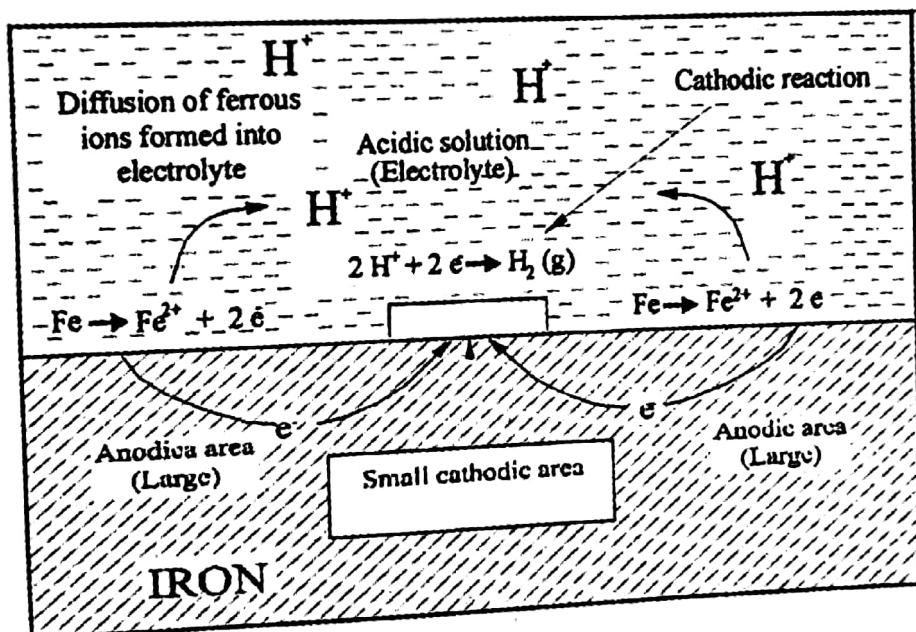
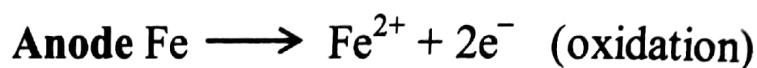


Fig. 5.2 Mechanism of wet corrosion by hydrogen evolution

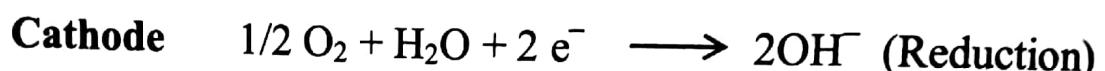
b) **Absorption of oxygen**

This type of corrosion takes place in neutral environments. A best example of this kind of corrosion is rusting of iron. In the presence of

atmospheric oxygen, corrosion takes place on the iron surface and there is formation of iron oxide film. If this film develops some cracks, anodic areas are created on the surface while the other parts act as cathodes.



The liberated electrons flow from anodic to cathodic areas through the metal and are accepted by the dissolved oxygen.



The Fe^{2+} ions and OH^- ions diffuse and react to form Fe(OH)_2 .



If enough oxygen is present, ferrous hydroxide is oxidised to ferric hydroxide

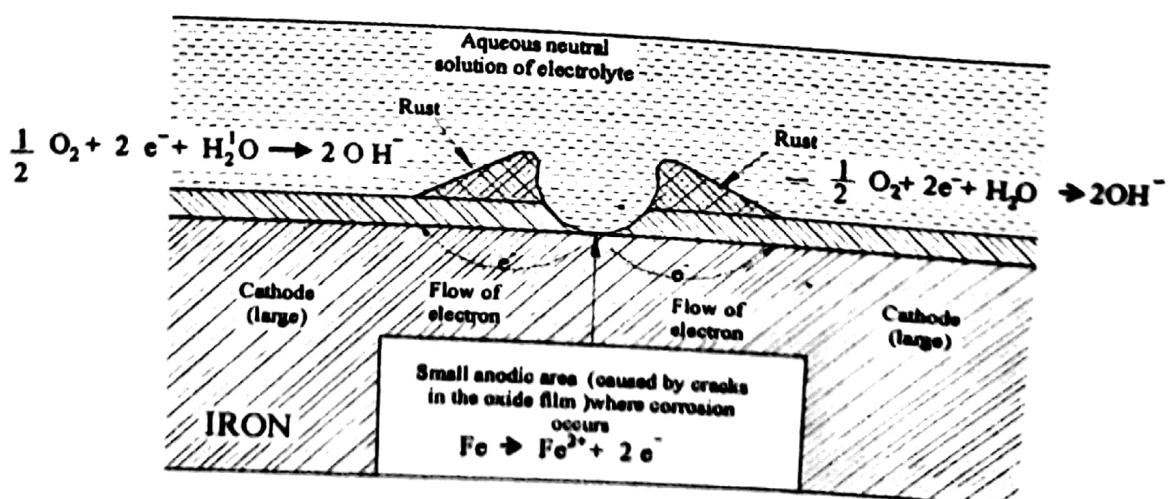
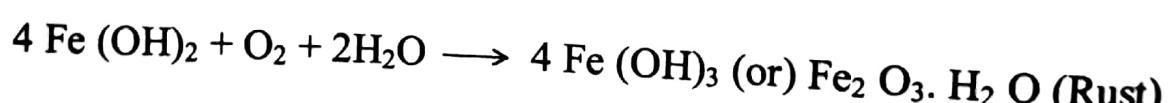
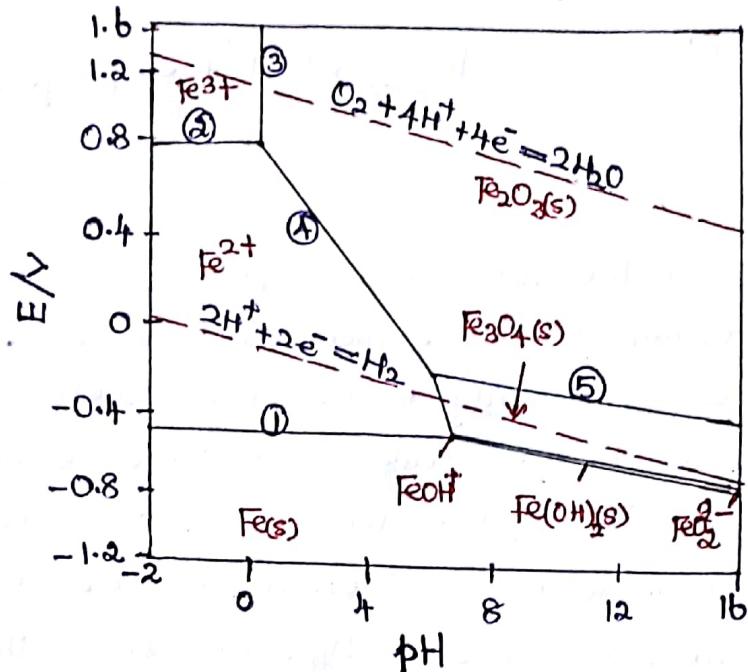


Fig. 5.3 Mechanism of wet corrosion by oxygen absorption

Pourbaix diagrams:

Pourbaix diagrams plot electrochemical stability for different redox states of an element as a function of pH.



Pourbaix diagram for iron at ionic concentrations of 1.0 mM.

Areas in the Pourbaix diagram represent the stability of species. More stable species tend to occupy larger areas.

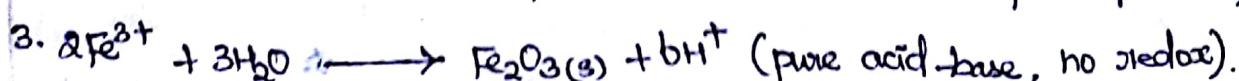
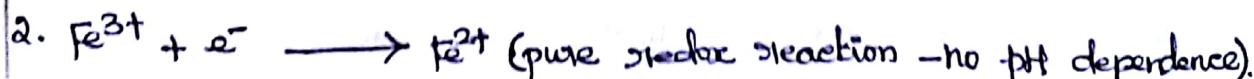
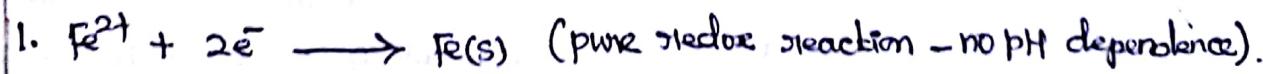
Lines mark places where two species exist in equilibrium.

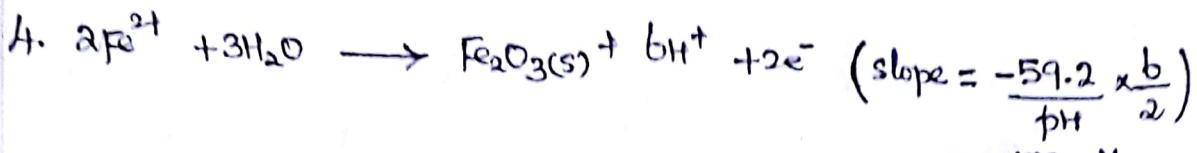
- * pure redox reactions are horizontal lines - these reactions are not pH dependent.

- * pure acid-base reactions are vertical lines - these do not depend on potential.

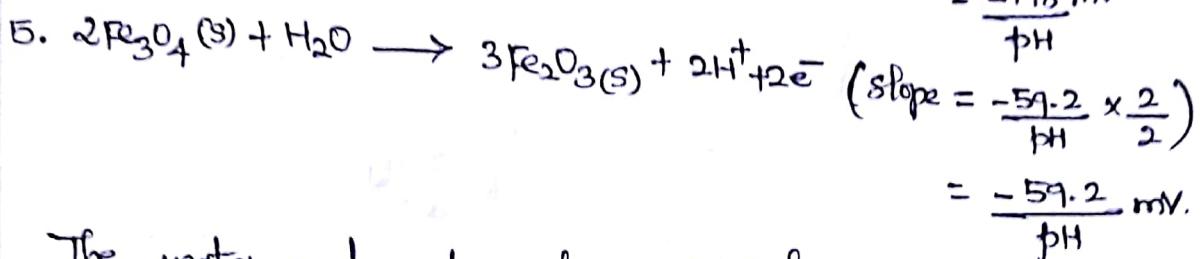
- * Reactions that are both acid-base and redox have a slope of $-\frac{0.05915V}{V} \times \frac{\text{No. of } H^+}{\text{No. of } e^-}$

The equilibria in the iron Pourbaix diagram (numbered on the plot).



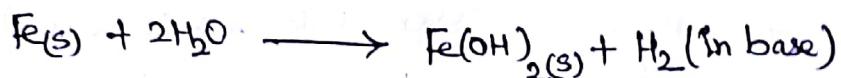
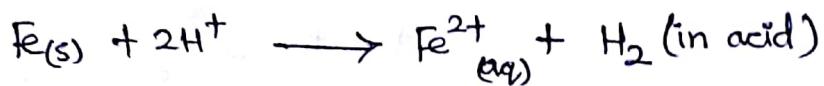


$$= -\frac{178}{\text{pH}} \text{ mV}$$

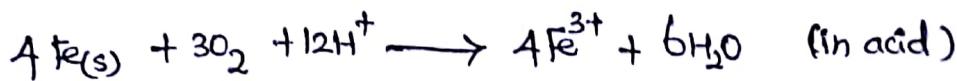


$$= -\frac{59.2}{\text{pH}} \text{ mV.}$$

The water redox lines have special significance on a potentiometer diagram for an element such as iron. Recall that liquid water is stable only in the region between the dotted lines. Below the H₂ line, water is unstable relative to hydrogen gas, and above the O₂ line, water is unstable with respect to oxygen. For active metals such as Fe, the region where the pure element is stable is typically below the H₂ line. This means that iron metal is unstable in contact with water, undergoing reactions.

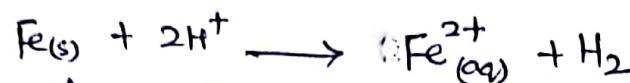


Iron (& most other metals) are also thermodynamically unstable in air-saturated water, where the potential of the solution is close to the O₂ line in the potentiometer diagram. Here the spontaneous reactions are,



The corrosion of iron is indeed rapid in parts of the potentiometer diagram where the element is oxidized to a soluble, ionic product such as Fe³⁺_(aq). However, solids such as Fe₂O₃ forms a protective coating on the metal that greatly impedes the corrosion reaction. This phenomenon is called passivation.

Draw a vertical line through the iron potentiocell diagram at the pH of tap water (about 6). At slightly acidic pH, iron is quite unstable with respect to corrosion by the reaction.



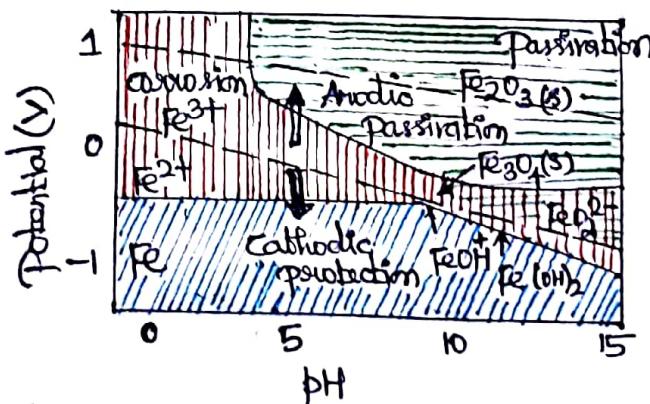
but only in water that contains relatively little oxygen, i.e., in solutions where the potential is near the H_2 line.

Saturating the water with air (O_2) oxygen moves the system closer to the O_2 line, where the most stable species is Fe_2O_3 and the corrosion reaction is



This oxidation reaction is orders of magnitude slower because the oxide that is formed passivates the surface. Therefore iron corrodes much more slowly in oxygenated solutions.

More generally, iron ore passivates whenever they oxidize to produce a solid product, and corrode whenever the product is ionic and soluble. This behavior can be summed up on the potentiocell diagram below,



The cathodic protection strategy is most frequently carried out by connecting a more active metal such as Mg (or) Zn to the iron (or) steel object. (Ex. the hull of a ship, or an underground gas pipeline) that is being protected.

Electrochemistry

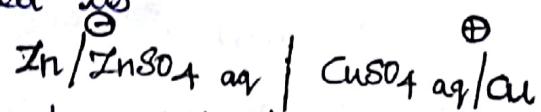
The branch of chemistry, which deals with the study of the conversion of chemical energy into electrical energy or vice-versa and their mutual relationship, is referred to as Electrochemistry.

Galvanic cells

A galvanic cell is a device which converts chemical energy into electrical energy. The galvanic cell usually consists of two electrolytic solutions in which two electrodes of different materials are dipped. The emf of such a cell is directly proportional to the intensity of the chemical reaction occurring in it. The reaction going on in a galvanic cell is the reverse of that taking place in an electrolytic cell. A galvanic cell is also called electrochemical cell. Daniel cell is a well known example of galvanic cell.

Daniel cell:

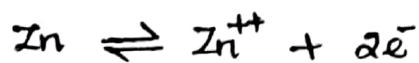
Daniel cell consists of In electrode dipped into ZnSO_4 solution and a Cu electrode dipped into CuSO_4 solution. The two solutions are separated by a porous pot. This allows electrical contact but prevents gross mixing. The cell may be represented as



When the two electrodes are connected by a wire, current flows in the circuit. The working of the cell may be illustrated by considering each electrode in turn.

Anode:

On account of high solution pressure, In passes into solution forming In^{+2} ions with the liberation of electrons. This process will continue until an equilibrium is reached between the metal and solution. The balance of force that operates between the metal and solution is called Potential.

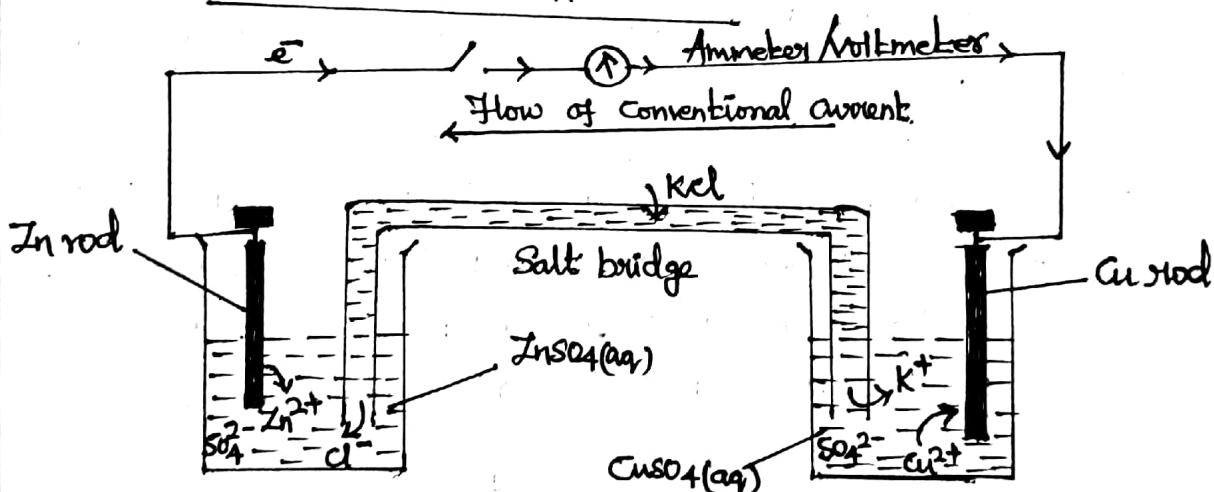
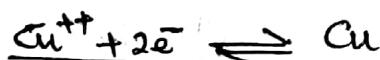


Cathode

The electrons liberated at the anode (Zn electrode) travel along external circuit and are made available at the Cu electrode. Hence Cu^{++} ions gain these electrons and get deposited as Cu.



Thus the movement of electrons from Zn to Cu produces current in the circuit. The net reaction is the sum of two electrode reactions. This is known as cell reaction.



The phenomenon of a metal passing into solution as metal ions with the liberation of electrons is known as oxidation (or) de-electronation. The electrode where it takes place is known as anode or oxidising electrode or negative electrode. The reverse phenomenon of the gain of electrons by a metal ion with the deposition of metal is known as reduction or electronation. The electrode where it occurs is known as cathode or reducing electrode or positive electrode.

According to International sign convention, the electrode where oxidation occurs is represented on the left-hand side and the reducing electrode on the right-hand side. The emf of the cell is the sum of the two electrode potentials.

$$E_{\text{cell}} = E_{\text{anode}} + E_{\text{cathode. (or)}} \quad \text{RP} \quad \text{RP}$$

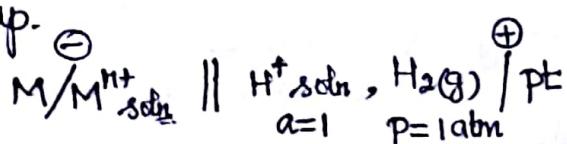
Electrode potential

The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution is called electrode potential.

Standard electrode potentials:

Single electrode potential of an electrode at a given temperature depends upon the activity (or concentration) of the ions in the surrounding solution. If the activity of the ions is unity and the temp. is 25°C , the potential developed at the electrode is called standard electrode potential. It is denoted by E° .

Standard electrode potential, E° of an electrode can be measured by coupling the electrode with Standard Hydrogen Electrode (SHE). If the electrode reaction is oxidation, the following cell is set up.



The emf of the above cell is determined using a potentiometer.

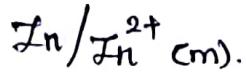
$$E_{\text{cell}} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

since $E_{\text{H}_2}^{\circ} = 0$, the emf of the cell is equal to the oxidation potential of the electrode (SHE or anode).

Sign Conventions:

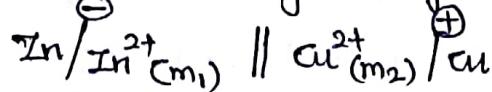
Certain conventions and notations are followed regarding electrodes and electrochemical cells. They are as follows.

1. A half cell such as In rod dipped in a solution of In^{2+} ions of concentration (m) is indicated by



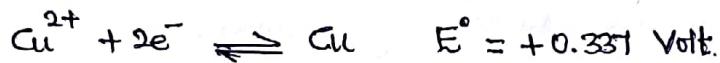
The vertical line denotes a solid phase in contact with a liquid phase.

- 2. A galvanic cell may be represented as:



Double vertical lines between the two half cells represent the liquid junction. Always the electrode where oxidation occurs is represented on the left-hand side. It is given a negative sign. The electrode where reduction occurs is represented on the right-hand side. It is given a positive sign.

- 3. According to IUPAC system, the electrode potential is given a positive value if the electrode reaction involves reduction when compared to SHE.



If the electrode reaction involves oxidation when compared to SHE, the electrode potential is given a negative sign.



- 4. The values of oxidation and reduction potentials are numerically equal but opposite in sign. That means the potential of the same electrode acting as anode will be opposite in sign to the one acting as cathode.

- 5. The emf of the cell must be positive for a cell reaction to be spontaneous.

Electrochemical series:

The electrochemical series is the arrangement of various electrode systems in the increasing order of their standard reduction potentials.

Electrode	Electrode reaction (Reduction)	E° (Volts)
Li^+/Li	$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3.04
K^+/K	$\text{K}^+ + e^- \rightleftharpoons \text{K}$	-2.92
Ca^{2+}/Ca	$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	-2.87
Na^+/Na	$\text{Na}^+ + e^- \rightleftharpoons \text{Na}$	-2.71
In^{2+}/In	$\text{In}^{2+} + 2e^- \rightleftharpoons \text{In}$	-0.7618

Fe^{2+}/Fe	$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.44
Cd^{2+}/Cd	$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}$	-0.40
Pb^{2+}/Pb	$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	-0.13
$\text{H}^+/\frac{1}{2}\text{H}_2$	$\text{H}^+ + e^- \rightleftharpoons \frac{1}{2}\text{H}_2$	± 0.0000
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+0.34
Ag^+/Ag	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+0.80
Hg^{2+}/Hg	$\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}$	+0.85
Au^{3+}/Au	$\text{Au}^{3+} + 3e^- \rightleftharpoons \text{Au}$	+1.42
$\frac{1}{2}\text{F}_2/\text{F}^-$	$\frac{1}{2}\text{F}_2 + e^- \rightleftharpoons \text{F}^-$	+2.87

Nernst Equation

Single electrode potential and cell emf are determined not only by the nature of the constituents opposing the electrodes but also by the temp and concentrations of the solutions (or more accurately activities) involved. When all the substances taking part in the reaction in a reversible cell are in their standard states, i.e., at unit activity, the emf is called the standard emf of the cell. It is denoted by E° . Similarly, when the activity of the solution in the electrode is unity, the potential developed is called standard electrode potential. It is also denoted by E° .

If the reaction under examination takes place for the passage of n Faraday, the standard free energy change (i.e., free energy change when all the reactants and products are at unit activity) ΔG° is given by

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

E° - standard emf of the cell (or) std. electrode potential.

Consider a general reversible reaction,



Applying law of Mass action,

$$K = \frac{a_1^l a_m^m}{a_A^a a_B^b} \quad K - \text{Equilibrium constant.}$$

According to Vant Hoff isotherm,

$$\Delta G_I = \Delta G_I^\circ + RT \ln \frac{a_1^l a_m^m}{a_A^a a_B^b}$$

But $\Delta G_I = -nFE$

$$\therefore -nFE = -nFE^\circ + RT \ln \frac{a_1^l a_m^m}{a_A^a a_B^b}$$

Multiply by (-) & divide by nF

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_1^l a_m^m}{a_A^a a_B^b}$$

If the solutions used in the cell are dilute, activities may be replaced by concentrations. Thus,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[I]^l [M]^m}{[A]^a [B]^b}$$

(or)

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[I]^l [M]^m}{[A]^a [B]^b}$$

At $T=25^\circ\text{C}$, the term $\frac{2.303 RT}{F}$ equals to 0.05915, hence

$$E = E^\circ - \frac{0.05915}{n} \log \frac{[I]^l [M]^m}{[A]^a [B]^b}$$

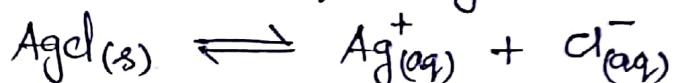
This is a general equation for the emf of a reversible cell or reversible electrode potential. This equation is known as Nernst equation. When the equation is applied to an electrode, E° is called the standard electrode potential.

Applications of Electrode potentials [Nernst Equation]

By measuring the emf of suitable galvanic cells, it is possible to calculate the changes in the thermodynamic functions ΔG° , ΔH° , ΔS° , solubility product, pH of a solution, activities of electrolytes and pK_a and pK_b .

Determination of solubility products of sparingly soluble salts.

When the sparingly soluble salt AgCl is dissolved in water, we have the following equilibrium,



According to the law of equilibrium,

$$K_{eq} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

Since the undissolved salt is present in the solid state, its concentration can be regarded as constant. Therefore,

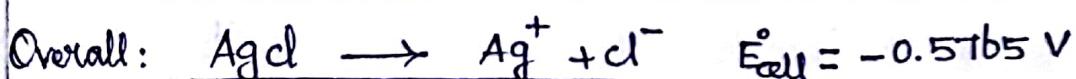
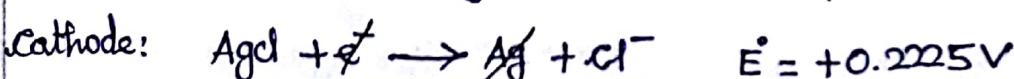
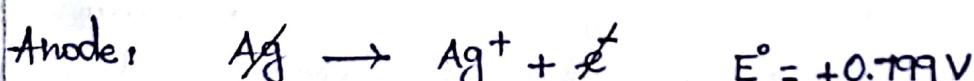
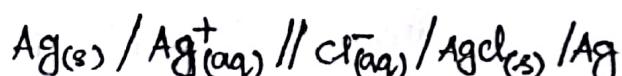
$$[\text{Ag}^+][\text{Cl}^-] = K \cdot [\text{AgCl}] = K \cdot \text{constant} = K_{sp}$$

(or)

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

The solubility product is equal to the ionic product in a saturated solution.

K_{sp} for AgCl may be determined from Emf measurements by employing a suitable cell.



The cell Emf is given by

$$E = E^\circ - \frac{RT}{nF} \ln K_{sp}$$

At equilibrium the cell would not be able to perform any useful work and hence $E_{cell} = 0$. Therefore

$$E^\circ = \frac{RT}{nF} \ln K_{sp}$$

At 298 K,

$$E^\circ = \frac{0.05915}{n} \log K_{sp}$$

$$\log K_{sp} = \frac{nE^\circ}{0.05915}$$

$$K_{sp} = \exp \left[\frac{nE^\circ}{0.05915} \right]$$

We also know that,

$$G^\circ_f = -RT \ln K_{sp}$$

$$G^\circ_f = -nFE^\circ$$

$$E^\circ = \frac{G^\circ_f}{-nF}$$

$$E^\circ = \frac{RT}{nF} \ln K_{sp}$$

Therefore, $K_{sp} = 1.76 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$

The solubility of AgCl may be evaluated from the solubility product. Since the concentration of Ag^+ equals that of Cl^- , we may write

$$[\text{Ag}^+] = [\text{Cl}^-] = (K_{sp})^{1/2} = (1.76 \times 10^{-10})^{1/2}$$

Hence the solubility of AgCl is $1.32 \times 10^{-5} \text{ mol dm}^{-3}$.

Determination of pH of a solution.

One of the most important applications of Emf measurements is the determination of the pH of solution. In principle, the activity of hydrogen ions or the concentration of hydrogen ions can be determined by setting a cell in which one of the electrodes is reversible to hydrogen ions. In practice the hydrogen electrode is combined with another reference electrode such as saturated calomel electrode (SCE) or any other reference electrode.

For the single hydrogen electrode $\text{Pt}/\text{H}_2(\text{g})$, H^+ soln, the electrode reaction can be written as $P=1\text{ atm}$ $a=?$



The potential of the electrode depends upon the pressure of H_2 gas and the activity (or concentration) of H^+ ions in solution.

$$E_{\text{H}_2} = E_{\text{H}_2}^\circ - \frac{2.303 \text{RT}}{\text{nF}} \log \frac{[\text{H}^+]}{[\text{H}_2]^{\frac{1}{2}}}$$

At low pressures, $[\text{H}_2]^{\frac{1}{2}} = 1\text{ atm}$,

$$E_{\text{H}_2} = E_{\text{H}_2}^\circ - \frac{2.303 \text{RT}}{\text{nF}} \log [\text{H}^+]$$

Since $E_{\text{H}_2}^\circ = 0$, $n=1$

$$E_{\text{H}_2} = - \frac{0.05915}{1} \log [\text{H}^+] \quad \dots \text{at } 25^\circ\text{C.}$$

$$E_{\text{H}_2} = 0.05915 \text{ pH}$$

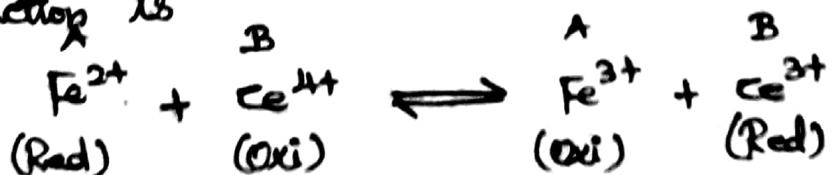
$$\therefore \text{pH} = \frac{E_{\text{H}_2}}{0.05915}$$

Using this equation, the pH of the given solution can be calculated.

Determinations of Equivalence point in redox titrations.

One of the widely used applications of emf measurement is to detect the equivalence point of a titration by measuring the emf of the cell.

Consider a redox titration between Fe^{2+} and Ce^{4+} , the overall reaction is



We can write two Nernst equations, describing potential of the solution.

$$E_{eq} = E_A^\circ - \frac{0.05915}{n_A} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \rightarrow ①$$

$$E_{eq} = E_B^\circ - \frac{0.05915}{n_B} \log \frac{[Ce^{3+}]}{[Ce^{4+}]} \quad \rightarrow ②$$

These equations can be rearranged as

$$-\log \frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{n_A(E_{eq} - E_A^\circ)}{0.05915} \quad \rightarrow ③$$

$$-\log \frac{[Ce^{3+}]}{[Ce^{4+}]} = \frac{n_B(E_{eq} - E_B^\circ)}{0.05915} \quad \rightarrow ④$$

At equivalence point we have mixed stoichiometric amount of Fe^{2+} and Ce^{4+} . Hence,

$$-\log \frac{[Fe^{3+}]}{[Fe^{2+}]} = \log \frac{[Ce^{4+}]}{[Ce^{3+}]}$$

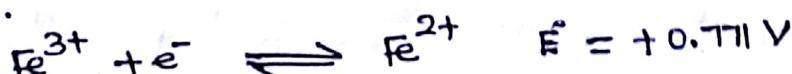
Therefore,

$$\frac{n_A(E_{eq} - E_A^\circ)}{0.05915} = -\frac{n_B(E_{eq} - E_B^\circ)}{0.05915}$$

and finally,

$$E_{eq} = \frac{n_A E_A^\circ + n_B E_B^\circ}{n_A + n_B}$$

The overall reactions can be described in terms of two half-cell reactions.



Hence,

$$E_{eq} = \frac{(1 \times 0.771) + (1 \times 1.610)}{1+1}$$

$$E_{eq} = 1.1905 V$$

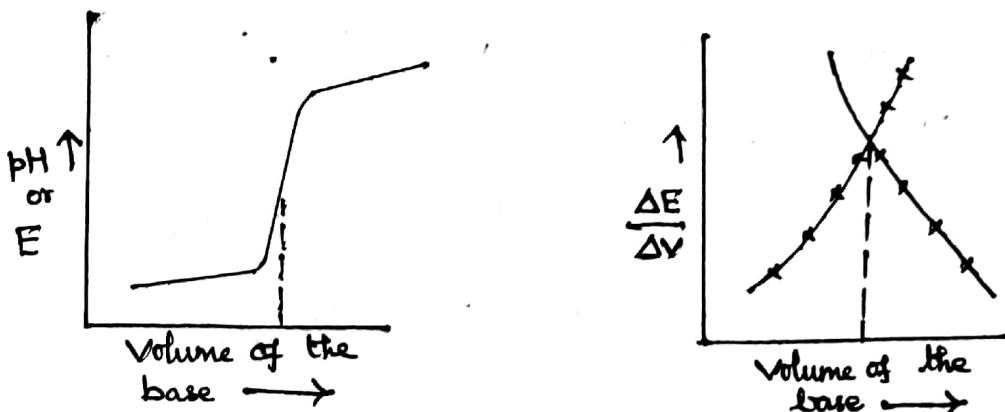
Acid - Base titrations:

In an acid-base titration, neutralisation process is accompanied by a change in concentration of H^+ or OH^- ions. In the titration of an acid such as HCl against NaOH, the pH of the solution rises gradually at first, then more rapidly until the equivalence point where a very sharp increase in pH for a very small addition of the base occurs. After the equivalence point, the pH increases only slightly.

To study the pH changes potentiometrically, an electrode sensitive to H^+ ions is immersed in the solution and then coupled with a suitable reference electrode. The potential, E of any form of hydrogen electrode is related to the pH of the solution:

$$E = 0.05915 \text{ pH} + E_{\text{ref}}$$

since E is proportional to pH, by measuring the emf at different stages and plotting it against the volume of the base, the end-point can be detected. This is the principle of acid-base titration.



The end point can be most accurately located by plotting $\Delta E/\Delta V$ against the volume of the base. $\Delta E/\Delta V$ has a maximum value in the end-point.

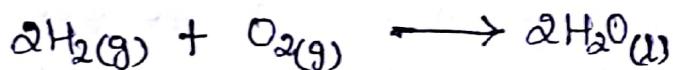
Standard Gibb's free energy of formation for water

The standard Gibb's free energy of formation of

a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states.

[1 bar of P, T = 25°C/298 K].

Let's look at the reaction of the formation of Water.



The Gibbs free energy relates the spontaneity of various reactions by looking at the change in enthalpy temperature and entropy. We can relate those by,

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

If we look at our reaction, it's clear that this is an exothermic reaction. Moles of gas are decreased and a liquid is formed so entropy is decreasing as well. We know that the formation of water is a spontaneous reaction, so ΔG° must be negative. Therefore, this reaction must be run at temperatures where the difference of the enthalpy and the product of entropy and temperature must be less than zero. (< 0)

The Gibbs free energy is also a state function, so looking at ΔG_f° , we can find $\Delta G_{\text{rxn}}^\circ$.

$$\Delta G_{\text{rxn}}^\circ = \sum \Delta G_{\text{prod}}^\circ - \sum \Delta G_{\text{react.}}^\circ$$

Both hydrogen gas and oxygen gas are in their standard states and have a Gibbs free energy of 0.

If you look at tabulated standard thermodynamic data at 25°C.

Species	phase (matter)	chemical formula	$\Delta G_f^\circ (\text{kJ/mol})$
Hydrogen	Gas	H ₂	0
Monoatomic Oxygen	Gas	O	231.7
Dioxygen	Gas	O ₂	0

Ozone	Gas	O ₃	163.2
Water	Liquid	H ₂ O	-237.14
Water	Gas	H ₂ O	-228.61

H₂O(l) has a Gibb's free energy of -237.14 kJ mol⁻¹.

Therefore,

$$\Delta G_{rxn}^{\circ} = -237.14 \text{ kJ mol}^{-1} - 0 \text{ kJ mol}^{-1}$$

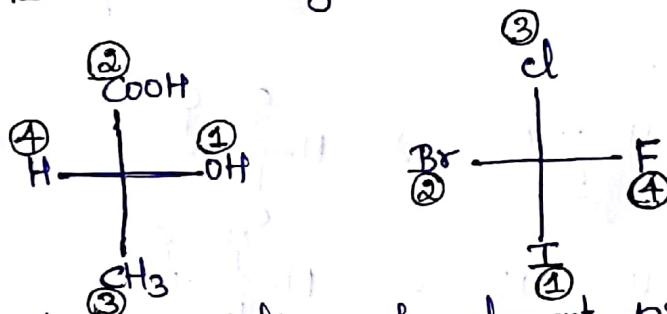
$$\therefore \Delta G_{rxn}^{\circ} = -237.14 \text{ kJ mol}^{-1}$$

RS configuration of a chiral centre

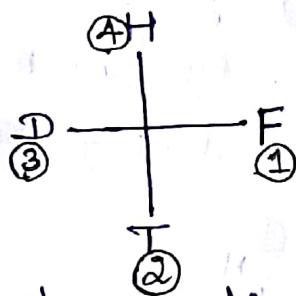
We can use the following set of rules to assign a letter, R or S, to describe the configuration of groups at a chiral centre in the molecule. The R,S configuration is also called the Cahn-Ingold-Prelog nomenclature. (Absolute Nomenclature).

Rules:

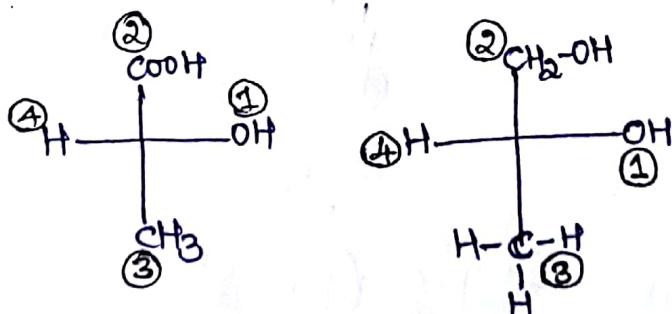
- * Identify chiral centre in molecule
- * Assign a priority number (1-4) to each substituent at the chiral centre. Atoms with higher atomic numbers get higher priority.



- * At chiral centre if isotopes of element present priority given should be based on "Atomic Mass".



- * At chiral centre if directly attached atoms are same, choose next atoms in sequence till priority decided.



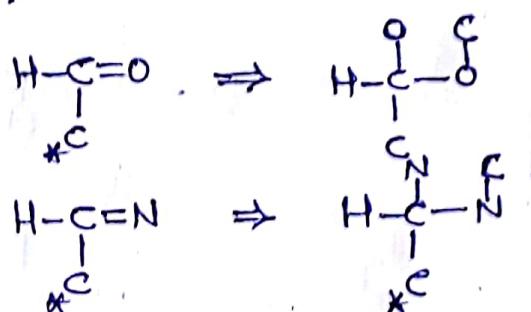
After giving priority keep least priority group (or)

atom away from the observer. See the priority direction of other groups except lowest priority group which is considered to be stereogenic centre.

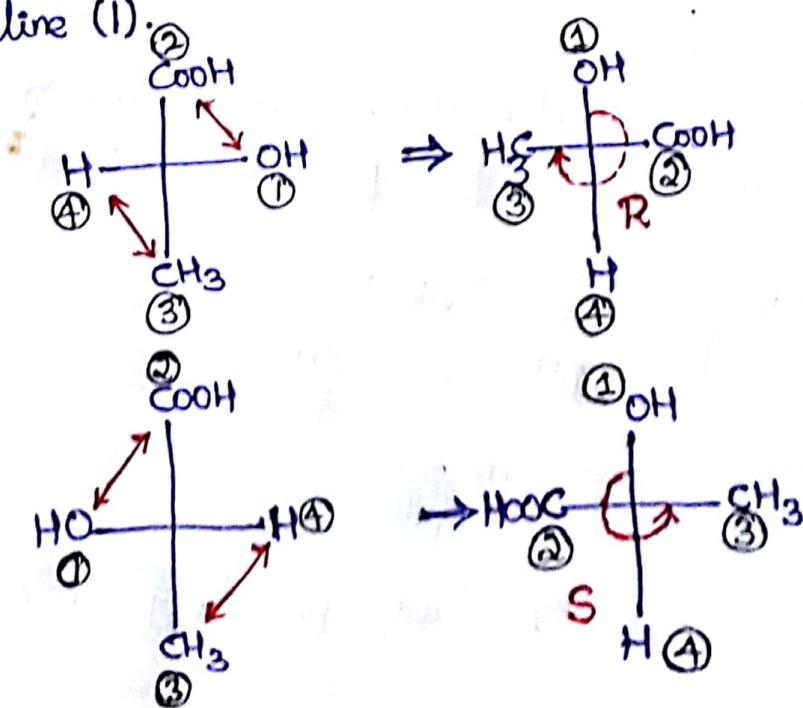
If the priority direction is clockwise configuration then that nomenclature is known as R configuration (rectus).

If the priority direction is anticlockwise configuration, nomenclature is S configuration (sinister).

* At chiral centres if unsaturation presence (double/triple bond) then duplication/triplication should be considered.



* If least priority group on horizontal line (-) take opposite configuration. By doing mutual exchange of two pairs of groups bring least priority group on vertical line (1).



Conformational Analysis of n-Butane

conformational Analysis:-

It is defined as the relative stabilities of the conformations of a compound and interpretation of its properties it depends on the following factors.

- (i) Torsional strain
- (ii) Angle strain
- (iii) Vander Waals strain
- (iv) Dipole - Dipole interactions.

(i) Torsional strain:-

The strain developed in a molecule by the bond-pair bond-pair repulsion, one on each C atom of a C-C single bond, is called torsional strain. The greater the torsional strain, the lower is the stability of a conformation.

(ii) Angle strain:-

Any deviation from the usual bond angle will create a strain in the molecule which is called angle strain. The greater the angle strain, the lower is the stability of a conformation.

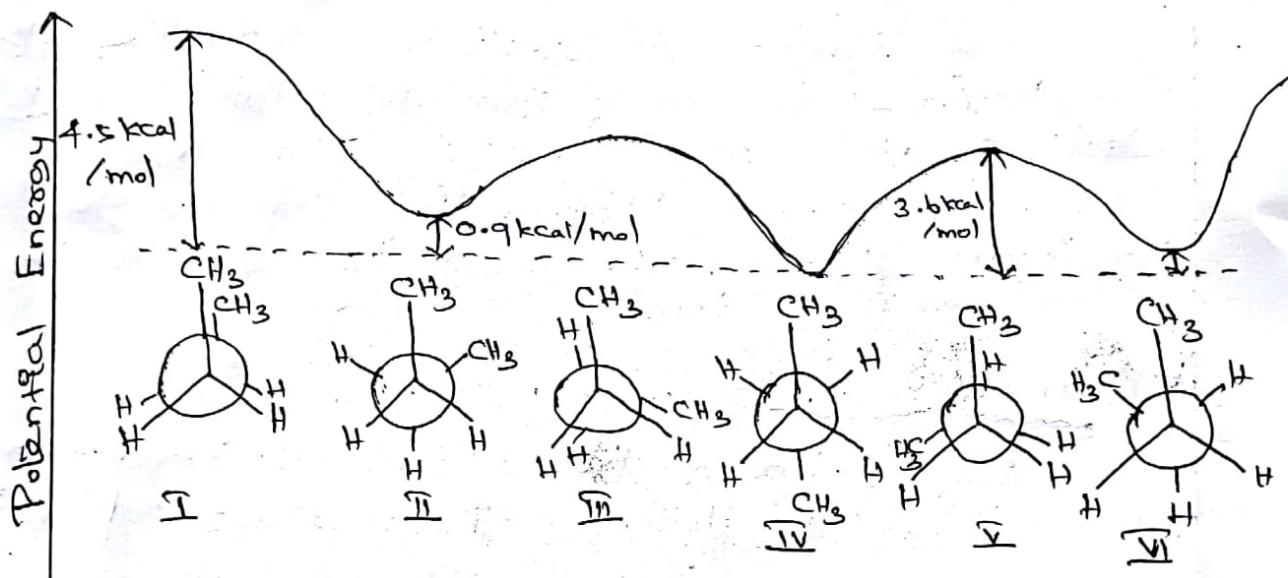
(iii) Steric strain (or) Vander Waals strain:-

If the distance between two substituents is less than the sum of their Vander Waals radii then a repulsive force generates due to repulsion between the electron clouds of the interacting substituents. The destabilizing interaction creates a strain in the molecule which is known as Vander Waals strain. The greater the size of the non-bonded substituents, the greater is the Vander Waals strain and less stability.

(iv) Dipole-Dipole Interaction :-

Non-bonded substituents on each C atom of a C-C single bond may undergo dipole-dipole interactions of which the H-bonding force is the strongest. If the non-bonded atoms have opposite charges, the stability of the conformation increases, otherwise the non-bonded atom have same charges, the stability of, the conformation decreases.

The potential energy of butane as a function of dihedral angle is given below:



Structure I - Total eclipsed. ($0^\circ \text{ & } 360^\circ$)

II & VI - Gauch conformation ($60^\circ \text{ & } 300^\circ$)

III & IV - Partially eclipsed ($120^\circ \text{ & } 240^\circ$)

II - Anti structure. (180°)

The order of increasing stability of the conformation of butane is as follows:

$$\text{I} < \text{IV} \equiv \text{V} < \text{II} \equiv \text{VI} < \text{III}$$

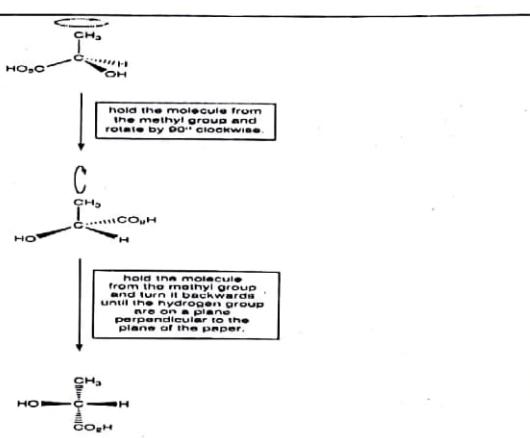
- * The staggered conformations (II, IV and VI) of butane are at energy minima and are thus the stable conformations of butane.
- * However, not all of the staggered conformations of butane are similar.
- * The conformations with a dihedral angle of $\pm 60^\circ$ between the two C-CH₃ bonds are called gauche conformations and the conformation in which the dihedral angle is 180° is called the anti conformation (VI).
- * The anti conformation (IV) does not have torsional strain because the groups are staggered and the methyl groups are far apart.
- * The methyl groups in the gauche conformations are close enough to each other and for this, the gauche conformation are destabilized by Vander Waals repulsions between non-bonded hydrogens on the two CH₃ groups.
- * This repulsion causes the gauche conformation to have approximately 0.9 kcal/mol more energy than anti conformation in which no such Vander Waals repulsions are present.
- * Therefore the anti conformation is more stable than a gauche conformation.
- * The eclipsed conformations (I, III and V) represent energy maxima in the potential energy diagram.
- * Eclipsed conformations III and V not only have torsional strain, they have Vanderwaals repulsions arising from the eclipsed methyl groups and hydrogen atoms.
- * The eclipsed conformation I has the greatest energy (least stable) of all because, in addition to torsional strain, there is large Vanderwaals repulsive force between the eclipsed methyl groups.

FISCHER, NEWMANN AND SAWHORSE PROJECTION FORMULAS:

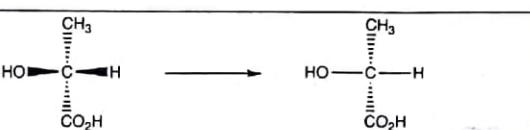
To convert this stereo formula into a Fischer projection use the following procedure:

Step 1: Hold the molecule so that

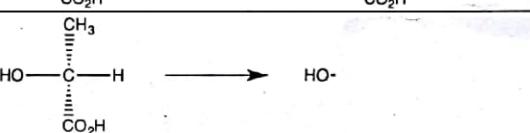
1. the chiral center is on the plane of the paper,
2. two bonds are coming out of the plane of the paper and are on a horizontal plane,
3. the two remaining bonds are going into the plane of the paper and are on a vertical plane



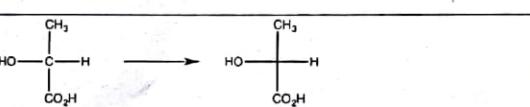
Step 2: Push the two bonds coming out of the plane of the paper onto the plane of the paper.



Step 3: Pull the two bonds going into the plane of the paper onto the plane of the paper.



Step 4: Omit the chiral atom symbol for convenience.



(i) Fischer Projection to Sawhorse Projection:

Fischer projection of a compound can be converted into Sawhorse projection; first in the eclipsed form (in Fischer projection the groups on neighbouring carbons are considered to be eclipsing each other), by holding the model in horizontal plane in such a way that the groups on the vertical line point above, and the last numbered chiral carbon faces the viewer. Then, one of the two carbons is rotated by an angle of 180° to get the staggered form (more stable or relaxed form). For example, Fischer projection of an optically active tartaric acid is converted into staggered Sawhorse projection as shown.

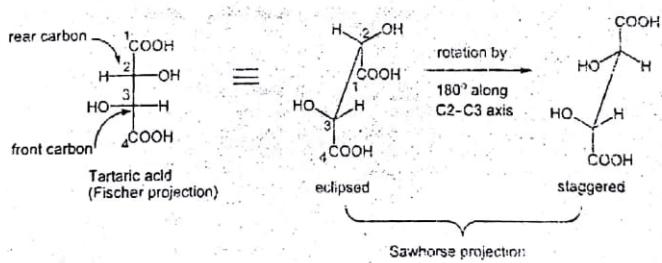


Fig. 2.5: Conversion of Fischer projection into Sawhorse projection

Sawhorse Projection to Fischer Projection:

First, the staggered Sawhorse projection is converted to an eclipsed projection. It is then held in the vertical plane in such a manner that the two groups pointing upwards are away from the viewer, i.e. both these groups are shown on the vertical line. Such a conversion for 2,3-dibromobutane is shown.

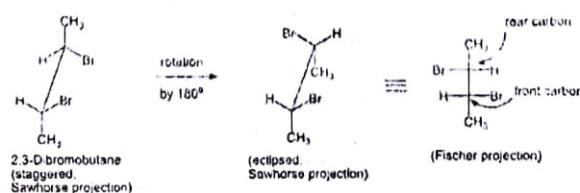


Fig. 2.6: Conversion of Sawhorse projection into Fischer projection

Sawhorse Projection to Newman Projection And then Fischer Projection:

Conversion of Sawhorse projection to Newman projection is quite easy. The molecule is viewed from front carbon (the central C-C bond being invisible) to get the staggered Newman projection. The rear carbon is rotated by 180° to get eclipsed Newman projection. Then, the molecule is held in the vertical plane, i.e. central bond is visible in the vertical plane in such a manner that front carbon is the lowest carbon.

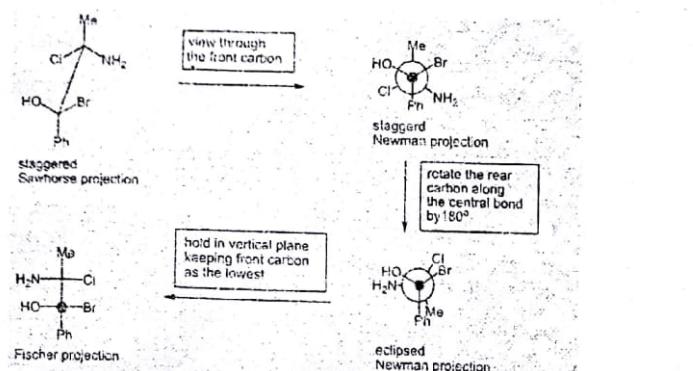


Fig. 2.7: Conversion of Sawhorse projection into Fischer projection via Newman projection

Fischer Projection to Newman Projection and then Sawhorse Projection:

The molecule is viewed through the lowest chiral carbon, which becomes the front carbon, and thus eclipsed Newman projection is drawn. It is then converted into staggered conformation. Finally, the molecule is viewed through the bond connecting the front carbon with rear carbon. Such a conversion of D-erythrose is illustrated in the following scheme.

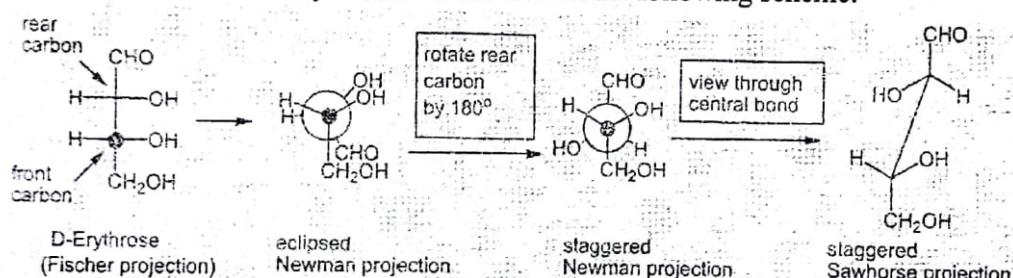


Fig. 2.8: Conversion of Fischer projection into Sawhorse projection via Newman projection

Symmetry:

Symmetry is defined in terms of elements and operations.

Each operation is performed relative to a point, line or plane - called a symmetry element.

There are 5 kinds of operations:

1. Identity E

2. n-Fold rotations C_n

3. Reflection σ

4. Inversion i

5. Improper n-Fold Rotation S_n

1. Identity (E):

In identity operation no change is made in the original molecule. We can say identity is the operation of not doing anything. We leave the system unchanged and identical to the original system.

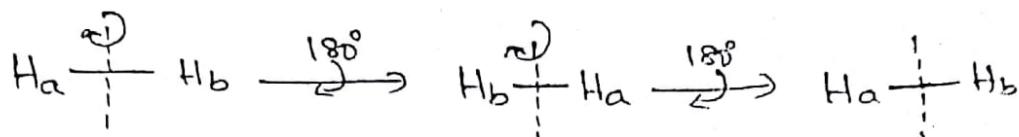
2. Rotation axis (or) Proper axis of Symmetry (C_n):

If an imaginary axis can be constructed in a molecule around which the molecule can be rotated through an angle (θ) to get an indistinguishable configuration, the molecule is said to possess a rotation axis.

The value of n (order of axis) can be calculated by,

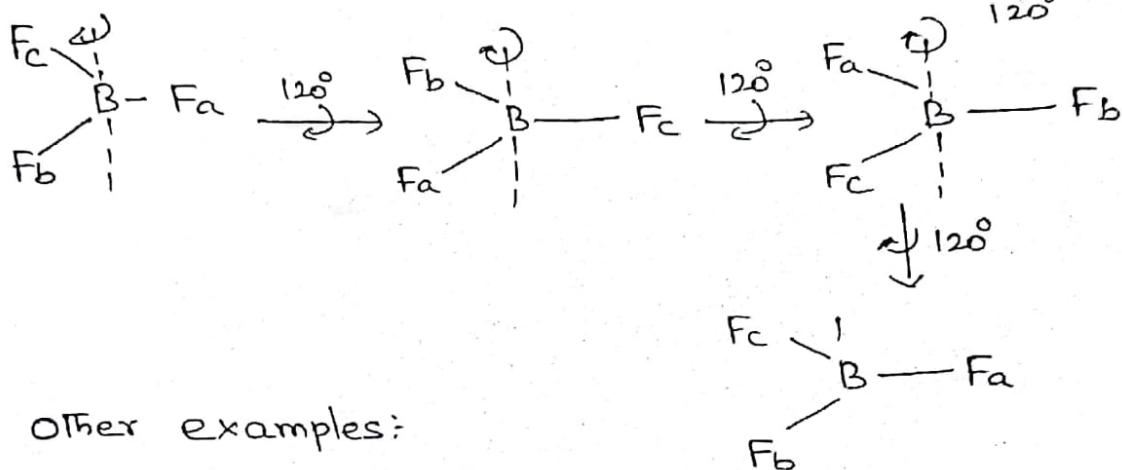
$$n = \frac{360^\circ}{\theta}$$

e.g.: C_2 axis



$$n = \frac{360^\circ}{180^\circ} = 2$$

C_3 axis.



Other examples:



$$n = \frac{360^\circ}{72^\circ} = 5 \quad (C_5 \text{ axis})$$

Cyclopentane

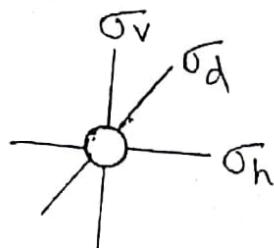


$$n = \frac{360^\circ}{60^\circ} = 6 \quad (C_6 \text{ axis})$$

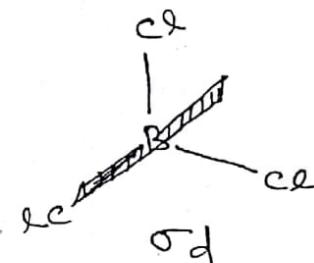
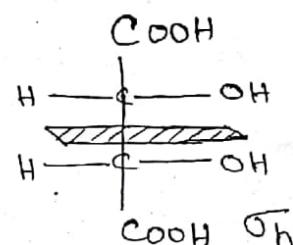
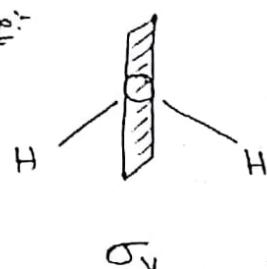
3. Plane of Symmetry (σ)

An imaginary plane that bisects molecule in such a way that the two parts are mirror images of each other. This element of symmetry is represented by symbol (σ).

A symmetry plane parallel with the principle axis is known vertical (σ_v) and one perpendicular to it horizontal (σ_h). A third type, the angle between two (2-fold) rotation axis perpendicular to the principle axis is dihedral (σ_d).



e.g.:

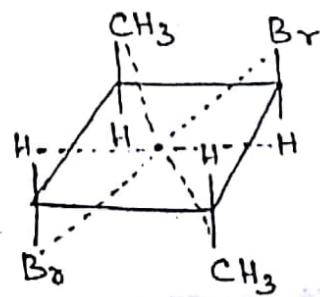
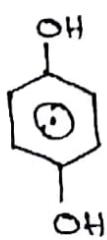
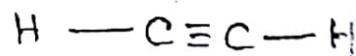
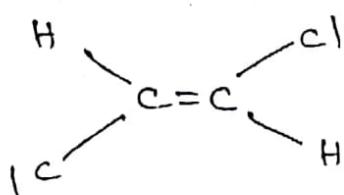


Other examples: NH_3 , SF_4 , O_2 , B_2H_6 etc,

4. Centre of Symmetry (i):

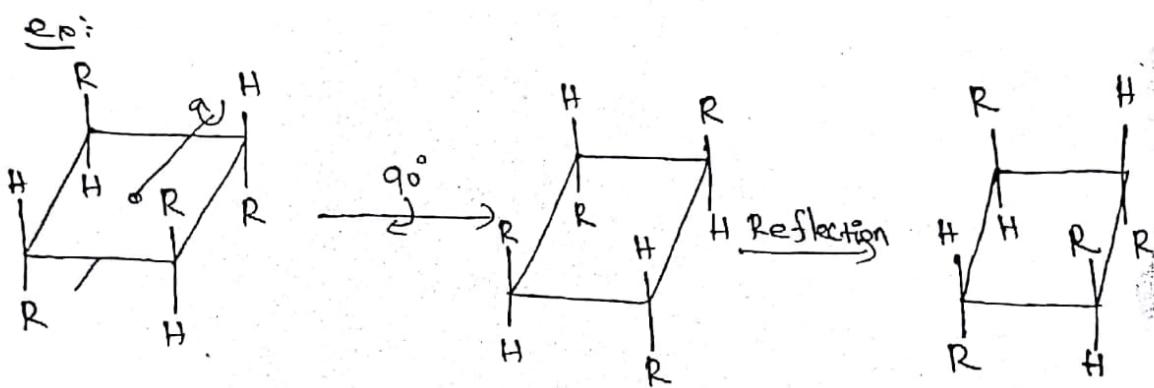
This is such a point through if a line drawn meets identical atoms of equal distance from the point in two opposite directions.

e.g.:



5. Alternating axis of Symmetry (or) Improper axis of symmetry: (S_n):

When a molecule has a n -fold alternating axis of symmetry is rotated through an angle $360^\circ/n$ about this axis then followed by the reflection in a plane perpendicular to this axis the molecule is indistinguishable from the original structure.

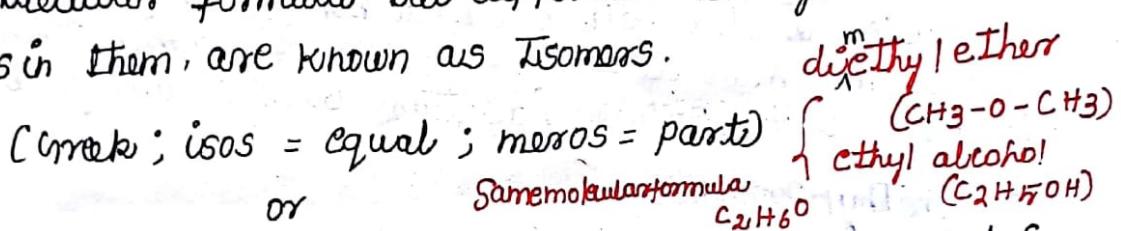


Stereochemistry

organic chemistry is a chemistry sub discipline involving the scientific study of the structure, properties, and reactions of organic compounds and organic materials. i.e., matter in its various forms that contain carbon atoms. Study of structure includes many physical and chemical methods to determine the chemical composition and the chemical constitution of organic compounds and materials.

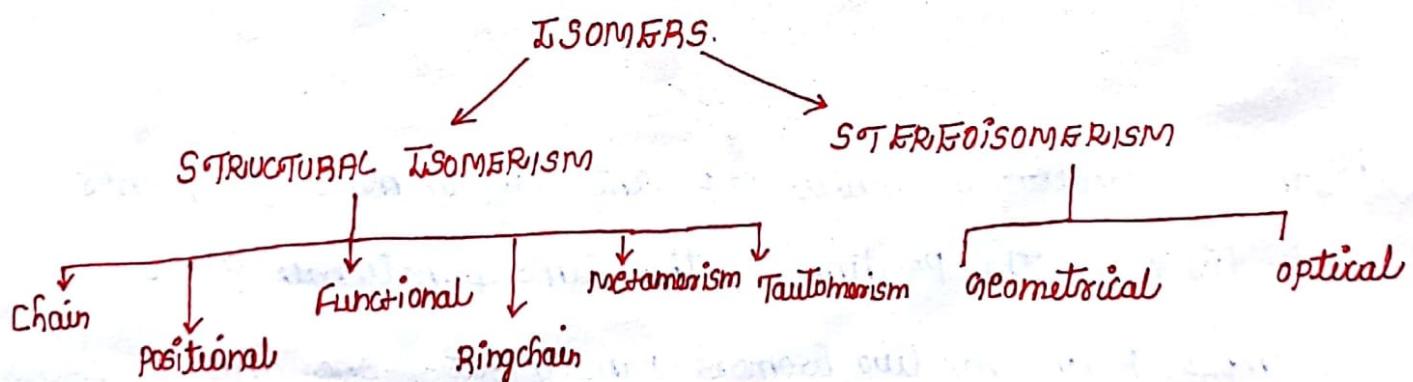
What is Isomerism

The organic compounds having the same molecular formula but different structures are known as Isomers. This phenomenon is known as Isomerism. In other words, the organic compounds having the same molecular formula but different arrangements of carbon atoms in them, are known as Isomers.



The presence of two or more compounds which has the same molecular formula is known as isomerism.

Classification of Isomerism



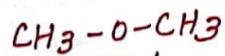
Structural Isomerism

This type of Isomerism is classified into 6 types

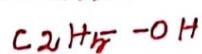
1. chain Isomerism
2. positional Isomerism
3. Functional Isomerism
4. Ring chain Isomerism
5. Metamerism Isomerism
6. Tautomerism Isomerism.

structural isomerism

↓
isomers differ from one
another in their structural arrangements



oxygen atoms bonded to
two carbon atoms

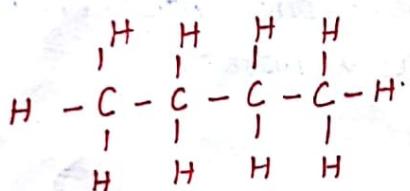


oxygen atoms bonded
to carbon & hydrogen atoms

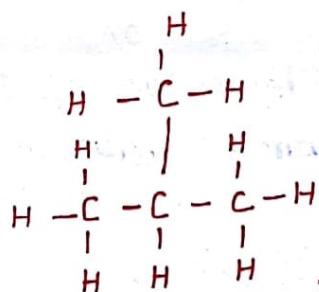
chain Isomerism

- The same molecular formula represents two or more compounds
- It differs in the nature of carbon chain (straight or branched)
- The isomers have different skeleton of carbon atoms.
- Example, C_4H_{10} (Butane) has two isomers namely butane and

2-methyl Propane

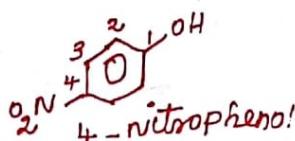


Butane

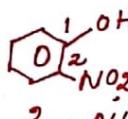


2-methyl propane

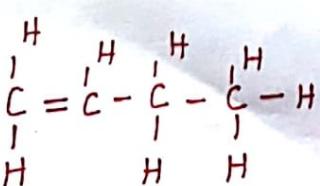
positional Isomerism



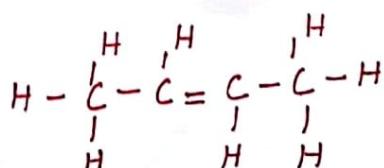
and



- The same molecular formula represents two or more compounds
- It differs in the position of the same functional group
- Example, Butene has two isomers namely But-1-ene and But-2-ene



But-1-ene

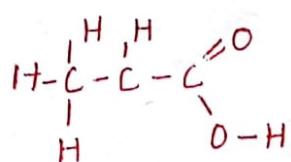


Different position of double bond
But-2-ene

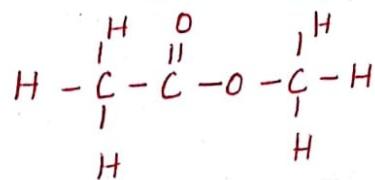
Functional Isomerism

②

- Same molecular formula but different functional groups & different properties. (Or)
- It differs in the nature of the functional group.
- Example. $C_3H_6O_2$ has two isomers namely propanoic acid and methyl ethanoate.



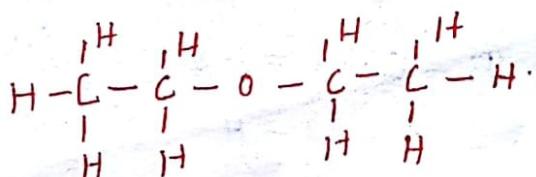
Propanoic Acid



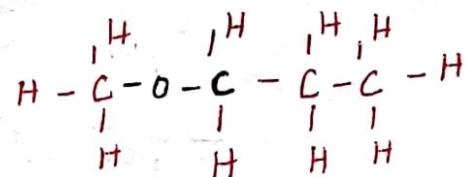
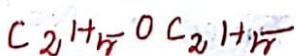
Methyl Ethanoate.

Metamerism Isomerism

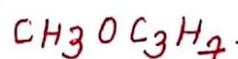
- The same molecular formula represents two or more compounds.
- It differs in the nature of the alkyl groups attached to the same functional group.
- Isomers differ in their structure due to difference in the numbers & distribution of carbon atoms around the functional grp.
- Example, Diethyl ether and methyl propyl ether are metamerical isomers.



Diethyl Ether



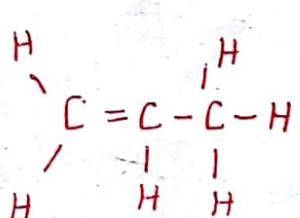
Methyl Propyl Ether



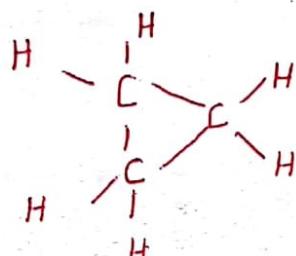
Number of carbon atoms on either side of the functional group are different.

RING CHAIN ISOMERISM

- The same molecular formula represents two or more compounds.
- It differs in the mode of linkage of carbon atoms.
- The isomers have either open chain or closed chain.
- Example. propane and cyclopropane are ring chain isomers.



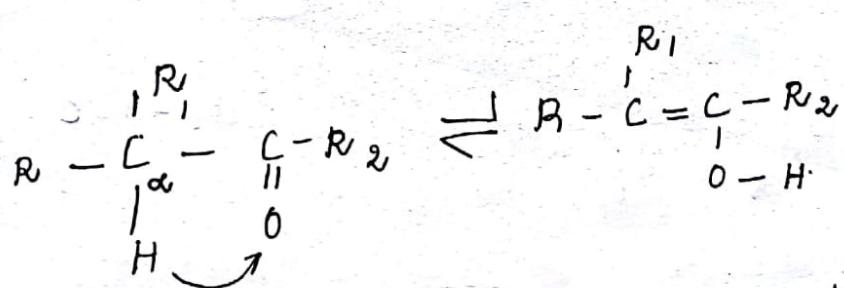
propane



cyclopropane

TAUTOMERISM ISOMERISM

Interconvertible keto and enol forms of a carbonyl compound are known as 'tautomers'. and their interconversion is called tautomerization. This special type of constitutional isomerism is called 'Tautomerism'.



where
 $\text{R}_2 = \text{H, alkyl}$

In organic chemistry, keto-enol tautomerism refers to a chemical equilibrium between a keto form and an enol. The enol & keto forms are said to be tautomers of each other. The interconversion of the two forms involves the movement of an alpha hydrogen and the shifting of bonding.

electrons; hence the isomerism qualifies as tautomerism. ③

A compound containing a carbonyl group ($C=O$) is normally in rapid equilibrium with an enol tautomer, which contains a pair of doubly bonded carbon atoms adjacent to a hydroxyl (-OH) group, $C=C-OH$. The keto form predominates at equilibrium for most ketones.

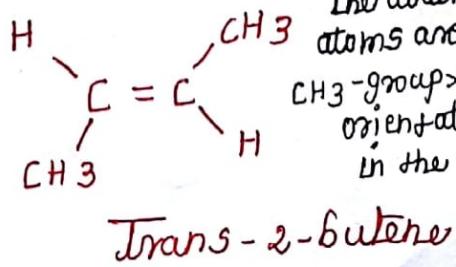
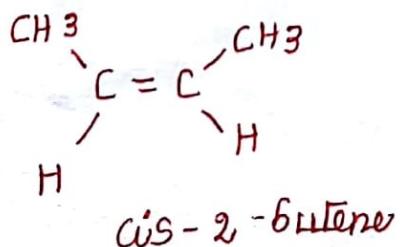
STEREISOMERISM

This type of isomerism differs in the spatial arrangement of atoms or groups. It is of two types

- i Geometrical Isomerism
- ii Optical Isomerism.

Geometrical Isomerism ↗

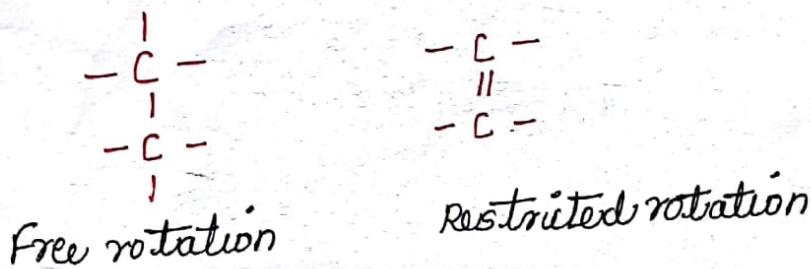
- The same molecular formula represents two or more compounds.
- It differs in the spatial arrangement of atoms or groups around carbon-carbon double bond.
- It is of two types - If same group are on same side then, it is called 'cis' isomers and if it is on opposite sides, then it is called 'trans' isomers.
- Example, cis-2-butene and trans-2-butene are 'cis' and 'trans' isomers.



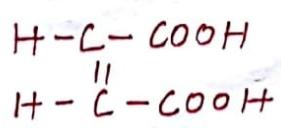
In both geometrical isomers the double bonded carbon atoms are attached to CH_3 -group & H-atom but the orientation of CH_3 & H atoms in the two isomers are different

Geometrical or cis-trans-isomerism

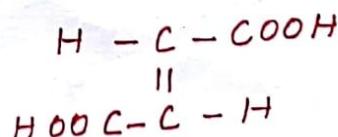
when two carbon atoms are linked by a single bond, there is free rotation about C-C bond. However, when two carbon atoms are linked by a double bond, the rotation is restricted.



The compounds, in which the rotation is restricted, with different group or atom on same carbon atom generally exhibit geometrical isomerism. This condition results either from double bond or from rings. Stereoisomers which differ in properties due to restricted rotation are known as geometrical isomers and the phenomenon is called geometrical isomerism. The isomer in which the same groups are present on the same side is called cis-isomer and the isomer in which the same groups are on the opposite side is called trans-isomer.



maleic acid



Fumaric acid

optical isomerism

- optical isomerism is a type of stereoisomerism.
- In which the isomers are identical in molecular weight and most chemical & physical properties but differ in their effect on the rotation of polarized light.
- Solutions of some organic compounds have the ability to rotate the plane of polarised light. These compounds are said to be optically active. This property of a compound is called optical activity. Optical activity in a compound is detected and measured by means of a Polarimeter. When a solution of a known concentration of an optically active material is placed in the polarimeter, the beam of polarised light is rotated through a certain number of degrees, either to the right (clockwise) or to the left (anticlockwise).

Dextrorotatory (d) or (+) form : complexes that rotates the plane of polarized light towards right are said to be Dextrorotatory or 'd' form.

Laevorotatory (l) or (-) form : while the complexes rotates towards left are called Laevorotatory (or) 'l' form

The 'd' and 'l' forms are mirror images and cannot be superimposed on each other. Such molecules or ions that cannot be superimposed are called chiral. Since these forms are related to each other as mirror images these are commonly called Enantiomers

Chiral and Achiral - Superimposable & non-superimposable ⑤

- Although everything has a mirror image, mirror images may or may not be superimposable.
- Some molecules are like hands. Left and right hands are mirror images, but they are not identical, or non-superimposable.
- A molecule (or object) that is not superimposable on its mirror image is said to be chiral.
- Other molecules are like socks. Two socks from a pair are mirror images that are superimposable. A socks and its mirror image are identical.
- A molecule or object that is superimposable on its mirror image is said to be "achiral"

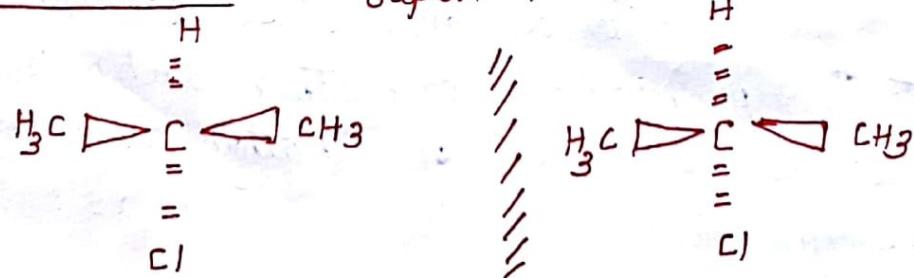


These molecules
are chiral and
exists as enantiomers

Chlorocodomethanesulphonic acid

Not superimposable : Enantiomers

If the four groups attached to a central carbon atom of a molecule are different, then the molecule is not superimposable on its mirror image. Such a carbon is called achiral carbon or asymmetric carbon. superimposable : no enantiomers.



But in the case of isopropyl chloride the molecules are chiral and cannot exist as enantiomers.

Stereoisomers

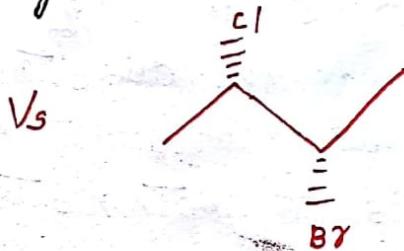
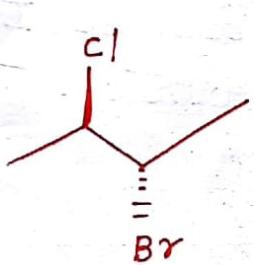
→ compounds with the same connectivity, different arrangement in space.

Enantiomers

→ stereoisomers that are non-superimposable mirror images; only properties that differ are direction (+ or -) of optical rotation.

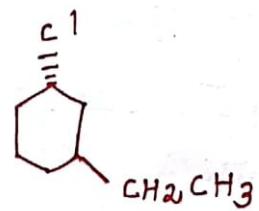
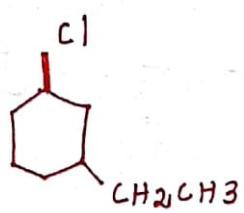
Diastereomers

→ stereoisomers that are not mirror images; different compounds with different physical properties.



These compounds are diastereomers of one another

A compound contained both a chlorine and a bromine atom but they differed in the way they occupied three-dimensional space. Notice that in one of the compounds the chlorine is going away from us into the page (it has a dashed bond) and the bromine is also going into the page. On the other compound, the bromine is the same as the first in that it's going into the page but notice how the chlorine now is a solid wedged bond coming out at us. Since the compounds are different in the configurations of the chlorine atoms but ^{the} same with the bromine atoms, they are diastereomers. Notice also how they are not mirror images of one another.



These two six-membered ring compounds represent diastereomers

Sometimes diastereomers can include compounds that are ring structures. For example consider two compounds with a six-membered ring that have two substituents each, a chlorine atom and an ethyl group. Note that the ethyl groups have the same configuration in both compounds, but the chlorine atoms labeled C^1 have opposite configurations. These compounds are diastereomers because they have same bond configuration at one stereocenter but different configurations at another stereocenter.

Enantiomers

1) Enantiomers are stereoisomers that are mirror images of each other.

2) Have identical physical properties except for the ability to rotate Plane-Polarised light.

3) Present in Pairs

4) Similar molecular shape

Diastereomers

Diastereomers are stereoisomers that aren't a mirror image of each other.

Distinct Physical Properties.

There can be several molecules

Different molecular shape.

Applications of electrochemical series (or) Nernst equations.

Definition

→ When various electrodes (metals) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electrochemical series.

i calculation of standard emf of the cell

The standard emf of a cell (E°) can be calculated if the standard electrode potential values are known using the following relation:

$$E_{\text{cell}}^\circ = E_{\text{R.H.E}}^\circ - E_{\text{L.H.E}}^\circ$$

ii relative ease of oxidation (or) reduction

Higher the value of standard reduction potential (+ve value) greater is the tendency to get reduced. (i.e. metals on the top (-ve value) are more easily oxidised).

- a) The fluorine has higher positive value of standard reduction potential (+2.87 V), and shows higher tendency towards reduction. ~~to gain electron~~
- b) The lithium has highest negative value (-3.01 V) and shows higher tendency towards oxidation.

iii Displacement of one element by the other

Metals which lie higher in the emf series can displace those elements which lie below them in the series.



For example, we may know whether Cu^{2+} will displace Zn^{2+} from the solution or vice-versa. We know that standard reduction potential of Cu and Zn^{2+} .

$$\text{i.e., } E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V and } E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V.}$$

So, Cu^{2+} has a great tendency to acquire Cu form, than Zn^{2+} has for acquiring Zn form.

iv determination of standard free energy change (ΔG°) and equilibrium constant for the reaction.

Standard electrode potential can also be used to determine the standard free energy change (ΔG°) and equilibrium constant (K) for the reaction. We know that:

$$\Delta G^\circ = RT \ln K = 2.303RT \log K.$$

$$\log K = \frac{\Delta G^\circ}{2.303RT} \quad (\text{also } \Delta G^\circ = hFE^\circ)$$

$$= \frac{hFE^\circ}{2.303RT}.$$

v. Hydrogen displacement behaviour

metals with negative reduction potential.

(i.e. the metals placed above H_2 in the emf series) will displace the hydrogen from an acid solution.

Example:

Zn reacts with dil H_2SO_4 to give H_2 but Ag does not, why?



$$E^\circ_{\text{Zn}} = -0.76 \text{ volt.}$$

The metal with positive reduction potential i.e., the metals placed below H₂ in the emf series) will not displace the hydrogen from an acid solution.



$$E^\circ_{Ag} = +0.80 \text{ volt}$$

iii predicting spontaneity (or) feasibility of redox reactions

Spontaneity of 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, the reaction is spontaneous (or) feasible ($\Delta G = -ve$).

ii) If E° of the cell is negative, the reaction is not spontaneous (or) not feasible ($\Delta G = +ve$).

With examples with good diagrams

Diagram showing standard reduction potentials for various elements.