Unit-III: Equilibrium Thermodynamics and Water Chemistry

Preamble

- Thermodynamics is a branch of science which deals quantitatively with heat-related energy.
- Thermodynamics can be defined as the study of energy, energy transformations and its relation to matter.
- The analysis of thermal systems is accomplished through the application of the governing thermal equilibrium among systems in physical contact (Zeroth law), conservation equations, namely *Conservation of Mass*, *Conservation of Energy* (1st law of thermodynamics), the 2nd law of thermodynamics and the property relations and also determinations of entropy (3rd law of thermodynamics).
- Energy can be viewed as the ability to cause changes.
- Whenever there is an interaction between energy and matter, thermodynamics is involved. Some examples include heating and air-conditioning systems, refrigerators, water heaters, etc.

Limitations of Thermodynamics

- It applies only to matter in bulk and not to individual atoms or molecules.
- It concerns only with the initial and final states of the system.
- It does not tell whether the reaction will be fast or slow.

Basic concepts of thermodynamics

System

A system is defined as a quantity of matter or a region in space chosen for study.

Surroundings

The mass or region outside the system is called the surroundings.

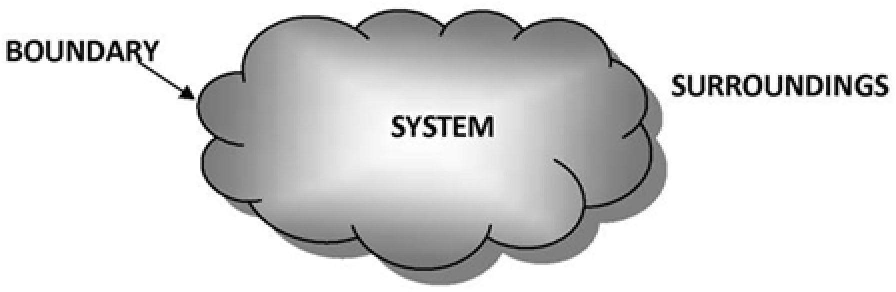


Fig. 1: System, surroundings, and boundary

Boundary: the real or imaginary surface that separates the system from its surroundings. The boundaries of a system can be fixed or movable. Mathematically, the boundary has zero thickness, no mass, and no volume.

Types of systems

Closed system or control mass: consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.

Examples: A gas kept in a cylinder fitted with movable piston. When the piston is raised, the gas expands and transfers energy (heat) in the form of work to the surroundings. Since the total amount of gas remains constant, there is no exchange of matter with the surroundings.

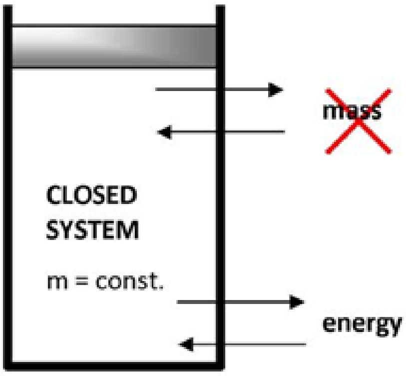


Fig. 2: Closed system, mass cannot cross the boundaries, but energy can.

Open system or control volume: is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.

Examples: A beaker containing hot water placed on a table. The water vapour (matter) and heat (energy) are transferred to the surroundings through the imaginary boundary.

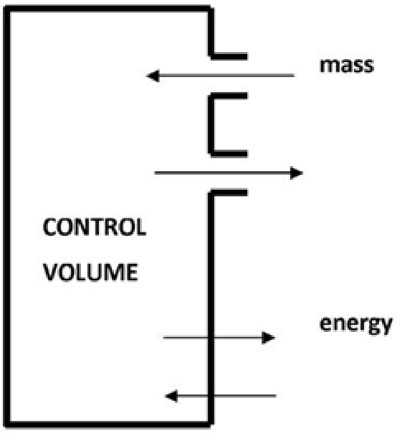


Fig. 3: Control volume, both mass and energy can cross the boundaries.

Isolated system: A closed system that does not communicate with the surroundings by any means.

Examples: Hot water in a thermo flask. Due to insulation, neither water (matter) nor heat (energy) can be exchanged with its surrounding.

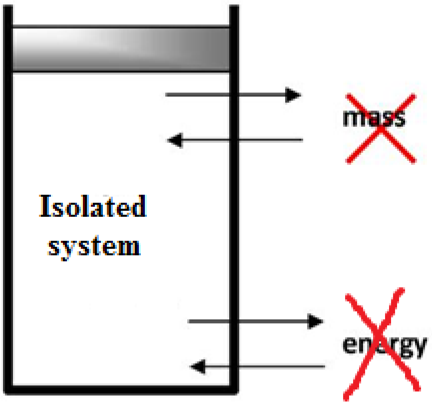


Fig.4 neither matter nor energy can be exchanged with its surrounding

Rigid system: A closed system that communicates with the surroundings by heat only.

Properties of a System

Any characteristic of a system is called a property.

Macroscopic system: A macroscopic system is one which consists of a large number of atoms, molecules or ions.

Macroscopic properties: The property associated with a large number of particles (a macroscopic system) is called as macroscopic properties.

Intensive properties: are those that are independent of the size (mass) of a system, such as temperature, pressure, and density. They are not additive.

Extensive properties: values that are dependent on size of the system such as mass, volume, and total energy U. They are additive.

- Generally, uppercase letters are used to denote extensive properties (except mass m), and lower case letters are used for intensive properties (except pressure P, temperature T).
- Extensive properties per unit mass are called specific properties, e.g. specific volume ($v=V/m$).

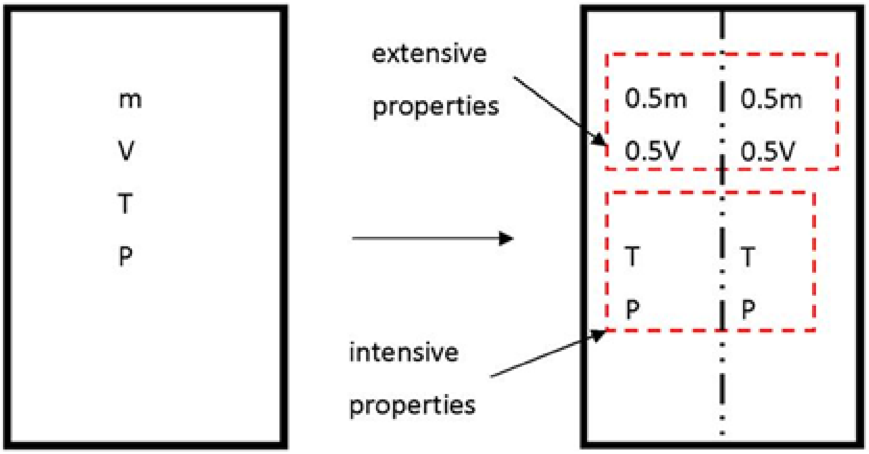


Fig.5. Intensive and extensive properties of a system.

Processes and Cycles

Any change a system undergoes from one equilibrium state to another is called a process, and the series of states through which a system passes during a process is called a path.

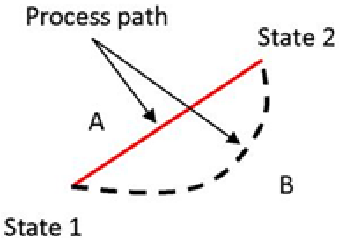


Fig. 6: To specify a process, initial and final states and path must be specified.

Isothermal: is a process during which the temperature ($dT = 0$) remains constant.

Adiabatic process: If no heat enters or leaves the system during any step of the process, the process is said to be adiabatic. This is achieved by carrying the process in an insulated container i.e. $dq = 0$.

Isobaric process: is a process during which the pressure remains constant.

Isometric or isochoric process: is process during which the specific volume remains constant.

Cyclic Process: A system is said to have undergone a *cycle* if it returns to its initial state at the end of the process. i.e. $dE = 0$, $dH = 0$.

Reversible process: It is a process in which the energy change in each step of the process can be reversed in direction by making a small change in any property of the system, such as temperature, pressure, etc. Two important criteria for a process to be reversible are

- The change must be performed at an infinitesimal slow rate.
- There must be no loss of energy due to friction and no finite temperature differences.

Irreversible process: It is a process in which the system or surroundings are not restored to their initial state at the end of the process.

All processes occurring spontaneously in nature are irreversible. They always tend to proceed in a definite direction and do not proceed in the opposite direction without the action of an external force. Irreversible processes take place spontaneously and not in infinitesimal slow steps that can be reversed.

Examples: Expansion and diffusion of gases flow of heat from a hotter body to a colder body, etc.

Difference between reversible and irreversible process

S.No	Reversible process	Irreversible process
1.	Driving force and opposing force differ by an infinitesimally small amount.	Driving force and opposing differ by a large amount.
2.	The work obtained is maximum.	The work obtained is not maximum.
3.	Reversible process takes place by infinitesimally small steps; the process would take infinite time for completion.	It requires only finite time for completion.
4.	It is unreal as it assumes the presence of a frictionless and weightless piston.	It is real and can be performed actually.

Endothermic Process: If heat is absorbed from its surroundings to carry out the reaction, then it is known as endothermic process.

Exothermic Process: If heat is liberated to its surroundings from the system to carry out the reaction, then it is known as exothermic process.

State and Equilibrium

At a given *state*, all the properties of a system have fixed values. Thus, if the value of even one property changes, the state will change to different one.

In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system. A system in equilibrium experiences no changes when it is isolated from its surroundings.

- **Thermal equilibrium**: when the temperature is the same throughout the entire system.
- **Mechanical equilibrium**: when there is no change in pressure at any point of the system. However, the pressure may vary within the system due to gravitational effects.
- **Phase equilibrium**: in a two phase system, when the mass of each phase reaches an equilibrium level.
- **Chemical equilibrium**: when the chemical composition of a system does not change with time, i.e., no chemical reactions occur.

State of a system and thermodynamic variables:

State of a system: A set of macroscopic properties such as pressure, volume, temperature etc., which describe the system is known as the “State of a system”. Whenever there is a change in any one of the macroscopic properties, the system is said to have undergone a change of state.

State Functions or state variable: State function or state variable is a thermodynamic property which depends only on the state of the system and independent of the path followed to bring about the change.

Examples: Temperature, volume, pressure and thermodynamic variables such as internal energy (E), enthalpy (H), entropy (S) etc.

Path functions or Path variables: Properties which depend on the followed to bring about the change are called as path functions (or) path variables.

Examples: Heat (q), work (W) etc.

Energy of the Thermodynamic system

Internal Energy [E] (or) [U]:

It is defined as “the heat change at constant volume”. The total energy content of the system is also known as internal energy.

It depends on its chemical nature, temperature, pressure and volume. The exact magnitude of this energy is not known. It is the sum of transitional, electronic, vibrational, rotational and nuclear energies.

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

It is not possible to calculate the absolute value of the internal energy of a system. But, change in enthalpy (ΔE) can be found out from the difference of energy of the initial state [E_{ini}] and the final state [E_{fin}].

$$\Delta E = E_{final} - E_{inital}$$

Δ_E = +ve, if E_{final} is greater than $E_{initial}$ and

Δ_E = -ve, if E_{final} is less than $E_{initial}$.

The change in internal energy accompanying a chemical (or) physical process is accurately measurable.

Enthalpy (or) Heat content (H)

It is defined as “the heat change at constant pressure”. When a quantity of heat Q is supplied to a system, let the internal change from E_A to E_B and the work done by the system be W.

$$Q = \Delta E + W$$

If the work done is due to expansion at constant pressure then,

$Q = \Delta E + P\Delta V$ (ΔV is the increase in volume)

$$Q = E_B - E_A + P(V_B - V_A) .$$

$$= E_B + PV_B - [E_A + PV_A]$$

$$= H_B - H_A .$$

‘H’ stands for E + PV . This quantity is called heat content (or) enthalpy of a system.

$$\Delta H = E_B - E_A + P(V_B - V_A)$$

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

Enthalpy is also state function.

The following conclusions are made from this equation.

Then (i) at constant pressure, $\Delta H > \Delta E$

(ii) If Volume is constant, (ie) $\Delta V = 0,$ then: $\Delta H = \Delta E$

Thus, at the constant volume, enthalpy change (or) heat absorbed (ΔH) is equal in internal energy (ΔE) at constant volume.

First law of thermodynamics

First law of thermodynamics states that, "energy can neither be created nor be destroyed, but it can be transferred from one form to another". This is also known as "Law of conservation of energy"

ΔE = q-W (or) (1)

q= ΔE +W or

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

For an infinitesimally small change, equation (1) may be written as

dE=dq-dw (2)

Where dE is the increase in energy, dq and dw represent small quantities of heat absorbed and external work done by the system respectively.

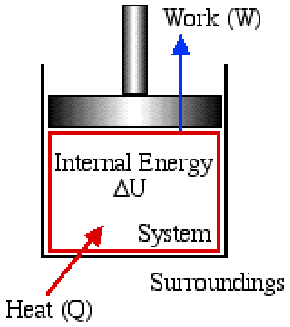
Equation(1) and (2) are the mathematical forms of the first law.

It is explained by the following derivation

Consider a cylinder having freely movable piston. Let the initial volume and the initial internal energy of the gas inside the cylinder be " V_1 " and " E_1 " respectively.

Let the pressure given by the piston be "P". Now small amount of heat (q) is given. So the gas inside the cylinder absorbs heat and expands. During the expansion, it pulls the piston upwards. So the given heat is converted into work.

Let the final volume and the final internal energy of the gas inside the cylinder be " V_2 " and " E_2 " respectively. [Fig]



Work done W = Pressure applied X displacement

$= P\ (V_2 - V_1)$

$W = P\Delta V$

Let the initial internal energy be E_1, the final internal energy be E_2, heat be q.

q= $E_1 + q = E_2 + W$

q= $[E_2 - E_1]$ +W

q= ΔE +W

q-W= ΔE (1)

For an infinitesimally small change, equation 1 may be

$dE = dq - dw$

Statement of first law of thermodynamics

It can be stated in different ways as follows.

1. Energy can neither be created nor destroyed, but it can be converted from one form to another form.
2. It is impossible for a machine to produce work continuously without consuming energy
3. The total energy of the universe is constant
4. Whenever one form of energy disappears, an equivalent amount of another form of energy appears.

In a cyclic process [i.e., in which the system is subjected to a series of operation such that it ultimately comes back to its initial state, so that initial and final states becomes identical].

$E_1 = E_2$, (or) $\Delta E = 0$

ΔE = q-w

0= q-w

q=w

(ie) the work done is equal to the heat absorbed in a cyclic process.

Case 1: In isothermal process, ΔE =0 then q=w

Case 2: In isochoric process, ΔV =0 then q= ΔE

Case 3: In isobaric process ΔP =0, then q= $\Delta E + P\Delta V$

Case 4: In adiabatic process q=0, $\Delta E = -w$

Limitations of First law of thermodynamics

The first law of thermodynamics does not provide answers for the following

1. The first law establishes a definite relationship between the heat absorbed and the work performed by a system in a process. But is puts no restriction on the direction of flow of heat.
2. According to first law, the energy of an isolated system remains constant during a specified change of heat. But it does not tell whether the reaction is feasible.
3. The first law states that energy of one form can be converted into another form. But it does not tell that heat energy cannot be completely converted in to an equivalent amount of work.

Application of first law of thermodynamics:

Heat Capacity:

It is defined as the amount of heat necessary to increase the temperature of the substance through 1°C.

Molar Heat Capacity: It is defined as the amount of heat absorbed by one mole of the substances to raise its temp by 1°C.

Heat Capacity is the rate of change of heat with temperature

$$C = \frac{dq}{dT} \quad \text{for one mole of substances}$$

First law of thermodynamics: dq = dE + Pdv

$$\therefore\ C = \frac{dE + Pdv}{dT} \qquad (1)$$

Molar heat capacity at constant volume (C_v)

At constant volume dv=0

$$\therefore\ C_v = \frac{dE}{dt} \qquad (2)$$

In terms of partial differentials:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V \qquad (3)$$

Increase in internal energy of the system per degree rise if temperature

Molar Heat Capacity at Constant Pressure (C_p)

At constant pressure, the equation 1 written as

$$C_P = \frac{dE}{dT} + P\left(\frac{dV}{dT}\right)$$

Upon partial differentiation,

$$C_p = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad (4)$$

W.K.T H = E + PV (5)

Differentiating equation with respect to T at constant P

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad (6)$$

Equation 4 and Equation 6 $\Rightarrow C_p = \left(\frac{\partial H}{\partial T}\right)_P$ (7)

C_p is defined as the increase in enthalpy of the system per degree rise of temperature.

Relation between C_v and C_p

By definition $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ (1)

But H = E + PV

$$\therefore C_p = \left[\frac{\partial(E+PV)}{\partial T}\right]_P$$

$$C_p = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad (2)$$

We know that E is a state function and regarded as a function of any of two variables P, V, and T. If we write E as function of V and T, then

E= f (T, V)

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

Dividing this equation by dT, keeping pressure constant,

We get,

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_v + \left(\frac{\partial E}{\partial V}\right)_T . \left(\frac{\partial V}{\partial T}\right)_P$$

(3)

Substituting the value $\left(\frac{\partial E}{\partial T}\right)_P$ in equation (2)

$$C_p = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T . \left(\frac{\partial V}{\partial T}\right)_P + \mathrm{P}\left(\frac{\partial V}{\partial T}\right)_P \quad (4)$$

By definition: $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

Equation (4) becomes

$$C_p = C_V + \left(\frac{\partial E}{\partial V}\right)_T . \left(\frac{\partial V}{\partial T}\right)_P + \mathrm{P}\left(\frac{\partial V}{\partial T}\right)_P \quad (5)$$

$$C_P - C_V = \left(\frac{\partial E}{\partial V}\right)_T . \left(\frac{\partial V}{\partial T}\right)_P + \mathrm{P}\left(\frac{\partial V}{\partial T}\right)_P \quad (6)$$

For an ideal gas E is independent of volume

i.e $\left(\frac{\partial E}{\partial V}\right)_T = 0$

$$\therefore \left(\frac{\partial E}{\partial V}\right)_T . \left(\frac{\partial V}{\partial T}\right)_P = 0$$

The equation (6) becomes

$$C_P - C_V = \mathrm{P}\left(\frac{\partial V}{\partial T}\right)_P \quad (7)$$

For one mole of an ideal gas PV=RT

Differentiating with respect to temperature at constant P

$$\mathrm{P}.\left(\frac{\partial V}{\partial T}\right)_P = \mathrm{R} \quad (8)$$

Comparing the equation (7) and (8)

$$C_P - C_V = \mathrm{R}$$

Limitations of the first law of thermodynamics/ Need for the 2nd law of thermodynamics

First law: does not provide the answers to the following

a. Whether the particular process / reaction is feasible
b. If so, to what extent do the process / reaction proceed?
c. Is it possible to convert completely internal energy into work?

So 2nd law of thermodynamics has been developed by Clausius and Kelvin to answer the above questions

Second law of thermodynamics

Only a fraction of heat can be converted in to work and the rest remains unavailable and unconverted i.e. 100% energy transformation is impossible.

The second law is based on the observations and experience. It is applicable only to cyclic process.

1. **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 on the machine.

2. **Kelvin Statement**

   It is impossible to take heat from hot body and convert it completely in to work by cyclic process without transferring a par to heat to a cold body.

In order to explain the spontaneity (feasibility) of physical and chemical process, the 2nd law of thermodynamics introduces two new thermodynamics functions, entropy and free energy.

ENTROPY

Entropy is measure of degree of disorder or randomness in the systems. It is also consider as a measure of unavailable form of energy.

Thus, when a system goes from a more orderly to less orderly state, randomness increases, and hence entropy the system increases.

Examples

- Solid changes to liquid, there is an increase in entropy
- Solidification occurs, entropy decreases
- Ice melted, entropy increases
- Flow of H_2O from hills. Decrease in order & increase in disorder

  $\therefore\ \Delta S \Rightarrow$ Increases
- Falling of an apple from tree

Mathematical Expression for Entropy

The change in entropy (ΔS) of a system is equal to the ratio of the heat exchange (q) to the temperature (T) of the reversible cyclic process.

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

Where q is the heat absorbed or evolved in calories

T is the temperature in degrees

Units of entropy:

Cal/deg (or) JK^{-1}

Significance of entropy

- Entropy & Disorder(randomness)

  Increase in entropy means change from an ordered to less ordered or disordered state.

  E.g.: All the natural process.

- Entropy and Unavailable energy

  Unavailable energy

  Entropy = $\frac{Unavailable\ \ energy}{Temperature}$

Entropy change in a Reversible process (Non – Spontaneous)

Consider an isothermal & reversible expansion of an ideal gas. If the system absorbs q amount of heat from the surroundings at temperature T, the increase in entropy of the system is given by

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

At the same time, surroundings lose the same amount of heat q at the same temperature T. This results in decrease of surroundings entropy

i.e. $\Delta S_{surroundings} = -\frac{q}{T}$

Hence, the total change in entropy of the process is given by

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$$

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

$$\Delta S_{Total} = 0$$

Entropy change in an Isothermal Process

According to I^{st} law of thermodynamics

$$q = \Delta E + W \qquad (1)$$

In a reversible isothermal expansion, there is no change of internal energy (dE=0)

So equation (1) becomes $q_{rev} = W$

The work done in the expansion of a n moles of a gas from a volume V_1 to V_2 at constant temperature T is given by

$$W = nRT \, l_n \frac{V_2}{V_1} \qquad (2)$$

Equation (2) is introduced in equation (1), we get

$$q_{rev} = nRT \, l_n \frac{V_2}{V_1}$$

$$T \, \Delta S = nRT \, l_n \frac{V_2}{V_1} \qquad \left(\because \ \Delta S = \frac{q}{T} \right)$$

$$\Delta S = \frac{1}{T} \, nRT \, l_n \frac{V_2}{V_1}$$

$$\Delta S = nR \, l_n \frac{V_2}{V_1}$$

$$\Delta S = 2.303 \ nR \log \frac{V_2}{V_1} \qquad (3)$$

Substitute V_1 and V_2 in equation (3), we get

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

<u>Entropy change in Physical Transformations</u>

Entropy change takes place even when the system undergoes physical transformations such as fusion, vaporization or transition from one crystalline form to another.

Let ΔH be the quality of heat absorbed in calories at constant T & P during the reversible physical transformation. Then the entropy change is given by

$$\Delta S = \frac{\Delta H}{T}$$

Example:

Latent heat of vaporization of H_2O = 540 cal. /g (at $100^\circ C$)

Latent heat of fusion of ice = 80 cal./g (at $0^\circ C$)

But the entropy change, ΔH = L X M

$$\therefore \ \Delta S = \frac{L.M}{M}$$

Where, L = Latent heat in calories

M = M.W.in g

T = Temp in Kelvin

Free Energy or Gibbs functions (G):

Gibbs free energy (G) and Helmholtz work function (A) are the thermodynamics function which helps in the development of criterion of spontaneity or feasibility of a process.

Gibbs free energy (G): Refers to "the capacity to do useful work"

W.K.T a part of the total energy of a system is converted into work and the rest is unavailable. The part of the energy which is converted into useful work is called available energy. "The isothermally available energy present in a system is called free energy (G).

It is mathematically defined as

$$G = H - TS$$

Where,

H is enthalpy of the system

S is the entropy of system

T is Temperature

Physical significance of the free energy

Free energy may be written as.

$$G = H - TS$$

At constant temperature, when a system changes its state, let G_1 changes to G_2, H_1 to H_2 and S_1 to S_2 then

$$G_1 = H_1 - T S_1 \qquad (1)$$

$$G_2 = H_2 - T S_2 \qquad (2)$$

The change in Gibbs functions, ΔG can be obtained by subtracting equation 1 from equation 2

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

It is already known that at constant pressure

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

Substituting this value of ΔH in equation 3, we get

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

But we know that

$$\Delta A = \Delta E - T\Delta S \qquad (5)$$

Comparing equations 4 and equation 5

$$\Delta G = \Delta A + P\Delta V \qquad (6)$$

But $\Delta A = -W_{rev}$

Substituting this value of $T\Delta S$ in equation 7

$$\Delta A = \Delta E - q \qquad (8)$$

According to the first law of thermodynamics

$$q = \Delta E + W$$

$$q - W = \Delta E$$

$$-W = \Delta E - q \qquad (9)$$

Comparing equation 8 and equation 9, we get

$$\Delta A = -W \qquad (10)$$

(or) $-\Delta A = W$

Since W is the maximum work obtainable, (i.e.), by reversible process, it is evident that decrease in the function A [i.e. $-\Delta A$] give the maximum work obtainable from the system during the given change.

<u>Work function (or) Helmholtz work Function (A)</u>

We also know that a part of internal energy of a system can be used at constant temperature to do useful work. “The part of the internal energy which is isothermally available to do useful work is called work function (A) of the system. It is mathematically defined as:

$$A = E - TS$$

Condition for spontaneity of a reaction or Condition for negative value of ΔG

W.K.T $\quad G = H - TS$

If the process is carried out at constant P & T,

Then $\quad (\Delta G)_{T,P} = \Delta H - T\Delta S$

For the process to be spontaneous ΔG_{sys} should be negative.

$$(\Delta G)_{T,P} = \Delta H - T\Delta S \qquad (1)$$

i) If ΔH = -Ve & ΔS = +Ve then ΔG = -Ve(spontaneous)

ii) If ΔH = -Ve & $\Delta S = 0$ then ΔG = -Ve(spontaneous)

iii) If $\Delta H = 0$ & $\Delta S = +\text{Ve}$ then $\Delta G = \text{-Ve}$(spontaneous)

iv) If $\Delta H = +\text{Ve}$ & $\Delta S = +\text{Ve}$ further $\Delta H < T\Delta S$ then $\Delta G = \text{-Ve}$(spontaneous)

v) If $\Delta H = \text{-Ve}$ & $\Delta S = \text{-Ve}$ further $\Delta H > T\Delta S$ then $\Delta G = \text{-Ve}$(spontaneous)

Equation (1) is the commonly used criterion of the feasibility of a process.

No Process is possible which results in an increase in the Gibbs free energy of the system, because according to equation (1) the Gibbs free energy always decreases in a spontaneous process.

Hence, for an irreversible or spontaneous process at constant T & P, $\Delta G < 0$.

Physical significance of the work function (A)

The part of the internal energy which is isothermally available to do useful work is known as work function of the system.

$$A = E - TS \tag{1}$$

At constant temperature, when a system changes its state, let A_1 changes to A_2, E_1 to E_2 and S_1 to S_2, then

$$A_1 = E_1 - TS_1 \tag{2}$$

$$A_2 = E_2 - TS_2 \tag{3}$$

The change in work function, ΔA can be obtained by subtracting equation 2 from equation 3

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \tag{4}$$

If the above change is brought out reversibly at temperature T and heat absorbed is equal to q_{rev}, then

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

Substituting this for ΔS in equation 4

$$\Delta A = \Delta E - q_{rev} \tag{5}$$

According to the first law of Thermodynamics

$$\Delta E = q - w \tag{6}$$

For a reversible process where work is done by the system [W is negative and it is maximum] equation 6 can be rewritten as

$$\Delta E = q_{rev} - W_{\max}$$

$$\Delta E - q_{rev} = - W_{\max} \qquad (7)$$

Comparing equations 5 and 7

$$- \Delta A = W_{\max} \qquad (8)$$

The decrease in the functions A gives the maximum work done by the system. So A is called work function. It is also called Helmholtz free energy

Gibb's – Helmholtz Equation

In terms of enthalpy and free energy (Relationship between G&H)

W.K.T $G = H - TS$

$H = E + PV$

$\therefore\ G = E + PV - TS$

By differentiation,

$$dG = dE + PdV + VdP - TdS - SdT \qquad (1)$$

Substituting dE value in equation (1), we get,

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

$$\therefore\ dG = VdP - SdT \qquad (2)$$

At constant P, dP = 0

$$\therefore\ dG = - SdT$$

(3)

For any two states of the system,

$$dG_1 = - S_1\, dT$$

$$dG_2 = - S_2\, dT$$

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

$$d\Delta G = - S_2\, dT + - S_1\, dT$$

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

$$= - \Delta S dT$$

$$\frac{d\Delta G}{dT} = \Delta S \qquad (4)$$

According to the defintion of free energy

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

$\frac{\Delta G - \Delta H}{T}$ = - ΔS substituting in equation (4)

We get,

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

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

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

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

This must useful equation of thermodynamics, as it represents the essential aspects of both 1st & 2nd laws.

Applications of Gibb's - Helmholtz equation

Calculation of enthalpy change of reaction (heat if reaction) occurring in galvanic cells.

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

$$-\Delta G = nF\,E^{\circ} \qquad (1)$$

Hence Gibb's - Helmholtz equation is written as

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

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

$$\Delta H = -nFE^{\circ} + nFT\left[\frac{\partial E^{\circ}}{\partial T}\right]_P$$

$$\Delta H = -nF\left[E^{\circ} - T\left(\frac{\partial E^{\circ}}{\partial T}\right)_P\right] \qquad (2)$$

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

(i) Calculation of energy entropy change

ΔH and ΔS are related by the equation

$$\Delta G = \Delta H - T\,\Delta S \qquad (3)$$

W.K.T $\Delta G = -nFE^{\circ}$ and ΔH can be calculated by the above equation (2)

Hence, ΔS can be calculated from the above equation.

Vant Hoff Isotherm (Expression for equilibrium constant)

W.K.T dG = VdP – SdT

At constant temperature, dT = 0

$$\therefore \left(dG\right)_T = VdP \qquad (1)$$

For 1 mole of an ideal gas PV = RT

$$V = \frac{RT}{P} \qquad (2)$$

Substituting (2) in (1), we get

$$\left(dG\right)_T = RT.\frac{dP}{P}$$

On integration,

$$\int \left(dG\right)_T = RT\int \frac{dP}{P}$$

$$G = RT\ln P + G^{\circ} \qquad (3)$$

Where G° is integration constant and referred to as standard free energy.

Consider a general gaseous reaction

$$aA + bB \rightarrow cC + dD$$

Free energy change, ΔG for the above reaction is given by

$$\Delta G = \Delta G_{\text{Products}} - \Delta G_{reac\,\text{tants}}$$

or

$$\Delta G = \left[cG_c + dG_d\right] - \left[aG_A + bG_b\right] \qquad (4)$$

Let the partial pressure of A, B, C and D are P_A, P_B, P_C and P_D respectively. Now the free energy of each substances (A, B, C, D) at a Temp T using equation(3) are given by

$$aG_A = aG^{\circ}A + a\,RT\ln P_A$$

$$bG_b = bG^\circ B + \text{bRTln}\, P_B$$

$$cG_C = cG^\circ{}_C + \text{cRTln}\, P_C$$

$$dG_D = dD^\circ{}_D + \text{dRTln}\, P_D$$

Substituting the value in Equation (4), we get

$$\Delta G = \left[cG^\circ{}_C + cRT\ln P_C + dD^\circ{}_D + dRT\ln P_D\right] - \left[aG^\circ A + aRT\ln P_A + bG^\circ B + bRT\ln P_B\right]$$

$$\Delta G = cG^\circ{}_C + cRT\ln P_C + dD^\circ{}_D + \text{dRTln}\, P_D - aG^\circ A - \text{aRTln}\, P_A - bG^\circ B - bRT\ln P_B$$

$$\Delta G = \left[cG^\circ{}_C + dD^\circ{}_D - aG^\circ A - bG^\circ B\right] + RT\left\{\ln[P_C]^c + \ln[P_D]^d - \ln[P_A]^a - \ln[P_B]^b\right\}$$

$$RT\ln\frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b}$$

$$\Delta G = \Delta G^\circ +$$

$$\Delta G_{\text{Products}} - \Delta G_{reac\,\text{tants}}$$

$$\therefore \quad \Delta G^\circ = \qquad (5)$$

Where ΔG° represents the standard free energy change for the given reaction.

W.K.T when the reaction is at equilibrium, $\Delta G = 0$

$\therefore$ equation (5) becomes

$$\Delta G^\circ = -RT\ln\left[\frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b}\right]_{eq}$$

$$\Delta G^\circ = -RT\ln K_{eq}$$

Where $K_{eq} = \dfrac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b}$

Substituting ΔG° in equation(5), we get

$$\Delta G = -RT\ln K_{eq} + RT\ln\frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} \qquad (6)$$

This equation is calledVant Hoff Isotherm and gives a quantitative relationship between free energy and equilibrium constant.

Difference between isothermal and adiabatic process:

Isothermal Process	Adiabatic Process

(i) Exchange of heat takes place between the system and its surroundings (ii) It Involves a change in heat ($dq \neq 0$)	No Exchange of heat takes place between the system and its surroundings It involves no change in heat ($dq=0$)

Difference between reversible and irreversible process:

Reversible Process	Irreversible Process
(i) It is a slow process and takes infinite time to complete	It Process fast and complete soon
(ii) In equilibrium state at all the stages of the operation	It is in equilibrium only at the initial and final stage of operation
(iii) Can be reversed by any of the thermodynamics variables	It cannot be reversed
(iv) Unreal process	Real process and performed actually

<u>Problems</u>:

1. Calculate the entropy change in the thermodynamics expansion of 2 moles of an ideal gas from a volume of 5 litres to a volume of 50 litres.

Solution

$$\Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

n= 2 moles

R= 1.987 Cals. $K^{-1} mol^{-1}$

V_2 = 50 litres

V_1 = 5 litres

$$\therefore \ \Delta S = 2.303 \text{ x } 2 \text{ x } 1.987 \text{ x } \log \frac{50}{5}$$

$$= 2.303 \text{ x } 2 \text{ x } 1.987 \text{ x } 1$$

= 9.152 e.u

2. One mole of an ideal gas expands isothermally to twice its original volume at $27^{\circ}C$. Calculate the entropy change during the process.

   Solution

$$\Delta S = 2.303 \text{ nRlog } \frac{V_2}{V_1}$$

$$= 2.303 \text{ x } 1 \text{ x}1.987 \text{ x } \log \frac{2}{1}$$

$$= 2.303 \text{ x } 1.987 \text{ x } 0.3010$$

$$= 1.3773 \text{ e.u}$$

3. One mole of an ideal gas at 300K expands reversibly and isothermally from $2x10^{-2} m^3$ to $4x10^{-2} m^3$. Calculate the entropy change for the gas.

Solution

$$\Delta S = 2.303 \text{ x } 1 \text{ x } 1.987 \text{ x } \log \frac{4x10^{-2}}{2x10^{-2}}$$

$$= 1.3773 \text{ e.u}$$

4. Calculate the change in energy accompanying the isothermal expansion of 5 moles of an ideal gas at 300K until its volume has increased six times

Solution

$$\Delta S = 2.303 \text{ x } 5 \text{ x } 1.987 \text{ x } \log \frac{6}{1}$$

$$= 2.303 \text{ x } 5 \text{ x } 1.987 \text{ x } 0.778$$

$$= 17.8 \text{ Cals /K}$$

5. Calculate the entropy change involved when one mole of liquid oxygen is converted in to gaseous oxygen at its boiling point of $-183^{\circ}C$. Enthalpy of vaporization of liquid oxygen is 6.820 J.

Solution

ΔS for vaporization $\Delta S_v = \dfrac{\Delta H_v}{T_b}$

ΔH_v = Molar latent heat of vaporization

T_b = boiling point $-183^{\circ}C + 273 = 90K$

$$\Delta S = \frac{6.82}{90} = 0.0757\text{eu}$$

6. Calculate the change in entropy when one gram mole of water is converted to vapour at its boiling point. Latent heat of vaporizations 540 Cal. /g.

Solution

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

ΔH_v = Latent heat of vaporization x moles of H_2O (M)

= 540 x 18

= 9720 Cal.

Latent heat of fusion of ice at 0 $^{\circ}C$ = 80 Cal/g

Latent heat of Vaporization of H_2O = 540 Cals /gm

$$\Delta S_v = \frac{9720}{373}$$

$$\Delta S_v = 26.06 \text{ e.u}$$

Latent heat of Vaporization of H_2o = 540 Cals /gm

Problems based on Gibbs free energy

1. ΔH and ΔS for a reaction at 27 $^{\circ}C$ are -10 K cals and 20 Cals K^{-1} respectively. What is ΔG for the reaction? Predict whether the reaction will be feasible or not?

Solution:

Free energy is expressed as

ΔG = ΔH - T ΔS

Given:

ΔH = -10K Cals or -10000 Cals

ΔS = 20 Cals K^{-1}

T = 27 x 273 = $300^{\circ}K$

$\therefore$ ΔG = -10000 – 300(20)

= -16,000 Cals or -16KCals

As ΔG is –ve, the reaction is feasible

2. ΔG for a reaction at $300^{\circ}K$ is -16KCals. ΔH for the reaction is -10KCals. What is the entropy of the reaction and what will be the ΔG at $330^{\circ}K$?

Solution:

The free energy change is expressed as

$$\Delta G = \Delta H - \text{T}\,\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

Given:

ΔG = -16 KCals

ΔH = -10 KCals

$$\therefore \quad \Delta S = \frac{(-10)-(-16)}{300} = 0.02 KCals\ K^{-1}$$

At $330^{\circ}K$

$$\Delta G = \Delta H - \text{T}\,\Delta S$$

= (-10) – 330 x 0.02

= - 10 - 6.6 = -16.6 KCals

3. Calculate the standard free energy change for the reaction,

$H_2(g)+I_2(g) \rightarrow 2HI(\text{g})$.

Given that the standard enthalpy change and standard entropy changes for the reaction are 52KJ and 165.2 JK^{-1} . Is this reaction spontaneous at 298K?

Solution:

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

Given:

ΔH° = 52 KJ or 5200 J

ΔS° = 165.2 J

T = 298K

$\therefore \quad \Delta G^{\circ}$ = 52000 – 298 x 165.2

= + 2770.4 J or

= + 2.77KJ

Since ΔG° has positive value, the reaction G not spontaneous at $298^{\circ}K$.

Problems based on Gibbs –Helmholtz equation

1. Gibbs free energy of a reaction at 300K as 310K are -29KCals and -29.5 K Cals respectively. Determine its ΔH and ΔS at 300K.

Solution:

According to Gibbs – Helmholtz equation

$$\Delta G = \Delta H + \mathrm{T}\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad (1)$$

Given:

T_1 : 300 K

T_2 : 310 K

G_1 : -29 Kcals

G_2 : -29.5 Kcals

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{(-29.5)-(-29)}{310-300}$$

$$\frac{-0.5}{10} = -0.05\text{KCals}$$

$\therefore$ ΔH at 300K, using equation (1)

$-29 = \Delta H + 300\ (-0.05)$

$\Delta H = -29 + 15$

$\Delta H = -14$ K Cals

Further

$$\Delta G = \Delta H - \mathrm{T}\,\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-14-(-29)}{300}$$

$\Delta S = +0.05$ K Cals K^{-1}.

2. Calculate ΔG° for cell reaction at 25 $^\circ C$. $Zn + FeSO_4 \rightarrow Fe + ZnSO_4$. The standard reduction potentials are $E^\circ(Zn^{2+}, Zn)$ = 0.76 v and $E^\circ(\mathrm{Fe}^{2+}, \mathrm{Fe})$ = -0.44 V. Predict whether the reaction is spontaneous or not?

Solution:

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

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

Where E° is end of the cell, n is the no of e^{-} transferred in the cell reaction, F is Faraday

$$E^{\circ}_{Cell} = E^{\circ}_{Cathode} - E^{\circ}_{Anode}$$

In the given system, Zn act as anode and Fe act as cathode

$$E^{\circ} = (-0.44) - (-0.766)$$

$$= + 0.32$$

$$\therefore \quad \Delta G = -nFE$$

$$= -2 \times 96{,}500 \times 0.32$$

ΔG = -61760 J . Since ΔG = - Ve, the reaction is spontaneous.

3. Calculate ΔG° for a Daniel cell Zn// $ZnSO_4$ // $CuSO_4$ //Cu at $25^{\circ}C$. Given E° = 1.1 V.

Solution:

The relation between free energy change and electrical energy is given by:

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

$$= -2 \times 96{,}500 \times 1.1$$

= -212300 Coulombs x Volt (or) Joules

= -212.3 KJ.

Free Energy change and Equilibrium Constant

4. Calculate ΔG° at 300K for a reaction when K_p =100.

Solution:

According to Vant Hoff isotherm

$$\Delta G^{\circ} = -RT\ln K_{eq}$$

$$\Delta G^{\circ} = -2.303\ RT\log K'$$

Where

R = 1.987 Cals $K^{-1}\ mol^{-1}$

T = $300^{\circ} K$

K = 100

$\therefore$ ΔG° = -2.303 x 1.987 x 300 x log 100

= -2.303 x 1.987 x 300 x 2

= -2.745.63 Cals

5. The Value of equilibrium constant for a reaction is found to be 10,000 at $25^{\circ} C$. Calculate ΔG° for the reaction.

ΔG° = -2.303 RTlogK

= -2.303 x 1.987 x 298 x log 10,000

= -2.303 x 1.987 x 298 x 4

= -5454.66 Cals

Important formulae to solve the problems

1. Entropy change for isothermal process

$$\Delta S = 2.303\ nR \log \frac{V_2}{V_1} \quad \text{or}$$

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

2. Entropy change in physical transformations

$$\Delta S = \frac{\Delta H}{T}$$

Where ΔH = L x M

L = Latent heat in Calories

M = M.wt in gms

T = Temp. in Kelvin

3. Relation between ΔG, ΔH and ΔS

i) $\Delta G = \Delta H - T\,\Delta S$

ii) $\Delta S = \dfrac{\Delta H - \Delta G}{T}$

iii) ΔG = -Ve, Reaction is spontaneous

= +Ve, Reaction is not spontaneous

= zero, Reaction is in equilibrium

4. Gibbs – Helmholtz equation to calculate heat or enthalpy of reaction, ΔH , ΔS etc.,

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

T in Kelvin

$$\Delta G = G_2 - G_1$$

$$dT = T_2 - T_1$$

$$\therefore \frac{d\Delta G}{dT} = \frac{G_2 - G_1}{T_2 - T_1}$$

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

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

5. Free energy change and electrical energy or Electrical work:

$$\Delta G = nFE^{\circ}$$

Where E° = emf of the cell

$= E_{cathode} - E_{anode}$

n = No. of e^- transferred in the cell reaction

F = Faraday (in Coulombs) 96,500

6. Vant Hoff Isotherm

(Relation between standard free energy change and equilibrium constant)

ΔG° = RTln K

ΔG° = -2.303 RTlogK

Where K = Equilibrium constant

T = in Kelvin

R= 1.987 Cals $K^{-1}mol^{-1}$

Model Questions

Part-A (2 Marks)

1. Calculate the entropy change involved when one mole of liquid oxygen is converted into gaseous oxygen at its boiling point of -183°C. Enthalpy of vaporization of liquid oxygen is 6.820J.
2. Distinguish between reversible and irreversible process.
3. Calculate ΔG^o at 300 k for a reaction when $K_{eq} = 100$. Given R = 1.987 $calSK^{-1}mol^{-1}$.
4. State first law of thermodynamics.
5. State the second law of thermodynamics.
6. What is the work function?
7. Bring out the differences between open and closed system.
8. What is meant by isolated system?
9. Define isobaric and isochoric process.
10. Define entropy.
11. Define free energy and spontaneity.
12. What is the significance of free energy?
13. Define enthalpy.
14. Why does entropy of a solid increase on fusion?
15. Define state and path functions.
16. Write the phase rule for one component system.
17. What do you mean by eutectic temperature in phase equilibria?
18. Define system and surrounding.
19. Write the limitations of first law of thermodynamics.
20. What are intensive and extensive properties? Give examples.
21. What is zeroth law of thermodynamics? Mention its significance.
22. What is condensed phase rule?
23. Define degree of freedom in phase equilibria.

Part-B (8 Marks)

1. Prove that $C_p - C_v = R$.
2. Derive Gibbs-Helmholtz equation. Mention two applications.
3. Derive the expression for Van’t Hoff isotherm for a general equation $aA + bB \rightarrow cC + dD$.
4. Construct a phase diagram for Lead-Silver system and explain it.
5. Discuss the application of phase rule to one component system.
6. The free energy change, ΔG for process is -138 kJ at 30 °C and -135 kJ at 40 °C. Calculate the change in enthalpy, ΔH accompanying the process at 35 °C.

7. Explain the physical significances of free energy and work function.

Nernst Equation for single electrode potential

Consider a general redox reaction,

$$M^{n+}_{(aq)} + e^{-} \rightarrow M_{(s)}$$

Where $M^{n+}_{(aq)} = Metal\ ion;\ M_{(s)} = pure\ metal;$

$n = Valency\ of\ the\ metal\ (Number\ of\ electrons\ involved\ in\ the\ redox\ reaction)$

For a reversible reaction, the free energy change (ΔG) and its equilibrium constant are related as,

$$\Delta G = \Delta G^{\circ} + RT\ln\frac{[Products]}{[Reactants]}$$

$$\Delta G = \Delta G^{\circ} + RT\ln\frac{[Products]}{[Reactants]}$$

---------- (1)

Where, ΔG^0 is known as the standard free energy change.

For a reversible reaction, the change in free energy is related to electrical energy as

$-\Delta G = nFE$ --------- (2) and **$-\Delta G^{\circ} = nFE^{\circ}$** ---------- (3)

Where, n = Number of electrons involved in the redox reaction;

F = Faraday (96,500 C);

E = Electrode potential (in Volts);

E° = Standard electrode potential (in volts)

Substituting equations (2) and (3) in (1),

$$-nFE = -nFE^{\circ} + RT\ln\frac{[Products]}{[Reactants]}$$

$$-nFE = -nFE^{\circ} + RT\ln\frac{[Products]}{[Reactants]}$$

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

$$-nFE^{\circ} + RT\ln\frac{[M_s]}{[M^{n+}][e^{-}]}$$

The activity/concentration of pure substances is equal to one and $[M_{(s)}] = 1$; $[e^{-}] = 1$.

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

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

---------- (4)

Dividing equation (4) by –nF,

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

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

Converting natural logarithm into decadic logarithm the above equation becomes,

$$E = E^{\circ} + 2.303 \frac{RT}{nF} \log_{10}[M^{n+}] \; E = E^{\circ} + 2.303 \frac{RT}{nF} \log_{10}[M^{n+}]$$

---------- (5)

Equation (5) is known as Nernst equation for electrode potential.

At 25 °C,

$$\frac{2.303RT}{nF} = \frac{0.0592}{n}$$

Therefore, equation (5) becomes

$$E_R = E_R^{\circ} + \frac{0.0592}{n} \log_{10}[M^{n+}] \; E_R = E_R^{\circ} + \frac{0.0592}{n} \log_{10}[M^{n+}]$$ ----------

(6)

Where, E_R and E_R° are reduction potential and standard reduction potentials respectively.

For the oxidation process, $M_{(s)} \rightarrow M^{n+}_{(aq)} + e^{-} \; M_{(s)} \rightarrow M^{n+}_{(aq)} + e^{-}$, the equation (6) becomes

$$E_{OX} = E_{OX}^{\circ} - \frac{0.0592}{n} \log_{10}[M^{n+}]$$

Where, $[M^{n+}]$ = Concentration of the metal ion (mol/dm^3); n = Number of electrons involved in the redox process.

Determination of Solubility of Sparingly soluble salts

- The ionic concentration of a solution can be calculated from the EMF of a concentration cell.
- In case of a sparingly soluble salt, the salt can be completely ionised even in saturated solutions, and the ionic concentration is proportional to the solubility of the salt.
- As an example, if we want to find the solubility of silver chloride, that can be done by measuring the EMF of the cell.

  Ag | N/100 AgNO3 | Glass || Saturated AgCl | Ag

The EMF of the cell at 25°C is given by the relation

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

- Here, n, the valence of $Ag^+ = 1$ and the concentration of Ag^+ in N/100 $AgNO_3$ solution is 0.01 gram ion per litre.
- Hence,

$$E = \frac{0.0591}{1} \log \frac{0.01}{C_1}$$

- From the above expression, the concentration of AgCl in gram ions of silver per litre can be calculated.
- By multiplying this by the molecular weight of silver chloride (143.5), the solubility of AgCl in grams per litre can be obtained.

Determination of pH Using Glass electrode

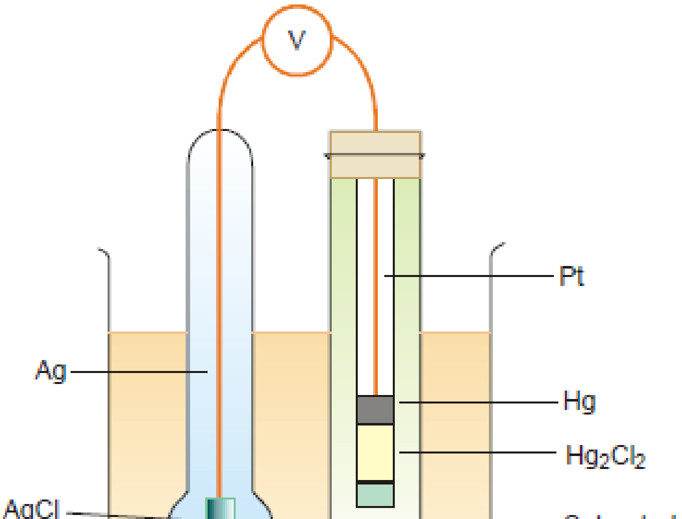
- A glass electrode is immersed in the solution for which we want to find the pH.
- It is coupled with a standard calomel electrode (SCE) to set-up an electrochemical cell.
- The EMF of the cell thus formed, can be determined experimentally.

Ag, AgCl |1M HCl | Glass || Solution of Unknown pH || SCE

The potential of the glass electrode, E_G, at 25°C is given by equation

$$E_G = E°_G + \frac{2.303RT}{F} pH$$

$$= E°_G + 0.0591\, pH$$



(Figure Courtesy: Essentials of Physical Chemistry – Arun Bahl, B.S.Bahl, G.D. Tuli)

We know that

$$E_{cell} = E_R - E_L$$

i.e.,

$$E_{cell} = E_{SCE} - E_G$$

Substituting the value of E_G from (A)

$$E_{cell} = E_{SCE} - E^{\circ}_G - 0.0591 \times pH$$

$$pH = \frac{E_{SCE} - E^{\circ}_G - E_{cell}}{0.0591}$$

- The electrode potential of calomel electrode is known while E_{cell} can be found experimentally.
- Therefore, we can find pH of a given solution if $E_G°$ is known.
- It can be determined by using a solution of known pH and measuring the E_{cell}.

This value of $E_G°$ is constant for a particular glass electrode and can be used for any subsequent determinations of pH of unknown solutions with the help of the equation given above.

Potentiometric titrations: Acid-Base

- In a potentiometric titration, a suitable electrode immersed in the solution to be titrated acts as the 'indicator'.
- The indicator electrode is paired with a reference electrode and the two electrodes are connected to an electronic voltmeter.
- The EMF of the indicator electrode changes gradually with the change of concentration of ions caused by the addition of titrant from the burette.
- The equivalence point is indicated by a sharp change in electrode potential.
- Since the potential of reference electrode is a constant, any change in the potential of the indicator electrode is reflected by a similar change in the cell potential.

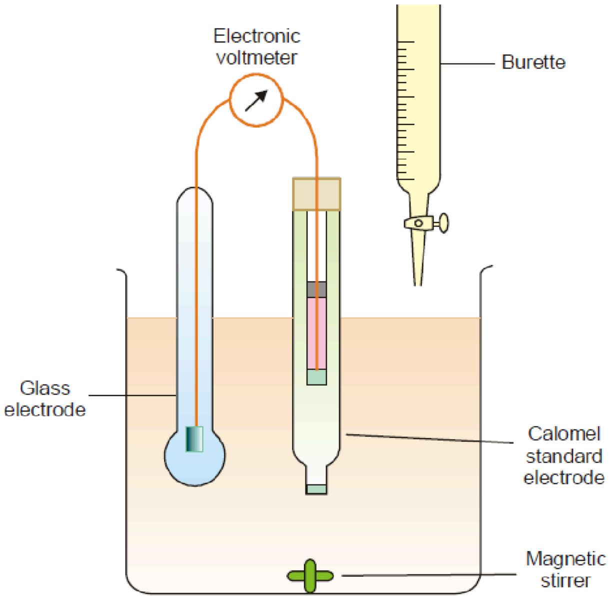
- Therefore, the equivalence point can be found by plotting a graph between the cell EMF and the volume of titrant added from the burette.
- A sharp rise in the curve shows the equivalence point and the corresponding volume on the graph is the volume of the solution used for the titration.
- The different types of potentiometric titrations are as follows:
  - (*a*) Acid-base titrations
  - (*b*) Oxidation-reduction titrations
  - (*c*) Precipitation titrations

Acid-base Titrations

- The apparatus used for potentiometric acid-base titrations is set-up as follows:
- A hydrogen electrode or a glass electrode is immersed in the solution of the acid whose strength is to be determined.
- The glass electrode is coupled with a standard calomel electrode.
- The cell thus formed is connected to the potentiometer or electronic voltmeter.
- When alkali is added, pH of the solution changes.
- The EMF of the cell also changes with pH of the solution in accordance with the relation.

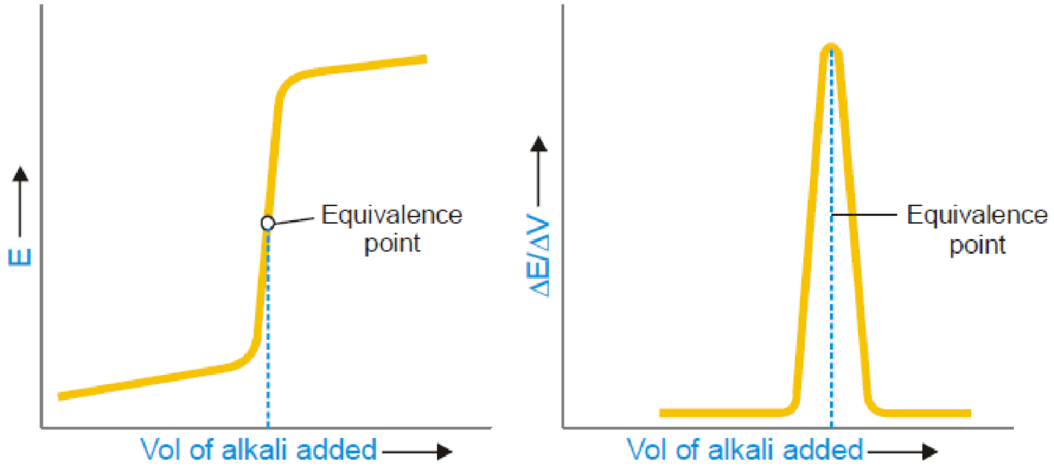
$$E = E^\circ + 0.0591\,\mathrm{pH}$$

- The standard alkali solution is then added from the burette in small volumes.
- After each addition, the EMF of the cell is recorded.
- The EMF is then plotted against the volume of alkali added.
- The shape of the curve for the titration of a strong acid against strong alkali (HCl versus NaOH) is shown in the following Fig.



(Figure Courtesy: Essentials of Physical Chemistry – Arun Bahl, B.S.Bahl, G.D. Tuli)

- The steepest portion of the curve indicates the equivalence point.
- However, when the solutions are very dilute, or weak acids or bases, are involved, the steepness of the curve is less marked and it is difficult to judge the end-point.
- In such a case, we plot the slope of the curve, ΔE/ΔV against the volume of alkali used, and the maximum of the curve indicates the end-point.



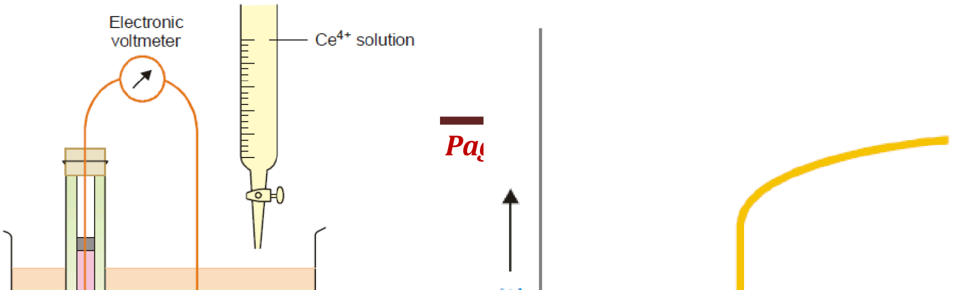
(Figure Courtesy: Essentials of Physical Chemistry – Arun Bahl, B.S.Bahl, G.D. Tuli)

Oxidation-reduction Titrations

- The titration of ferrous ions (Fe^{2+}) with ceric ions (Ce^{4+}) is an example of oxidation-reduction (or redox) titration.
- Fe^{2+} ion is oxidized to Fe^{3+} ion, while Ce^{4+} is reduced to Ce^{3+} ion.

$$\mathbf{Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}}$$

- The indicator electrode is a platinum strip dipping in the solution of Fe^{2+} ions, and it is connected to a standard calomel electrode.
- The Ce^{4+} solution is added from the burette and the cell potential is recorded after each addition.
- The potential of the platinum electrode depends on the ratio $[Fe^{3+}]/[Fe^{2+}]$.
- Therefore, the cell potential changes with the addition of Ce^{4+} ions from the burette.
- At the equivalence point, there is a sharp rise of potential which indicates the endpoint.
- Potentiometric titrations of this type are particularly useful for coloured solutions for which an indicator cannot be used.



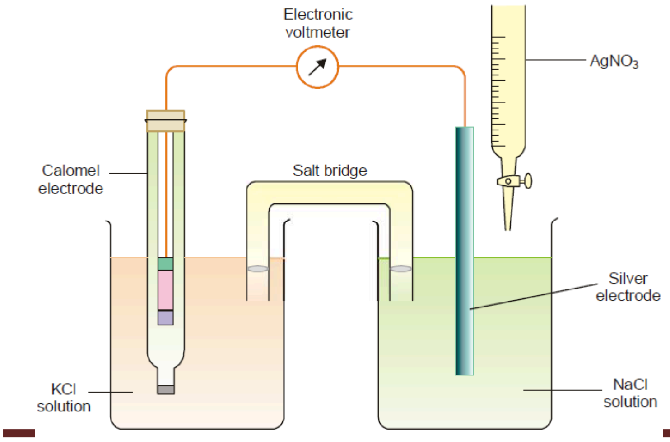
(Figure Courtesy: Essentials of Physical Chemistry – Arun Bahl, B.S.Bahl, G.D. Tuli)

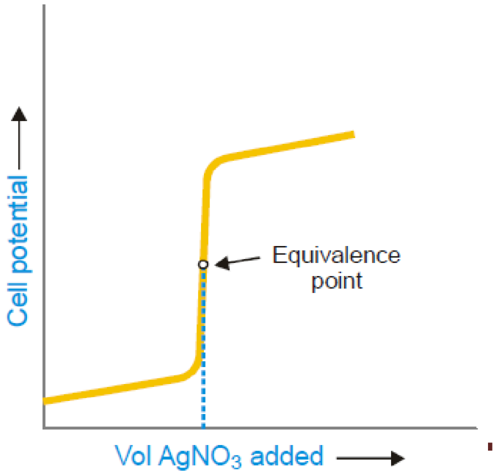
Precipitation Titration

- A typical precipitation titration is that of sodium chloride solution against silver nitrate solution.
- A silver electrode dipping in the unknown sodium chloride solution is coupled with a calomel electrode through a salt bridge.
- Any change in the cell potential is due to changes in concentration of Ag^+ ions around the silver electrode.

$$\mathbf{Ag^+ + \mathit{e} \longrightarrow Ag}$$

- Initially the concentration of Ag^+ ions will be zero and the addition of silver nitrate from the burette, causes the precipitation of silver.
- Now the solution will contain a small concentration of Ag^+ ions formed by the slight dissociation of silver chloride.
- This concentration will increase slightly as Cl^- ions are removed in order to maintain the solubility product $\mathbf{K_{SP} = [Ag^+][Cl^-]}$.
- After the equivalence point, the concentration of Ag^+ ions and, also the potential of silver electrode will rise very sharply owing to the presence of excess of Ag^+ ions.
- The volume of $AgNO_3$ solution used to reach the equivalence point is obtained from the point of inflection in the graph.





(Figure Courtesy: Essentials of Physical Chemistry – Arun Bahl, B.S.Bahl, G.D. Tuli)

Estimation of total, permanent and temporary hardness of water (EDTA method)

Principle:

- Hardness in water is due to the presence of dissolved salts of calcium and magnesium.
- It is unfit for drinking, bathing, washing and it also forms scales in boilers.
- The estimation of hardness is based on complexometric titration.
- Hardness of water is determined by titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent.
- EDTA is insoluble in water, the disodium salt of EDTA is taken for this experiment.
- EDTA can form four or six coordination bonds with a metal ion.

Estimation of Total Hardness

- Total hardness is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium ions.
- It is estimated by titrating the water sample against EDTA using Eriochrome Black-T (EBT) indicator.
- Initially EBT forms a weak EBT-Ca^{2+}/Mg^{2+} wine red coloured complex with Ca^{2+}/Mg^{2+} ions present in the hard water.
- Upon the addition of EDTA solution, Ca^{2+}/Mg^{2+} ions preferably forms a stable EDTA-Ca^{2+}/Mg^{2+} complex with EDTA leaving the free EBT indicator in solution which is steel blue in colour in the presence of ammonia buffer (mixture of ammonium chloride and ammonium hydroxide, pH 10).

$$\text{Eriochrome Black-T} + Ca^{2+}/Mg^{2+} \longrightarrow \underset{\text{(Wine red)}}{\text{Eriochrome Black-T-}Ca^{2+}/Mg^{2+}}$$

$$\underset{\text{(Wine red)}}{\text{Eriochrome Black-T-}Ca^{2+}/Mg^{2+}} + \text{EDTA} \longrightarrow \text{EDTA-}Ca^{2+}/Mg^{2+} + \underset{\text{(Steel blue)}}{\text{Eriochrome Black-T}}$$

Estimation of Permanent Hardness

- Permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium ions.
- Permanent hardness cannot be removed by boiling.
- The filtrate obtained from the above step contains permanent hardness producing substances and is estimated against EDTA using EBT indicator.

Estimation of Temporary Hardness

- Temporary hardness is due to the presence of bicarbonates of calcium and magnesium ions.
- It can be easily removed by boiling.
- When water is boiled, temporary hardness producing substances (bicarbonates) are precipitated as insoluble carbonates or hydroxides.
- This precipitate can be removed by filtration.
- The temporary hardness is calculated from the total and permanent hardness.
- Temporary Hardness = Total Hardness - Permanent Hardness

Calculation

1 ml of 0.01 M EDTA ≡ 1 mg of CaCO3

V1 ml of EDTA ≡ V1 mg of CaCO3

<u>Calculation of total hardness</u>

Volume of EDTA solution consumed = ……….. ml

Volume of hard water taken = ………… ml

$$\frac{Volume\ of\ EDTA\ solution\ consumed}{\text{Volume of the hard water taken}}$$

$$\frac{Volume\ of\ EDTA\ solution\ consumed}{\text{Volume of the hard water taken}}$$

Total hardness =

X 1000 ppm

= ………………….. ppm

<u>Calculation of permanent hardness</u>

Volume of EDTA solution consumed = ……….. ml

Volume of boiled water taken = ………… ml

Permanent Hardness = $\frac{\text{Volume of EDTA solution consumed}}{\text{Volume of the boiled water taken}}$

$\frac{\text{Volume of EDTA solution consumed}}{\text{Volume of the boiled water taken}}$ X 1000 ppm

= ………………….. ppm

Calculation of temporary hardness

Temporary hardness of the given sample of water

= Total hardness - Permanent hardness

= ……………….. ppm

Determination of Chloride Ion Concentration by Argentometry (Mohr’s Method)

- This method determines the chloride ion concentration of a solution by titration with silver nitrate. As the silver nitrate solution is slowly added, a precipitate of silver chloride forms.
- The end point of the titration occurs when all the chloride ions are precipitated.
- Then additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.
- This method can be used to determine the chloride ion concentration of water samples from many sources such as seawater, stream water, river water and estuary water.

(*Refer: Laboratory manual for calculations and result*)

Corrosion

It is the gradual destruction of metals by chemical, electrochemical or biochemical interaction with the environment.

Causes of Corrosion

Metals occur in nature as their oxides, sulphides, carbonates etc. The chemically combined state is thermodynamically more stable. When we extract a metal from its ore, the metal is in a higher energy state, which is thermodynamically unstable. So it tries to go back to the stable state by chemical or electrochemical interaction with the environment.

Consequences or effects of Corrosion

1. Efficiency of the machine decreases.
2. Plant has to be shut down due to failure.
3. Product is contaminated.
4. The toxic products of corrosion cause health hazards.
5. There is a necessity to over design to allow for corrosion.

Classification or Theories of Corrosion

1. Dry or Chemical Corrosion
2. Wet or Electrochemical Corrosion

I. Dry or Chemical Corrosion

It is due to the attack on metal surface by atmospheric gases like O_2, SO_2, H_2S etc. (e.g.) Tarnishing of silver by H2S.

There are three types of dry or chemical corrosion.

1. Oxidation Corrosion
2. Corrosion by Hydrogen
3. Liquid Metal Corrosion

(1) Oxidation Corrosion

It is due to the direct attack of oxygen on metal surface in the absence of moisture. Alkali and Alkaline earth metals are corroded at low temperatures. At high temperatures, most metals except Au, Pt and Ag are oxidized.

Mechanism

i) Oxidation occurs at the surface of the metal to form M^{2+} ions.

$$M \longrightarrow M^{2+} + 2e^-$$

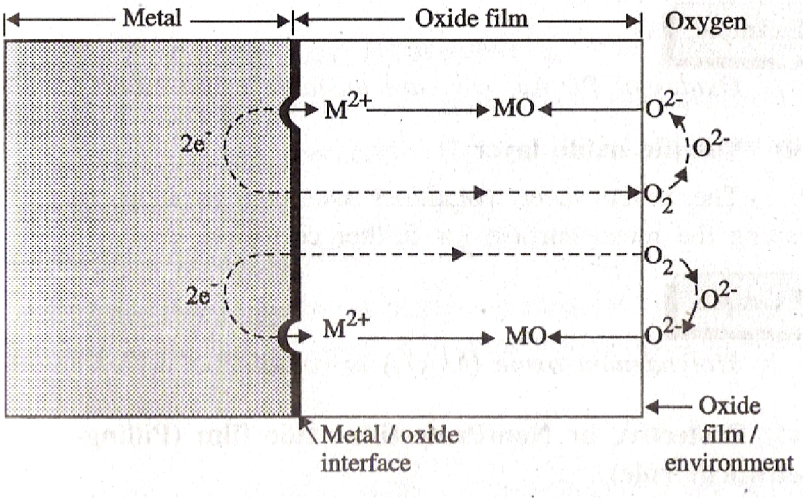
ii) Oxygen takes up the electrons. O_2 is reduced to O^{2-}

$$\frac{1}{2} O_2 + 2e- \longrightarrow O^{2-}$$

iii) O^{2-} ion reacts with M^{2+} to form metal oxide.

$$M^{2+} + O^{2-} \longrightarrow MO$$

The metal surface is converted to a monolayer of metal oxide. Further corrosion occurs by diffusion of M^{2+} ion through the metal oxide barrier. The growth of oxide film is perpendicular to the metal surface.



Different types of oxide films are formed.

(i) **Porous and Non-Porous Oxide Film (or) Pilling-Bedworth Rule:** The ratio of the volume of oxide formed to the volume of metal consumed is called Pilling-Bedworth ratio or Pilling – Bedworth rule.

(a) If the volume of the oxide layer formed is less than the volume of the metal consumed, the oxide layer is porous.

e.g. The volumes of oxides of alkali and alkaline earth metals are less than the volume of the metal consumed. So the oxide layer is porous and non-protective.

(b) If the volume of the oxide layer formed is greater than the volume of the metal consumed, the oxide layer is non-porous.

e.g. The volumes of oxides of heavy metals such as Pb, Sn are greater than the volumes of the metal consumed. So the oxide layer is non-porous and protective.

(ii) **Stable Oxide Layer:** A stable oxide layer is firmly adsorbed on the metal surface. The layer is impervious and prevents further corrosion. So the layer itself acts as a protective coating. (E.g.) Oxides of Al, Cu etc.

(iii) Unstable oxide Layer: This is mainly produced on the surface of noble metals such Ag, Au, Pt, etc. The unstable oxide decomposes to stable metal and oxygen.

$$\text{Metal Oxide} \longrightarrow \text{Metal} + \text{Oxygen}$$

(iv) Volatile Oxide: The oxide film volatilizes as soon as it is formed. It leaves fresh metal surface for further continuous attack. e.g. Molybdenum oxide MoO_3.

(2) Corrosion by Hydrogen

(a) Hydrogen embrittlement

Definition: Loss in ductility of a material in the presence of hydrogen is known as hydrogen embrittlement.

This type of corrosion occurs when a metal is exposed to hydrogen environment. Iron liberates atomic hydrogen by reacting with H_2S.

$$Fe + H_2S \longrightarrow FeS + 2H$$

Hydrogen atoms diffuse into the metal matrix in this atomic form and get collected in the voids present inside the metal

$$H + H \longrightarrow H_2$$

When the pressure of the gas increases, cracks and blisters develop on the metal.

(b) Decarburization

Definition: It is the process of decrease in the carbon content of steel.

At high temperature, molecular hydrogen decomposes to atomic hydrogen.

$$H \xrightarrow{\text{High Temperature}} 2H$$

When steel is exposed to this environment, carbon in the steel reacts with atomic hydrogen.

$$C + 4H \longrightarrow CH_4$$

Hence the carbon content in steel decreases. Collection of methane gas in the voids of steel develops high pressure and causes cracking.

(3) Liquid Metal Corrosion: It is due to the chemical action of flowing liquid metal at high temperature. It involves:

(i) The dissolution of a solid metal by the liquid metal.

(ii) The Penetration of liquid metal into the solid metal.

II. Wet (or) Electrochemical Corrosion:

It occurs under the following conditions.

(i) When two dissimilar metals or alloys are in contact with each other in presence of an aqueous solution or moisture.

(ii) When the metal is exposed to an electrolyte with varying amounts of oxygen.

Mechanism of Wet Corrosion

(1) Metal dissolution occurs at the anode.

$$M \longrightarrow M^{n+} + ne^-$$

(2) Reduction reaction occurs at the cathode in different environments.

(a) Acidic environment: Here hydrogen gas is evolved at the cathode.

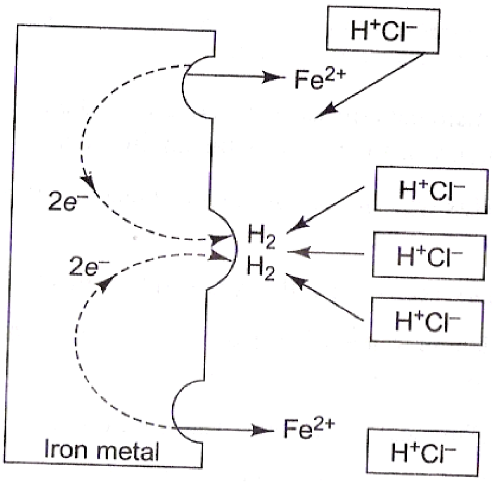
$$2\,H^+ + 2e^- \longrightarrow H_2$$

(b) Neutral environment: In neutral or slightly alkaline medium, hydroxide ions are formed at the cathode.

$$\tfrac{1}{2}\,O_2 + 2e^- + H_2O \longrightarrow 2OH^-$$

(a) **Hydrogen Evolution type corrosion (In Acidic Medium)**

All metals above hydrogen in the electrochemical series tend to get dissolved in acidic solution with simultaneous evolution of H_2 gas.



E.g. when iron comes into contact with non-oxidizing acid like HCl, hydrogen evolution occurs.

At anode: Iron is oxidized to Fe^{2+}

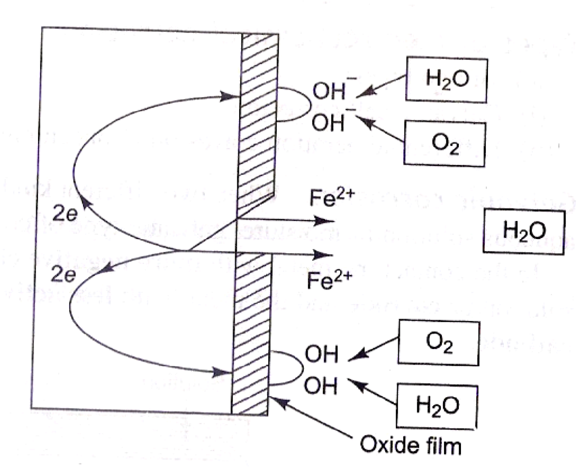
$$Fe \longrightarrow Fe^{2+} + 2e^-$$

At cathode: H^+ ion is reduced to H_2.

$$2\,H^+ + 2e^- \longrightarrow H_2 \uparrow$$

(b) Absorption of Oxygen (or) Formation of hydroxide ion type corrosion (In neutral or weakly alkaline medium)

The surface of iron is normally coated with a thin film of iron oxide. But if some cracks develop on the film, anodic areas are created on the surface. The rest of the metal part acts as cathode.



E.g. when iron is in contact with an electrolyte solution in presence of oxygen, OH- ions are formed.

At anode: Iron is oxidized to Fe^{2+}

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

At cathode: O_2 is reduced to OH^-.

$$\tfrac{1}{2}\,O_2 + 2e^- + H_2O \longrightarrow 2OH^-$$

Overall Reaction

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

If enough oxygen is present, $Fe(OH)_2$ is oxidized to $Fe(OH)_3$.

$$4\,Fe(OH)_2 + O_2 + H_2O \longrightarrow 4Fe(OH)_3\,(\text{rust})$$

Differences between chemical corrosion and electrochemical corrosion:

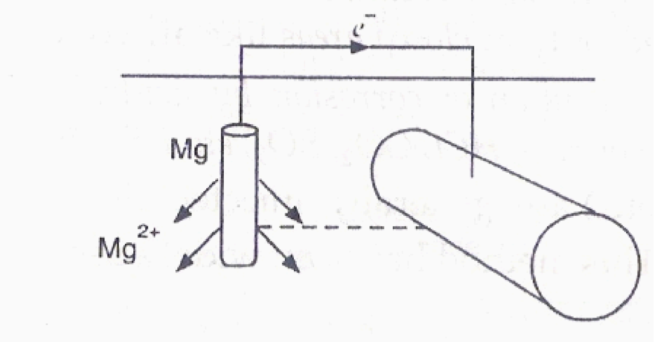
S.No	Chemical Corrosion	Electrochemical Corrosion

1.	It occurs in dry condition	It occurs in presence of moisture or electrolyte
2.	It occurs by the direct chemical attack on the metal by the environment	It occurs by the formation of a large number of anodic and cathodic areas.
3.	Even a homogenous metal surface is corroded.	Only heterogeneous or bimetallic surface is corroded
4.	Corrosion products gather at the place of corrosion	Corrosion occurs at the anode, while the products formed elsewhere
5.	It is a self-controlled process	It is a continuous process
6.	It takes place by adsorption mechanism	It follows electrochemical reaction
7.	(e.g.) Mild scale formation on iron surface	(e.g.) Rusting of iron under moist atmosphere

Corrosion control: The rate of corrosion can be controlled by modifying the metal or environment.

Cathodic Protection: The metal to be protected is made to act like a cathode. This is achieved in two ways.

a) **Sacrificial anodic protection:** In this method the more active metals like Zn, Mg, etc. are attached to base metal (cathode) which is to be protected from corrosion. The anodic metals (Zn or Mg) being more reactive undergoes corrosion but base metal remains unaffected.



Metal to be protected

Here the metal to be protected is made cathode by connecting it to a more active metal (anodic metal) called sacrificial anode. Only the corrosion concentrates on more active metal.

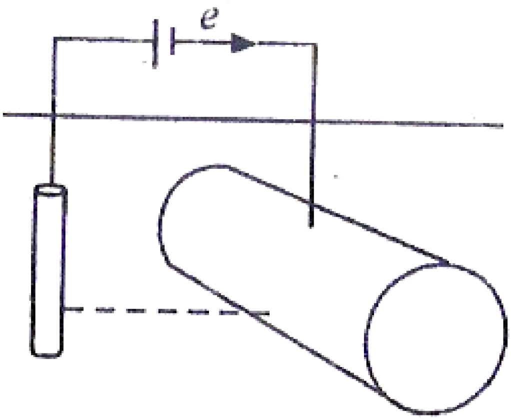
The sacrificial anodes have to be replaced from time to time after complete corrosion. The method is used for protecting buried pipeline, ship hulls, and industrial water tank. Several hundred kilometers long zinc wire is buried along oil pipe line in Alaska is an example for sacrificial anodic protection method.

Applications

1. Protection of buried pipelines, underground cables
2. Protection of ships and boats
3. Calcium metal is used to minimize engine corrosion
4. Magnesium sheets are inserted into domestic water boilers to prevent rust formation.

b) Impressed current cathodic protection method

Here an impressed current is applied in an opposite direction to nullify the corrosion current. Thus the corroding metal is converted to cathode from anode. The negative terminal of battery is connected to the metal to be protected. The positive terminal is connected to an inert electrode like graphite. The anode is buried in a 'back-fill' (containing a mixture of gypsum, coke breeze and sodium sulphate) to increase electrical contact.



Mg **Metal to be protected**

Applications

Protection of tanks, transmission line towers, underground water pipes, oil pipe line, ships etc.

Limitations

1. It is little costlier than Sacrificial anodic protection method.
2. It fails when current is switched off.