

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – I – Thermodynamics-II – SCY1316

1. INTRODUCTION

Need of Second Law of Thermodynamics

- 1. First law states that "heat can be converted completely into work". Actually, it is found that, only a fraction of quantity of heat may be converted into work in a cyclic process (i.e., efficiency of such conversion is not 100%).
- 2. The second law provides a mean for calculating the efficiency of this conversion.
- 3. The second law of thermodynamics states that, work can always be converted into heat but heat cannot be completely converted into work without leaving a permanent change in the system or surroundings.

Limitations of First Law and Need of Second Law

- 1. The first law of thermodynamics states that "One form of energy can be converted into another form but the total energy remains constant". It does not indicate the direction of the flow of energy. Further, it does not explain whether the conversion process / reaction will occur spontaneously or non-spontaneously.
- 2. First law also states that "heat can be converted completely into work". But actually, it is found that only a fraction of quantity of heat may be converted into work in a cyclic process. i.e., efficiency of such conversion is not 100%. The second law provide a mean for calculating the efficiency of this conversion.

The Second Law of Thermodynamics

- **1.** Clausius Statement: It is impossible to construct a machine which can transfer heat from a cold reservoir to a hot reservoir in a cyclic process, unless some external work is done on the machine.
- **2. Kelvin–Planck Statement:** It is impossible to take heat from a hot reservoir and convert it into work in a cyclic process without transferring a part of heat to the cold reservoir.
- **3.** Entropy Statement: Whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the universe (system and surroundings).

2. THE CARNOT CYCLE (THE CONCEPT OF ENTROPY)

The Carnot cycle is a reversible cycle which demonstrates the maximum convertibility of heat into work.

The Carnot's Reversible Engine

Sadi Carnot imagined a theoretical engine which is free from all defects of practical engines. Its efficiency is maximum and it is an ideal heat engine. This ideal heat engine operating ideal conditions can convert only a part of the absorbed heat into work. The fraction of the total heat converted into work by an engine is considered as its efficiency.

It works on a cycle consisting of two reversible isothermal and two reversible adiabatic processes. For carrying out this cycle change (Fig. 1.1):

- 1. One mole on an ideal gas (working substance) is enclosed in the cylinder with the help of a weightless and frictionless piston.
- 2. The source is kept at a fixed higher temperature T_1 and from which any amount of heat can be drawn.
- 3. The sink is kept at a lower temperature T_2 to which any amount of heat can be rejected.
- 4. A perfectly insulated stand is also provided so that the working substance (1 mole of an ideal gas) can undergo adiabatic change.



Fig. 1.1: The Carnot's Ideal Heat Engine

The Carnot Cycle

To prove that only a fraction of heat (absorbed at higher temperature) can be converted into work and to get an expression for efficiency in terms of temperature of the source and the sink, we have to consider a series of cyclic operations, called Carnot cycle.

The Carnot cycle consists of four steps (Fig. 1.2):

- 1. Isothermal reversible expansion
- 2. Adiabatic reversible expansion
- 3. Isothermal reversible compression
- 4. Adiabatic reversible compression

1. Isothermal Reversible Expansion

In the first part of the cycle, the cylinder is placed in a source at temperature T_1 . The gas is then allowed to expand isothermally and reversibly until the gas expands from volume V_1 to V_2 . Meanwhile, the pressure changes from P_1 to P_2 . During this isothermal expansion, let the amount of heat absorbed be q_1 . In the pressure–volume graph the line AB represents this change.

During this part of the cycle, the change in internal energy is (as per the First law of Thermodynamics):

$$\Delta E_1 = q_1 - w_1 \qquad \dots \dots (1)$$

Since the expansion is isothermal,



Fig. 1.2: The Carnot Cycle

2. Adiabatic Reversible Expansion

In the second part of the cycle, the cylinder is placed on the insulated stand. The gas is allowed to expand adiabatically and reversibly from the state P_2 , V_2 at T_1 to a new state P_3 , V_3 . In an adiabatic change q=0 and all the work is done at the expense of internal energy of the system. Hence its temperature falls. Let the temperature drop from T_1 to T_2 . In the P-V graph, the line BC represents this change.

For this adiabatic change, the change in internal energy is,

 $\Delta E_2 = -w_2$ since q=0(3)

Since the expansion is adiabatic,

Work done,
$$w_2 = -C_V(T_2 - T_1)$$
(4)

3. Isothermal Reversible Compression

In the third stage of the cycle, the cylinder is kept in a sink at temperature T_2 . The gas is isothermally compressed to volume V₄. During this isothermal compression, the amount of heat rejected to the sink be q_2 .

During this part of the cycle, the change in internal energy is

$$\Delta E_3 = -q_2 - w_3 \qquad \dots \dots (5)$$

(since the heat is rejected to the sink, negative sign is given to the amount of heat)

Since, the compression is isothermal,

Work done,
$$w_3 = RT_2 ln\left(\frac{V_4}{V_3}\right)$$

Work done, $w_3 = -RT_2 ln\left(\frac{V_3}{V_4}\right)$ (6)

4. Adiabatic Reversible Compression

In the last part of the cycle, the cylinder is placed on the insulated stand. The gas is compressed adiabatically and reversibly from P₄, V₄ at T₂ to its initial state P₁, V₁ at T₁. In P-V graph, the line DA represents this change.

Here again q=0.

Hence change in internal energy is

$$\Delta E_4 = -w_4 \qquad since \ q=0 \qquad \dots (7)$$

Since, the compression is adiabatic

Work done,
$$w_4 = -C_V(T_1 - T_2)$$

Work done, $w_4 = C_V(T_2 - T_1)$ (8)

The total change in internal energy ΔE for the whole cycle must be zero, since the system comes back to its initial state. Hence,

$$\Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 = 0$$

$$q_1 - w_1 - w_2 - q_2 - w_3 - w_4 = 0$$

$$q_1 - q_2 = w_1 + w_2 + w_3 + w_4$$

$$q_1 - q_2 = W$$
(9)

Here *W* is the total work done in the cycle. Since all the steps are reversible, work done must be maximum. i.e., The amount of heat converted into work is $q_1 - q_2$.

Hence its efficiency (η) is,

 $\eta = \frac{\text{Amount of heat converted into work (or) Maximum Workdone}}{\text{Total heat absorbed}}$ $\eta = \frac{q_1 - q_2}{q_1} = \frac{W}{q_1} \qquad \dots \dots (10)$

Where *W* is the maximum work done by the system; q_1 is the amount of heat absorbed by the system from the source at a higher temperature T_1 .

To get an expression for efficiency in terms of temperature of the source and the sink,

$$W = w_1 + w_2 + w_3 + w$$

$$\eta = RT_1 ln\left(\frac{V_2}{V_1}\right) - C_V(T_2 - T_1) - RT_2 ln\left(\frac{V_3}{V_4}\right) + C_V(T_2 - T_1)$$

$$\eta = RT_1 ln\left(\frac{V_2}{V_1}\right) - RT_2 ln\left(\frac{V_3}{V_4}\right) \qquad \dots (11)$$

For an isothermal process $\Delta E=0$. Therefore, from the first law of thermodynamics,

$$\Delta E_{1} = q_{1} - w_{1}$$

$$q_{1} = w_{1} \quad Since \ \Delta E = 0 \text{ for an isothermal process}$$

$$q_{1} = RT_{1} \ln \left(\frac{v_{2}}{v_{1}}\right) \qquad \dots (12)$$

Therefore, efficiency (η) is written from equations as:

$$\frac{W}{q_{1}} = \frac{\frac{RT_{1} ln\left(\frac{V_{2}}{V_{1}}\right) - RT_{2} ln\left(\frac{V_{3}}{V_{4}}\right)}{RT_{1} ln\left(\frac{V_{2}}{V_{1}}\right)}}{\frac{W}{q_{1}} = 1 - \frac{RT_{2} ln\left(\frac{V_{3}}{V_{4}}\right)}{RT_{1} ln\left(\frac{V_{2}}{V_{1}}\right)} \dots (13)$$

The expression for a reversible adiabatic process of an ideal gas in term of temperature and volume is written as:

$$TV^{\gamma-1} = a \text{ constant}$$

For an adiabatic expansion (states 2 and 3, the temperature-volume expression is written as:

$$T_1 V_2^{\gamma - 1} = T_2 V_3^{\gamma - 1} \qquad \dots \dots (14)$$

For an adiabatic compression (states 4 and 1, the temperature-volume expression is written as:

$$T_1 V_1^{\gamma - 1} = T_2 V_4^{\gamma - 1} \qquad \dots \dots (15)$$

On dividing (14) by (15) and comparing the equations, we obtain:

$$\frac{V_2}{V_1} = \frac{V_3}{V_{14}} \qquad \dots \dots (16)$$

Substituting (16) in equation (13), we get

$$\eta = 1 - \frac{T_2}{T_1} \qquad \dots \dots (17)$$

Comparison of equations (10) and (16) shows that:

$$\eta = \frac{T_1 - T_2}{T_1} \qquad \dots \dots (18)$$

Equation (17) gives us the efficiency of Carnot's engine in terms of the temperature of the source and the sink. Equation (18) is the mathematical expression for the second law.

3. ENTROPY

1. Entropy Definitions

- \checkmark Entropy is a measure of degree of disorder or randomness in the system.
- \checkmark Entropy is also considered as a measure of unavailable form of energy.

Mathematical Statement: The change in entropy is equal to the ratio of heat change occurs to the temperature in a reversible cyclic process.

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

Where, q is the heat absorbed or evolved in calories and T is the temperature in degrees.

2. Characteristics of Entropy

- ✓ The unit of entropy is calories degree⁻¹. It is also called as entropy unit (e.u). The unit of entropy in S.I. unit is Joules per Kelvin (JK^{-1}) .
- ✓ Entropy is a state function. The entropy change of a system is determined by the initial and final states only, and not on the path taken by the system.
- ✓ The entropy change is an extensive property. Its value depends upon the amount of substance involved (in moles).
- ✓ So, the unit of entropy is also written as *cals/deg/moles* (or) in S.I. unit JK^{-1} mole⁻¹.

3. Entropy and Disorder (Randomness)

Entropy is a measure of randomness or disorder in the system. Increase in entropy means change from an ordered to less ordered or disordered state (Fig. 1.3).



Entropy increases

Fig. 1.3: Physical Representation of the Degree of Disorder

There is always decrease in order and increase in disorder and therefore entropy increases.

4. Entropy and Spontaneity

A spontaneous process is always accompanied by an increase in entropy.

Let us consider a molecular system in states *A* and *B*. In state *A*, all the molecules are arranged and highly ordered while in state *B*, the molecules are present at random and it is highly disordered.

By definition, the entropy of state A is low and that of state B is high. Hence, an increase of entropy occurs in the change from state A to state B.

According to the law of chance, state *A* is less probable and state *B* is more probable. ie. The change from state *A* to state *B* is spontaneous (Fig. 1.4).

Hence, we can say that a change in a system which is accompanied by an increase in entropy tends to be spontaneous.



Fig. 1.4: Entropy and Spontaneity

5. Entropy and Unavailable Energy

When heat is supplied to the system, some portion of the heat is used up in doing work. This portion of heat is called workable or available energy. The remaining portion of heat which remains uncovered called unavailable energy. The second law of thermodynamics says that entropy is a measure of unavailable energy. Hence entropy can be defined as unavailable energy per unit temperature.

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

6. Entropy Change in Reversible Process

Consider an isothermal reversible expansion of an ideal gas at temperature T.

During the expansion, let q be the amount of heat absorbed by system from the surroundings.

Hence, the change in entropy of the 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.

Hence, the change in entropy of the surroundings $=\frac{-q}{T}$

 $[Total change in entropy of the process]_{\Delta S_{total}} = [Entropy change in system]_{\Delta S_{sys}} + [Entropy change in surr]_{\Delta S_{surr}}$

$$\Delta S_{total} = \frac{q}{T} + \left(\frac{-q}{T}\right)$$
$$\Delta S_{total} = 0$$

Therefore, the entropy change in a reversible isothermal process is zero. In other words, the entropy remains constant during a reversible process.

7. Entropy Change in Irreversible Process (Entropy Change of the Universe)

Let a system be at higher temperature T_1 and its surroundings at lower temperature T_2 . Consider a quantity of heat q passes irreversibly from system to surroundings. Then,

Decrease in entropy of system,
$$(\Delta S)_{sys} = \frac{-q}{T_1}$$

Increase in entropy of surroundings, $(\Delta S)_{surr} = \frac{+q}{T_2}$

Net entropy change of process,
$$\Delta S_{total} = -\frac{q}{T_1} + \frac{q}{T_2}$$

$$\Delta S_{total} = \frac{q}{T_2} - \frac{q}{T_1}$$

$$\Delta S_{total} = q \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta S_{total} = q \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

But $T_1 > T_2$, and hence $T_1 - T_2$ is positive.

$$(or) S_{total} > 0$$

Hence during an irreversible process, the entropy of the system increases. The total change in entropy of the system and its surroundings is called as entropy change of the Universe. Since all-natural processes that take place spontaneously are irreversible processes, the entropy of the Universe always increases.

4. ENTROPY CHANGE FOR AN IDEAL GAS (APPLICATIONS OF SECOND LAW OF THERMODYNAMICS)

Entropy is a state function. The entropy change of a system is determined by the initial and final states only and not on the path taken by the system.

> Entropy is an extensive property because its value depends upon the amount of substance involved i.e., its value depends on any two of the three variables T, P and V.

1. Entropy Change as a Function of *T* and *V*

According to the first law of thermodynamics:

$$d\mathbf{q} = d\mathbf{E} + \mathbf{P}d\mathbf{V} \qquad \dots (1)$$

By definition, dq = T dS

Substituting the value of dq in equation (1), we have

$$T dS = dE + P dV \qquad \dots (2)$$

 \succ By definition,

$$C_{V} = \frac{dE}{dT}$$
$$dE = C_{V}dT$$

Substituting the value of dE in equation (2), we have

$$T dS = C_V dT + P dV \qquad \dots (3)$$

- For 1 mole of an ideal gas, PV = RT $P = \frac{RT}{V}$
- Substituting in equation (3), we have

$$T dS = C_V dT + \frac{RT}{V} dV$$

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V}$$

...(4)

For a finite change of state of the system, the entropy change ΔS can be obtained by integrating equation (4) between limits of initial state 1 and final state 2 i.e., between S_1 and S_2 ; T_1 and T_2 and V_1 and V_2 assuming that C_v remains constant over the temperature range involved.

$$\int_{S_1}^{S_2} dS = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

(or)

$$[S]_{S_{1}}^{S_{2}} = C_{v} [\ln T]_{T_{1}}^{T_{2}} + R [\ln V]_{V_{1}}^{V_{2}}$$
$$[S_{2} - S_{1}] = C_{v} [\ln T_{2} - \ln T_{1}] + R [\ln V_{2} - \ln V_{1}]$$
$$\Delta S = C_{v} \ln \frac{T_{2}}{T_{1}} + R \ln \frac{V_{2}}{V_{1}}$$

➢ For 'n' moles of an ideal gas,

(or)

$$\Delta S = nC_{v} \ln \frac{T_{2}}{T_{1}} + nR \ln \frac{V_{2}}{V_{1}} \qquad ...(5)$$

$$\Delta S = 2.303 nC_{V} \log \frac{T_{2}}{T_{1}} + 2.303 nR \log \frac{V_{2}}{V_{1}}$$

2. Entropy Change as a Function of *T* and *P*

Let P_1 be the pressure of the ideal gas in the initial state and P_2 in the final state, then for 1 mole of an ideal gas,

$$P_1 V_1 = R T_1 \quad \text{and}$$

$$P_2 V_2 = R T_2$$
(or)
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1}$$

Substituting the value $\frac{V_2}{V_1}$ in equation (5), we have

$$\Delta \mathbf{S} = \mathbf{C}_{\mathbf{v}} \ln \frac{T_2}{T_1} + \mathbf{R} \ln \frac{P_1 T_2}{P_2 T_1}$$

$$\Delta \mathbf{S} = \mathbf{C}_{v} \ln \frac{T_{2}}{T_{1}} + \mathbf{R} \ln \frac{P_{1}}{P_{2}} + \mathbf{R} \ln \frac{T_{2}}{T_{1}}$$

$$\Delta \mathbf{S} = (\mathbf{C}_{v} + \mathbf{R}) \ln \frac{T_{2}}{T_{1}} + \mathbf{R} \ln \frac{P_{1}}{P_{2}}$$

$$\Delta \mathbf{S} = \mathbf{C}_{\mathbf{P}} \ln \frac{T_2}{T_1} + \mathbf{R} \ln \frac{P_1}{P_2} \qquad \qquad \begin{bmatrix} \because \mathbf{C}_{\mathbf{P}} - \mathbf{C}_{\mathbf{V}} = \mathbf{R} \end{bmatrix}$$

For 'n' moles of an ideal gas,

$$\Delta S = nC_{\rm P} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \qquad ...(7)$$

(8)

3. Entropy Change for an Isothermal Process

Since an isothermal process is carried out at constant temperature, the change in temperature, (ΔT) is zero. Therefore,

 $\Delta S = 2.303 n C_{\rm P} \log \frac{T_2}{T_1} + 2.303 n R \log \frac{P_1}{P_2}$

$$\Delta T = T_2 - T_1 = 0$$

$$T_1 = T_2$$
...(1)

Entropy change as a function of *T* and *V* is given by the expression:

$$\Delta \mathbf{S} = 2.303 n \,\mathrm{C_v} \log \frac{T_2}{T_1} + 2.303 n \,\mathrm{R} \log \frac{V_2}{V_1} \qquad \dots (2)$$

> For an isothermal process, $T_1 = T_2$ and the expression for the change in entropy for *n* moles of ideal gas using the expression (2) is written as:

$$\Delta S = 2.303 \, n \, \mathrm{R} \, \log \frac{V_2}{V_1} \qquad ...(3)$$

> Entropy change as a function of *T* and *P* is given by the expression:

$$\Delta \mathbf{S} = \frac{2.303 n \,\mathrm{C}_{\mathrm{P}} \log \frac{T_2}{T_1} + 2.303 n \,\mathrm{R} \log \frac{P_1}{P_2} \qquad \dots (4)$$

The expression for the change in entropy for an isothermal process $(T_1 = T_2)$ for *n* moles of ideal gas using the expression (4) is written as:

$$\Delta S = 2.303 \, n \, \mathrm{R} \, \log \frac{P_1}{P_2} \qquad ...(5)$$

4. Entropy Change for an Isobaric Process

Since the isobaric process is carried out at constant pressure, the change in pressure, (ΔP) is zero. Therefore,

$$\Delta P = P_2 - P_1 = 0$$

 $P_1 = P_2$...(1)

Entropy change as a function of *T* and *P* is given by the expression:

$$\Delta S = \frac{2.303 n C_P \log \frac{T_2}{T_1}}{T_1} + \frac{2.303 n R \log \frac{P_1}{P_2}}{T_1} \dots (2)$$

So, the entropy change for an isobaric process $(P_1 = P_2)$ is written as:

$$\Delta S = 2.303 n C_{\rm P} \log \frac{T_2}{T_1} \qquad \dots (3)$$

5. Entropy Change for an Isochoric Process

Since an isochoric process is carried at constant volume, the change in volume, (ΔV) is zero. Therefore,

$$\Delta \mathbf{V} = \mathbf{V}_2 - \mathbf{V}_1 = \mathbf{0}$$
$$\mathbf{V}_1 = \mathbf{V}_2$$

Entropy change as a function of *T* and *V* is given by the expression:

$$\Delta \mathbf{S} = \frac{2.303nC_V \log \frac{T_2}{T_1}}{T_1} + \frac{2.303n R \log \frac{V_2}{V_1}}{T_1} \dots \dots (1)$$

So, the entropy change for an isochoric process $(V_1 = V_2)$ is written as:

$$\Delta S = 2.303 n C_V \log \frac{T_2}{T_1} \dots (2)$$

6. Entropy Change of Phase Transitions

- The change of a substance from one form to another is known as phase transitions. Such changes occur at definite temperatures and are accompanied by entropy change.
- During these transitions either heat is absorbed or evolved (ie: the entropy either increases or decreases).
- > The entropy change for these transformations is given by:

$$\Delta \mathbf{S}_{\mathrm{trans}} = \frac{q_{rev}}{T}$$

where,

- \checkmark q_{rev} is the heat absorbed or evolved
- ✓ T temperature of transition
- \checkmark q_{rev} is actually the molar enthalpy change of the substance

1. Entropy of Vapourisation

It is defined as the change in entropy when one mole of a liquid substance change into vapours at its boiling point.



✓ where, ΔH_{vapour} is the latent heat of vaporization. Latent heat of vapourisation of water is 540 cals/gm.

2. Entropy Of Fusion

It is defined as the change in entropy when one mole of a solid substance changes into liquid form at its melting point.

ΔS_{fusion}	ΔH_{fusion}	
	- T	

✓ where, ΔH_{fusion} is the latent heat of fusion. Latent heat of fusion of ice at 0°C is 80 cals/gm.

Note:

$\Delta S =$	$L \times M$
	Т

 \checkmark where, *L* is the latent heat in calories; *M* is the molecular weight in grams; *T* is the temperature in Kelvin.

3. Entropy of Sublimation

It is defined as the change in entropy when one mole of a solid substance changes into vapour at a particular temperature.



5. NEED FOR THE INTRODUCTION OF NEW THERMODYNAMIC FUNCTIONS

 \blacktriangleright It is understood clearly that, for a process to be spontaneous ΔS_{Total} should be greater than zero.

i.e., $\Delta S_{Total} > 0$ (or) $\Delta S_{sys} + \Delta S_{surr} > 0$

- Hence, in order to decide the spontaneity of a process, we have to consider the change in entropy of the system as well as surroundings.
- So, Gibbs free energy (G) and Helmholtz work function (A) are the thermodynamic functions which can be applied only to system so that it can be used as criterion of spontaneity of a process.

1. Helmholtz Work Function (A)

- We also know that a part of internal energy of a system can be used at constant temperature to do useful work.
- A 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:

$$A = E - \dots(5)$$

where,

- \checkmark *E* is internal energy of the system
- \checkmark *S* is the entropy of system and
- \checkmark *T* is the temperature.

2. Physical Significance of the Work Function (A)

The work function is given by

$$A = E - TS \qquad \dots \dots (1)$$

For a small change in a reversible system at constant temperature,

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

But by definition,

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

 \therefore Equation (2) is written as

$$\Gamma\Delta S = q_{rev} \qquad \dots (3)$$

Substituting T Δ S in equation (2), we get

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

But according to first law of thermodynamics:

$$\Delta E = q - w \qquad \dots (5)$$
$$\Delta E - q = - w_{max}$$

Comparing equation (4) and (5),

 $\Delta A = -w$ $\Delta A = -w_{max}$ [Since for an isothermal reversible process, work obtained is maximum]

So the decrease in the work function A in any process at constant temperature gives the maximum work that can be obtained from the system.

3. Gibbs Free Energy (G)

- Gibbs free energy refers to "the capacity to do useful work". We know that a part of the total energy of a system is converted into work and the rest is unavailable. The part of energy which is converted into useful work is called available energy.
- The isothermally available energy present in a system to do useful work is called as free energy (G).
- ➢ It is mathematically defined as:

$$G = H - TS \qquad \dots (1)$$

where,

- \checkmark *H* is enthalpy of the system
- \checkmark *S* is the entropy of system and
- \checkmark *T* is the temperature.
- \succ For an isothermal process occurring at temperature *T*, if the system undergoes a change from the initial state to final state, then

 $G_1 = H_1 - TS_1$ (for the initial state) ...(2)

$$G_2 = H_2 - TS_2$$
 (for the initial state) ...(3)

Subtracting (3) from (2)

$$(G_2 - G_1) = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = \Delta H - T \Delta S \qquad \dots (4)$$

where,

- $\checkmark \Delta G$ is the change in free energy of the system
- $\checkmark \Delta H$ is the change in enthalpy of the system
- $\checkmark \Delta S$ is the change in entropy of the system

4. Physical Significance of the Free Energy (G)

The free energy is measure of the useful work obtainable from a system through a reversible, isothermal process at constant pressure. It is given by

$$G = H - TS \qquad \dots \dots (1)$$

For a small change in a reversible system at constant temperature,

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

But by definition, $\Delta H = \Delta E + P \Delta V$

 \therefore Equation (2) is written as

$$\Delta G = \Delta E + P \Delta V - T \Delta S \qquad \dots (3)$$

We know that, $\Delta A = \Delta E - T \Delta S$

Hence equation (3) can be written as:

 $\Delta G = \Delta A + P\Delta V \qquad \dots (4)$ Since $\Delta A = -w_{max}$ $\Delta G = -w_{max} + P\Delta V$ $-\Delta G = w_{max} - P\Delta V$

→ Where, $P\Delta V$ is the work done by expansion and w_{max} is the maximum work that can be obtained from the system.

 \succ Therefore,

 $w_{max} - P\Delta V = Network \text{ or Useful work}$

Hence, $-\Delta G = w_{useful}$

So, the decrease in free energy accompanying a process at constant temperature and pressure is equal to the useful work obtainable from the system.

6. THERMODYNAMIC CRITERION OF SPONTANEITY IN TERMS OF FREE ENERGY CHANGE

- Consider a process which is carried out at constant temperature, *T*.
- \blacktriangleright Suppose q is the amount of heat lost by surroundings and gained by the system, then

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} \qquad \dots \dots (1)$$

The entropy change of the surroundings is given by:

$$\Delta S_{surr} = -\frac{q}{T} \qquad \dots \dots (2)$$

(Negative sign indicates that the heat has been lost by the surroundings).

> Now heat gained by system at constant temperature represents its enthalpy change.

i.e., Heat gained by the system, $q = (\Delta H)_{SVS}$

From (2),

$$\Delta S_{surr} = -\frac{q}{T}$$

(or)

$$\Delta S_{surr} = -\frac{(\Delta H)_{sys}}{T} \qquad [\because q = (\Delta H)_{sys}] \quad ...(3)$$

Substituting the value ΔS_{surr} in equation (1), we get

$$\Delta S_{Total} = \Delta S_{sys} - \frac{(\Delta H)_{sys}}{T}$$

Multiplying by T on both sides, we get

$$T \Delta S_{Total} = T \left[\Delta S_{sys} - \frac{(\Delta H)_{sys}}{T} \right]$$

$$T \Delta S_{Total} = T \Delta S_{sys} - (\Delta H)_{sys}$$

 $\left(\Delta H\right)_{sys} - T \Delta S_{sys} = -T \Delta S_{Total}$

$$(\Delta G)_{sys} = -T \Delta S_{Total} \qquad [:: \Delta G = \Delta H - T \Delta S] \quad ...(4)$$

Equation (4) is the basis for criterion of spontaneity in terms of free energy change of the system only.

- \blacktriangleright We know that, for a process to be spontaneous ΔS_{Total} should be positive.
- > In other words, for a process to be spontaneous ΔG_{sys} should be negative.
- i.e., for a process at particular temperature and pressure to be spontaneous, the free energy change of the system must be less than zero.

$$(\Delta G)_{T,P} < 0 \qquad \dots \dots (5)$$

 \succ From equation (4),

- ✓ If ΔS_{Total} is positive, (ΔG) *T*, *P* = −, then the process is spontaneous.
- ✓ If $\Delta S_{Total} = 0$, (ΔG) *T*, *P* = 0, then the process is represents equilibrium.
- ✓ If ΔS *Total* is negative, (ΔG) *T*, *P* = +, then the process is non-spontaneous.
- → Hence for an irreversible or spontaneous process at constant temperature and pressure $\Delta G < 0$, and at equilibrium under isothermal and isobaric conditions $\Delta G = 0$.

7. GIBB'S – HELMHOLTZ EQUATION

We know that, G = H - TS and H = E + PV

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

Upon differentiation, dG = dE + P dV + V dP - T dS - S dT(1)

But according to first law and second law of thermodynamics,

$$dE = dq - P \, dV$$
 (First law)

$$dq = T \, dS$$
 (Second law)

$$\therefore dE = T \, dS - P \, dV$$

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

$$dG = T dS - P dV + P dV + V dP - T dS - S dT$$

$$dG = V dP - S dT \qquad \dots (2)$$

At constant Pressure, dP = 0

$$dG = -S dT$$

For any two states of the system,

$$dG_1 = -S_1 dT$$

$$dG_2 = -S_2 dT$$

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

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

$$d\Delta G = -(S_2 - S_1) dT$$

$$d\Delta G = -\Delta S dT$$

$$\frac{d\Delta G}{dT} = -\Delta S \qquad \dots (3)$$

But according to the definition of free energy change,

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

Substituting $-\Delta S$ in to the equation (3), we have

$$\frac{\Delta G - \Delta H}{T} = \left(\frac{d\Delta G}{d\Gamma}\right)_{p}$$
$$\Delta G - \Delta H = T \left(\frac{d\Delta G}{d\Gamma}\right)_{p}$$
$$\Delta G = \Delta H + T \left(\frac{d\Delta G}{d\Gamma}\right)_{p} \qquad \dots (4)$$

> The equation (4) is known as the Gibb's – Helmholtz equation.

Variation of Free Energy with Temperature at Constant Pressure (Another form Gibbs Helmholtz Equation)

The Gibbs free energy, G is defined as:

$$G = H - TS \qquad \dots \dots (1)$$
Upon differentiation,

$$dG = dH - TdS - SdT$$

$$dG = dH - TdS - SdT \qquad [\because H = E + PV]$$

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

$$dG = TdS + VdP - TdS - SdT \qquad [\because dE + PdV = TdS]$$

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

If the process is isobaric (constant pressure), dP = 0, therefore, equation (2) can be written as:

$$\left(\frac{\partial G}{\partial T_P}\right)_P = -S \qquad \dots (3)$$

Since entropy is always positive, the negative sign indicates that at constant pressure, G decreases with rise in temperature.

If we substitute the value of S in equation (1), we get

$$G = H + T \left(\frac{\partial G}{\partial T}\right)_P \qquad \dots \dots (4)$$

Dividing by T² on both sides gives,

$$\frac{G}{T^2} = \frac{H}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P$$

$$\frac{G}{T^2} - \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P = \frac{H}{T^2} \qquad \dots (5)$$

$$\frac{1}{T} \left(\frac{G}{T} - \left(\frac{\partial G}{\partial T} \right)_P \right) = \frac{H}{T^2}$$

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

On differentiating and neglecting higher terms, we get

$$\left[\frac{d(G/T)}{dT}\right]_{P} = -\frac{H}{T^{2}} \qquad \dots (6)$$

Equation (6) is another form of Gibb's-Helmholtz equation.

Applications of Gibb's-Helmholtz Equation

(i) Calculation of Enthalpy Change of the Reaction (Heat of 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 free energy, then

$$-\Delta G^{\circ} = nFE^{\circ} \qquad \dots \dots (1)$$

Hence, Gibb's-Helmholtz equation is given as:

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

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

$$-nFE^{\circ} = \Delta H - nFT \left(\frac{\partial E^{\circ}}{\partial T} \right)_{P}$$

$$\Delta H = -nFE^{\circ} + nFT \left(\frac{\partial E^{\circ}}{\partial T} \right)_{P}$$

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

≻ Knowing the value of E° and the temperature coefficient ($\partial E^{\circ} / \partial T$) of the cell reaction, it is possible to evaluate the enthalpy change (ΔH) of the reaction.

(ii) Calculation of Entropy Change

 \blacktriangleright Δ H and Δ S are related by the equation:

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

We know that $\Delta G = -nFE^{\circ}$ and ΔH can be calculated by the above equation (2). Hence ΔS can be calculated easily from the above equation (3).

8. CLAPEYRON EQUATION

According to thermodynamics, the change of free energy with change of temperature and pressure is expressed as:

$$d\mathbf{G} = \mathbf{V}d\mathbf{P} - \mathbf{S}d\mathbf{T} \qquad \dots (1)$$

➢ For two phases in equilibrium, we have

$$d\mathbf{G}_1 = \mathbf{V}_1 d\mathbf{P} - \mathbf{S}_1 d\mathbf{T} \qquad \dots (2)$$

$$d\mathbf{G}_2 = \mathbf{V}_2 d\mathbf{P} - \mathbf{S}_2 d\mathbf{T} \qquad \dots (3)$$

> The free energy change for the process at equilibrium

 $\therefore \mathbf{V}_1 d\mathbf{P} - \mathbf{S}_1 d\mathbf{T} = \mathbf{V}_2 d\mathbf{P} - \mathbf{S}_2 d\mathbf{T}$

 $d\mathbf{G}_1 = d\mathbf{G}_2$

On rearranging

...

$$V_{1}dP - V_{2}dP = S_{1}dT - S_{2}dT$$
(or)
$$(V_{1} - V_{2})dP = (S_{1} - S_{2})dT$$

$$\frac{dP}{dT} = \frac{(S_{1} - S_{2})}{(V_{1} - V_{2})}$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad \dots (4)$$

When there is a change of state from solid to liquid (melting), or liquid to vapours (vapourisation), or solid to vapours (sublimation), there is a change in entropy.

If one mole of liquid changes reversibly, it would absorb molar heat of vapourisation (ΔH_V) at a temperature equal to its boiling point. In this case the entropy change is given by:

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

Substituting ΔS in equation (4), we get

(or)
$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$
$$\frac{dP}{dT} = \frac{\Delta H}{T(V_2 - V_1)} \qquad \dots (4)$$

This equation is known as Clapeyron equation.

9. CLAUSIUS-CLAPEYRON EQUATION

> The Clapeyron equation for a liquid – vapour system is written as:

$$\frac{d\mathbf{P}}{d\mathbf{T}} = \frac{\Delta \mathbf{H}_{\mathbf{V}}}{\mathbf{T}(\mathbf{V}_2 - \mathbf{V}_1)}$$

This equation can be simplified by neglecting the small volume of liquid in comparison with the volume of vapour. The equation in such a case becomes:

$$\frac{d\mathbf{P}}{d\mathbf{T}} = \frac{\Delta \mathbf{H}_{\mathbf{V}}}{\mathbf{T}\mathbf{V}_{2}} \qquad \dots (1)$$

Suppose the vapour obeys the ideal gas laws:

$$\mathbf{V}_2 = \frac{RT}{\mathbf{P}}$$

Substituting V_2 in equation (5), we have

$$\frac{dP}{dT} = \frac{\Delta H_V}{T \times \left(\frac{RT}{P}\right)}$$
$$\frac{dP}{dT} = \frac{\Delta H_V \times P}{RT^2} \qquad \dots (2)$$

The equation (2) is known as Clausius–Clapeyron equation.

Integrated Form of Clausius-Clapeyron Equation

By rearranging the above equation, we have

$$\frac{d\mathbf{P}}{\mathbf{P}} = \frac{\Delta \mathbf{H}_{\mathbf{V}}}{\mathbf{R}} \times \frac{d\mathbf{T}}{\mathbf{T}^2}$$

If ΔH is considered as constant, we may integrate the above equation between suitable initial and final limits as:

$$\int_{P_{1}}^{P_{2}} \frac{dP}{P} = \frac{\Delta H_{V}}{R} \int_{T_{1}}^{T_{2}} \frac{dT}{T^{2}}$$

$$\left[\ln P\right]_{P_{1}}^{P_{2}} = \frac{\Delta H_{V}}{R} \times \left[-\frac{1}{T}\right]_{T_{1}}^{T_{2}}$$

$$\left[\ln P_{2} - \ln P_{1}\right] = -\frac{\Delta H_{V}}{R} \times \left[\frac{1}{T_{2}} - \frac{1}{T_{1}}\right]$$

$$2.303 \log \frac{P_{2}}{P_{1}} = \frac{\Delta H_{V}}{R} \times \left[\frac{1}{T_{1}} - \frac{1}{T_{2}}\right]$$

$$\log \frac{P_{2}}{P_{1}} = \frac{\Delta H_{V}}{2.303R} \times \left[\frac{T_{2} - T_{1}}{T_{2}T_{1}}\right] \dots (3)$$

Equation (3) is known as integrated form of Clapeyron – Clausius equation. It can be used to calculate the heat of vapourisation from the vapour pressure data at two different temperatures.

10. SOLVED PROBLEMS

Entropy Change in Isothermal Process

1. One mole of an ideal gas expands isothermally to twice its original volume at 27°C. Calculate the entropy change during the process.

Solution

> Entropy change in an isothermal expansion of an ideal gas is given by:

$$\Delta S = \frac{2.303 \times n \times R \times \log \frac{V_2}{V_1}}{Given: n = 1 \text{ mol} ; V_1 = 1 ; R = 1.987 \text{ cal. } K^{-1} \text{ mol}^{-1} ; V_2 = 2$$
$$\Delta S = \frac{2.303 \times 1 \times 1.987 \times \log \frac{2}{1}}{\Delta S} = 2.303 \times 1.987 \times 0.3010$$
$$\Delta S = 1.3773 \text{ e.u.}$$

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

Solution

> Entropy change in an isothermal expansion of an ideal gas is given by:

$$\Delta S = 2.303 \times n \times R \times \log \frac{V_2}{V_1}$$

Given: 2 mol ;
$$V_1 = 5$$
 litres ; $R = 1.987$ cal. K^{-1} mol⁻¹ ; $V_2 = 50$ litres

$$\Delta S = \frac{2.303 \times 2 \times 1.987 \times \log \frac{50}{5}}{\Delta S} = 2.303 \times 2 \times 1.987 \times 1$$

$$\Delta S = 9.152$$
 e.u.

3. Helium, weighing 4 gm, is expanded from 1 atm to one tenth to the original pressure at 30°C. Calculate the change in its entropy, assuming it to be an ideal gas.

Solution

 \succ We know that:

$$\Delta S = 2.303 \times n \times R \times \log \frac{P_1}{P_2}$$
Number of moles, = Weight (in gm)
n Weight (in gm)
Mol. Wt. = $\frac{4}{4} = 1$ mole
Given: R= 1.987 cal. K⁻¹ mol⁻¹; P₁ = 1 atm; P₂ = $\frac{1}{10}$ atm

$$\Delta S = 2.303 \times 1 \times 1.987 \times \log \frac{1}{\frac{1}{10}}$$

$$\Delta S = 4.57$$
 e.u.

Entropy of Phase Transitions

4. Calculate the entropy change when one mole of water is converted into steam, reversibly, at its boiling point. Latent heat of vapourisation is 540 cal.g⁻¹.

Solution

Given: $L_v = 540 \text{ cal.g}^{-1};$ $\Delta H_v = L_v \times \text{Molecular weight of water}$ $= 540 \times 18 = 9720 \text{ cals.}$

 $T_b = 100 + 273 = 373 \text{ K}$

 ΔS for vaporization is given by:

$$\Delta S_{v} = \frac{\Delta H_{v}}{T_{b}}$$
$$\Delta S_{v} = \frac{9720}{373}$$
$$\Delta S_{v} = 26.06 \text{ e.u.}$$

5. Calculate the entropy change involved when one mole of liquid oxygen is converted into gaseous oxygen at its boiling point of −183°C. Entropy of vaporization of liquid oxygen is 6.82 J.

Solution

Given: $\Delta H_v = 6.82 \text{ J}; \qquad T_b = -183 + 273 = 90 \text{ K}$

 Δ S for vaporization is given by:

$$\Delta S_{\nu} = \frac{\Delta H_{\nu}}{T_{b}}$$
$$\Delta S_{\nu} = \frac{6.82}{90}$$
$$\Delta S_{\nu} = 0.0757 \text{ e.u.}$$

6. Calculate the entropy changes for the fusion and vaporization of one mole of water at normal melting point (273 K) and at normal boiling point (373K). The molar enthalpy of fusion = 6.01 kJ mol^{-1} and the molar enthalpy of vaporization = $40.79 \text{ kJ mol}^{-1}$.

Given:

$$\Delta H_{\text{fusion}} = 6.01 \text{ kJ mol}^{-1} \text{ or } 6010 \text{ J mol}^{-1}; \qquad T_{\text{fusion}} = 273 \text{ K}$$

$$\Delta H_v = 40.79 \text{ kJ mol}^{-1} \text{ or } 40790 \text{ J mol}^{-1}; \qquad T_v = 373 \text{ K}$$
(i) ΔS for fusion is given by:

$$\Delta S_f = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

$$\Delta S_f = \frac{6010}{273}$$

$$\Delta S_f = 22.01 \text{ JK}^{-1} \text{ mol}^{-1}.$$
(ii) ΔS for vaporization is given by:

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

$$\Delta S_{\nu} = \frac{40790}{373}$$
$$\Delta S_{\nu} = 109.3 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Free Energy Change and Spontaneity

 Predict whether the following reaction is spontaneous at 25°C.
 C (g) + H₂O (l)→CO (g) + H₂ (g) ΔH = 31.4 k cal / mol and ΔS = 32 cal / deg at 25°C.

Solution

Given:

 $\Delta H = 31.4$ kcals (or) 31,400 cals; $\Delta S = 32$ cals deg⁻¹; T = 25 + 273 = 298 K

The free energy change is expressed as:

 $\Delta G = \Delta H - T\Delta S$ $\Delta G = 31,400 - 298 (32)$ $\Delta G = 31,400 - 9,536$ $\Delta G = 21,864 \text{ cal mole}^{-1} (\text{or}) 21.86 \text{ kcal mole}^{-1}.$

Since ΔG is positive, the reaction is not spontaneous.

8. ΔH and ΔS for a reaction at 27°C are -10 kcals and 20 cals K⁻¹ respectively. What is ΔG for the reaction? Predict whether the reaction will be feasible or not?

Solution

Given:

 $\Delta H = -10$ kcals (or) -10,000 cals; $\Delta S = 20$ cals K⁻¹; T = 27 + 273 = 300 K

The free energy change is expressed as:

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

$$\Delta G = -10,000 - 300 (20)$$

$$\Delta G = -16,000$$

$$\Delta G = -16 \text{ kcals}$$

As ΔG is negative, the reaction is feasible.

9. ΔG for a reaction at 300 K is - 16 kcals. ΔH for the reaction is - 10 kcals. What is the entropy of the reaction and what will be ΔG at 330 K?

Solution

Given: $\Delta G = -16$ kcals; $\Delta H = -16$ kcals; T = 300 K

The free energy change is expressed as:

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

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

$$\Delta S = \frac{-10 - (-16)}{300}$$

$$\Delta S = 0.02 \text{ kcals K}^{-1}.$$
At 330 K
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -10 - 330 (0.02)$$

$$\Delta G = -16.6 \text{ kcals}.$$

Gibbs-Helmholtz Equation

10. The free energy change, ΔG for a process is -138 at 30°C and -135 kJ at 40°C. Calculate the change in entropy and ΔH accompanying the process at 35°C.

Solution

$$\Delta G_1 = -138 \text{ kJ}; \quad \Delta G_2 = -135 \text{ kJ}; \quad d\Delta G = \Delta G_2 - \Delta G_1 = -135 - (-138) = 3 \text{ kJ};$$

$$T_1 = 30^{\circ}\text{C} = 273 + 30 = 303 \text{ K}; \quad T_2 = 40^{\circ}\text{C} = 273 + 40 = 313 \text{ K};$$

$$dT = T_2 - T_1 = 313 - 303 = 10 \text{ K}$$

According to Gibbs-Helmholtz equation:

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

The change in free energy ΔG at 35°C may be taken as the average value of ΔG at 30°C and 40°C.

$$T = \left(\frac{T_1 + T_2}{2}\right) = \frac{303 + 313}{2} = 308 \, K$$

The free energy change is expressed as:

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

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

$$\Delta S = \frac{-228.9 - (-136.5)}{308}$$

$$\Delta S = \frac{-92.4}{308}$$

$$\Delta S = -0.3 \text{ kJ K}^{-1}$$

$$\Delta S = -300 \text{ JK}^{-1}$$

11. Gibbs free energy of a reaction at 300 K and 310 K are -29 kcals and -29.5 kcals respectively. Determine its ΔH and ΔS at 300 K.

Solution

Given:

 $\Delta G_1 = -29 \text{ kcals}; \quad \Delta G_2 = -29.5 \text{ kcals}; \quad d\Delta G = \Delta G_2 - \Delta G_1 = -29.5 - (-29)$

= -0.5 kcals; $T_1 = 300$ K; $T_2 = 310$ K; $dT = T_2 - T_1 = 310 - 300 = 10$ K

According to Gibbs-Helmholtz equation:

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

 $\therefore \Delta H$ at 300 K,

$$-29 = \Delta H + 300 \left(\frac{-0.5}{10}\right)$$
$$-29 = \Delta H - 15$$
$$\Delta H = -29 + 15$$
$$\Delta H = -14 \text{ kcals}$$

The free energy change is expressed as:

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

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

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

$$\Delta S = \frac{15}{300}$$

$$\Delta S = 0.05 \text{ kcals K}^{-1}$$

$$\Delta S = 50 \text{ cals K}^{-1}$$

Applications of Gibbs-Helmholtz Equation

12. Calculate ΔG° for a Daniel cell, Zn/ZnSO₄//CuSO₄//Cu at 25°C. Given E° = 1.1V.

Solution

Given:

 $E_{cell}^{o} = +1.1V$; n= 2; F = 96,500 Coulombs

We know that:

 $\Delta G = -nFE^{\circ}_{cell}$ $\Delta G = -2 \times 96500 \times 1.1$ $\Delta G = -212300 \text{ (Coulombs × Volts = Joules)}$ $\Delta G = -212.3 \text{ kJ}$

Since ΔG is negative, the reaction is spontaneous.

13. The emf of a standard cadmium cell at 298 K is 1.01832 V and the temperature coefficient of emf of cell is -5.0×10^{-5} VK⁻¹. Calculate the values of Δ G, Δ H and Δ S for the cell reaction.

Solution

Given:

$$E_{cell} = 1.01832 \text{ V}; \quad n = 2; \quad \left(\frac{\partial E_{cell}}{\partial T}\right) = -5.0 \times 10^{-5} \text{ V K}^{-1}; \quad T = 298 \text{ K}$$

We know that:

$$\Delta G = -nFE_{cell}$$

$$\Delta G = -2 \times 96500 \times 1.01832 \text{ (coulombs } \times \text{ volts } = \text{ joules)}$$

$$\Delta G = -19653 \text{ J (or) } -196.53 \text{ kJ}$$

From the Gibbs-Helmholtz equation:

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

$$\Delta H = -2 \times 96500 \left[1.01832 - (298 \times -5 \times 10^{-5}) \right]$$

$$\Delta H = -2 \times 96500 \left[1.01832 - (-0.0149) \right]$$

$$\Delta H = -2 \times 96500 \left[1.01832 + 0.0149 \right]$$

$$\Delta H = -2 \times 96500 \times 1.03322$$

$$\Delta H = -199411.4 \text{ J (or)} - 199.4 \text{ kJ}$$

Further we know that:

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

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

$$\Delta S = \frac{-199.4 - (-196.5)}{298}$$

$$\Delta S = \frac{-2.9}{298}$$

$$\Delta S = -0.0097 \text{ kJ. K}^{-1} \text{ (or)} - 9.7 \text{ J.K}^{-1}$$

14. Calculate ΔG° for the cell reaction at 25°C, Zn + FeSO₄ \rightarrow Fe + ZnSO₄. The standard reduction potentials are $E^{\circ}(z_n^{2+}/z_n) = -0.76$ V and $E^{\circ}(Fe^{2+}/Fe) = -0.44$ V. Predict whether the reaction is spontaneous.

Given:

$$E_{Zn^{2+}/Zn}^{o} = -0.76V$$
; $E_{Fe^{2+}/Fe}^{o} = -0.44V$; $n=2$; $F = 96,500$ Coulombs

In the given system, Zn acts as anode and Fe acts as cathode.

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

$$E_{cell}^{\circ} = E_{Fe^{2+}/Fe}^{o} - E_{Zn^{2+}/Zn}^{o} = -0.44 - (-0.76) = +0.32 \text{ V}$$
We know that:

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

$$\Delta G = -2 \times 96500 \times 0.32$$

$$\Delta G = -61760 \text{ (Coulombs × Volts = Joules)}$$

$$\Delta G = -61.76 \text{ kJ}$$

Since ΔG is negative, the reaction is spontaneous.

Clausius-Clapeyron Equation

15. The vapour pressure of water at 100°C is 760 mm. What will be the vapour pressure at 95°C? The heat of vapourisation of water in the temperature range is 41.27 kJ mol⁻¹.

Solution

Given:

 $P_1 = 760 \text{ mm};$ $T_1 = 100 + 273 = 373 \text{ K};$ $T_2 = 95 + 273 = 368 \text{ K};$

 $\Delta H_V = 41.27 \text{ kJ mol}^{-1}$ or 41270 J mol}{-1}; R = 8.314 JK^{-1} mol^{-1}. The Clapeyron-Clausius equation for liquid-vapour equilibria is given by:

$$\log \frac{P_2}{P_1} = \frac{\Delta H_V}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$
$$\log \frac{P_2}{760} = \frac{41270}{2.303 \times 8.314} \left[\frac{368 - 373}{368 \times 373} \right]$$
$$\log P_2 - \log 760 = \frac{-206350}{2628213}$$
$$\log P_2 = -0.0785 + \log 760$$
$$\log P_2 = -0.0785 + 2.8808$$
$$\log P_2 = 2.8023$$
$$P_2 = \text{antilog of } 2.8023$$
$$P_2 = 634.3 \text{ mm.}$$

16. The vapour pressures of water at 95°C and 100°C are 634 and 760 mm, respectively. Calculate the molar heat of vapourisation, ∆Hv of water between 95°C and 100°C.

Solution

Given: $P_1 = 634 \text{ mm};$ $P_2 = 760 \text{ mm};$ $T_1 = 95 + 273 = 368 \text{ K};$ $T_2 = 100 + 273 = 373 \text{ K};$ $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}.$ The vapour pressures at different temperatures and molar heat of vapourisation are related by the equation:

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{760}{634} = \frac{\Delta H_v}{2.303 \times 8.314} \left[\frac{373 - 368}{368 \times 373} \right]$$

$$0.0787 = \frac{\Delta H_v}{19.1471} \left[\frac{5}{137264} \right]$$

$$\Delta H_v = \frac{0.0787 \times 19.1471 \times 137264}{5}$$

$$\Delta H_v = 41368 \text{ Jmol}^{-1} \text{ (or) } 41.368 \text{ kJ mol}^{-1}.$$

11.CHEMICAL POTENTIAL (or) PARTIAL MOLAR FREE ENERGY

Expression for Chemical Potential in terms of other Quantities

Let us consider the extensive property, free energy (G).

Suppose the system consists of 'n' constituents (in solution or in a heterogeneous system) and let the amount of each constituent in the system be $n_1, n_2, n_3 \dots$ moles.

Therefore, the property G is a function of not only temperature and pressure but also the amounts of different constituents present in the system. Hence, we have:

$$\boldsymbol{G} = \boldsymbol{f}(\boldsymbol{T}, \boldsymbol{P}, \boldsymbol{n_1}, \boldsymbol{n_2}, \boldsymbol{n_3} \dots) \quad \dots (1)$$

If there is a small change in the temperature, pressure and the amounts of the different constituents, then the change in the property G is given by:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,n_3\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,n_3\dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \dots \quad (2)$$

In equation (2), the first term on the right hand side gives the change in the value of G with temperature when pressure and compositions of different constituents are kept constant; the second term gives the change in the value of G with pressure when the temperature and compositions of different constituents are kept constant; and the remaining quantities in the right hand side gives the change in the value of G with a change in the amount of a constituent when temperature, pressure and the amounts of other constituents are kept constants.

If the temperature and pressure of the system are kept constant, then dT = 0 and dP = 0. Therefore, the equation (2) becomes:

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 + \dots \quad (3)$$

Each derivative on the right-hand side is called partial molar property and is represented by putting a bar over the symbol of that particular property i.e.: \bar{G}_1 , \bar{G}_2 , \bar{G}_3 for the 1st, 2nd and 3rd constituents respectively. Therefore, we have:

$$\bar{G}_{1} = \left(\frac{\partial G}{\partial n_{1}}\right)_{T,P,n_{2},n_{3}\dots}$$
$$\bar{G}_{2} = \left(\frac{\partial G}{\partial n_{2}}\right)_{T,P,n_{1},n_{3}\dots}$$
$$\bar{G}_{3} = \left(\frac{\partial G}{\partial n_{3}}\right)_{T,P,n_{1},n_{2}\dots}$$
and so on....

In general, for the component 'i', we have:

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2\dots}\dots(4)$$

In equation (4), the quantity \bar{G}_i is called as the *partial molar free energy or chemical potential and* is usually represented by the symbol μ .

$$\boldsymbol{\mu}_{i} = \overline{\boldsymbol{G}}_{i} = \left(\frac{\partial \boldsymbol{G}}{\partial \boldsymbol{n}_{i}}\right)_{T,P,\boldsymbol{n}_{1},\boldsymbol{n}_{2}...} \dots (5)$$

Using the definition of μ_i or \overline{G}_i , the equation (3) can be written as:

$$(dG)_{T,P,N} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots \quad (6)$$

Where, the subscript N stands for constant composition.

In equation (6), on the right-hand side, the first term gives the contribution of the first constituent to the total free energy of the system; the second term gives the contribution of the second constituent to the total free energy of the system and so on...

Obviously, μ_1 , μ_2 , μ_3 etc. give the contribution per mole to the total free energy.

Therefore, the chemical potential of a constituent may be defined as "the chemical potential of a constituent in a mixture is its contribution to the total free energy of the system of a constant composition at constant temperature and pressure".

It may also be noted that, the free energy is an extensive property, but the *chemical potential is an intensive property because it refers to one mole of the substance*.

12.GIBBS-DUHEM EQUATION

Let us consider the extensive property, free energy (G).

Suppose the system consists of 'n' constituents (in solution or in a heterogeneous system) and let the amount of each constituent in the system be $n_1, n_2, n_3 \dots$ moles.

Therefore, the property G is a function of not only temperature and pressure but also the amounts of different constituents present in the system. Hence, we have:

$$G = f(T, P, n_1, n_2, n_3 \dots) \dots (1)$$

If there is a small change in the temperature, pressure and the amounts of the different constituents, then the change in the property G is given by:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,n_3\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,n_3\dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \dots \quad (2)$$

In equation (2), the first term on the right hand side gives the change in the value of G with temperature when pressure and compositions of different constituents are kept constant; the second term gives the change in the value of G with pressure when the temperature and compositions of different constituents are kept constant; and the remaining quantities in the right hand side gives the change in the value of G with a change in the amount of a constituent when temperature, pressure and the amounts of other constituents are kept constants.

If the temperature and pressure of the system are kept constant, then dT = 0 and dP = 0. Therefore, the equation (2) becomes:

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3\dots} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_1,n_2\dots} dn_3 + \dots$$
(3)

Each derivative on the right-hand side is called partial molar property and is represented by putting a bar over the symbol of that particular property i.e.: \bar{G}_1 , \bar{G}_2 , \bar{G}_3 for the 1st, 2nd and 3rd constituents respectively. Therefore, we have:

$$\bar{G}_{1} = \left(\frac{\partial G}{\partial n_{1}}\right)_{T,P,n_{2},n_{3}\dots}$$
$$\bar{G}_{2} = \left(\frac{\partial G}{\partial n_{2}}\right)_{T,P,n_{1},n_{3}\dots}$$
$$\bar{G}_{3} = \left(\frac{\partial G}{\partial n_{3}}\right)_{T,P,n_{1},n_{2}\dots} and so on\dots$$

In general, for the component 'i', we have:

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2\dots} \dots (4)$$

In equation (4), the quantity \overline{G}_i is called as the *partial molar free energy or chemical potential and* is usually represented by the symbol μ .

$$\mu_i = \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2\dots} \dots (5)$$

Using the definition of μ_i or \overline{G}_i , the equation (3) can be written as:

$$(dG)_{T,P,N} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots \quad (6)$$

For a system of definite composition, represented by the number of moles n_1 , n_2 , n_3 ... etc. the equation (6) on integration gives:

$$G_{T,P,N} = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots$$
 (7)

Differentiating the equation (7) under the conditions of constant temperature and pressure but varying composition, we get:

$$(dG)_{T,P} = (\mu_1 dn_1 + n_1 d\mu_1) + (\mu_2 dn_2 + n_2 d\mu_2) + (\mu_3 dn_3 + n_3 d\mu_3)... \quad \dots (8)$$

Comparing equations (6) and (8), we get:

$$\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots$$

= $(\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots) + (n_1 d\mu_1 + n_2 d\mu_2) + n_3 d\mu_3) \dots$
 $n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 \dots = 0$

(or)

$$\sum n_i d\mu_i = 0 \quad \dots (9)$$

Equation (9) is applicable to a system at constant temperature and pressure, and is called as *Gibbs-Duhem equation*.

13.VARIATION OF CHEMICAL POTENTIAL WITH TEMPERATURE AND PRESSURE

In order to study the variation of chemical potential with temperature and pressure, let us first derive the expressions for the variation of free energy with T and P.

We know that, the free energy is a function of T, P and composition of a system.

$$\boldsymbol{G} = \boldsymbol{f}(\boldsymbol{T}, \boldsymbol{P}, \boldsymbol{n_1}, \boldsymbol{n_2}, \boldsymbol{n_3} \dots) \quad \dots (1)$$

If there is a small change in the temperature, pressure and the amounts of the different constituents, then the change in the property G is given by:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,n_3\dots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,n_3\dots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3\dots} dn_1 + \dots \quad (2)$$

If a system is closed one, there is no change in the number of moles of various constituents present in the system and hence dn_1 , dn_2 , dn_3 ...etc. will be zero.

Therefore, the equation (2) reduces to:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N,} dP \dots$$
(3)

For a closed system, we also know that, the total differential equation is given by:

$$dG = VdP - SdT$$
$$dG = -SdT + VdP \dots (4)$$

Comparing the coefficients of equations (3) and (4), we have:

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N} \quad \dots (5)$$
$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \quad \dots (6)$$

The equations (5) and (6) gives the variation of free energy with T and P for a closed system.

14.FUGACITY, ACTIVITY AND ACTIVITY COEFFICIENT

Fugacity may be defined as a substitute for pressure to explain the behaviour of real gas and activity is defined as the substitute for the concentration to explain the behaviour of a non-ideal solution.

Thus, in a mixture of real gasses, the chemical potential μ_i of any constituent *i* is given by:

$$\mu_i = \mu_i^o + RT ln f_i \quad \dots (1)$$

Where f_i is the fugacity of the constituent *i* in the mixture.

Similarly, in a non-ideal solution, the chemical potential μ_i of any constituent *i* is given by:

$$\mu_i = \mu_i^o + RT lna_i \quad \dots (2)$$

Where a_i is the fugacity of the constituent *i* in the mixture.

Thus, to explain the behaviour of real gases, the pressure has to be corrected by multiplying with a suitable factor to get the fugacity, that is:

$$f = \gamma \times P \quad \dots (3)$$

Where γ is called the activity coefficient of the gas.

From equation (3), we have:

$$\gamma = \frac{f}{P} \quad \dots (4)$$

Hence, the activity coefficient of a gas may be defined as the ratio of the fugacity of the gas to the pressure of the gas in the same state.

Similarly, in a non-ideal solution, the concentration has to be corrected by multiplying with a suitable factor to get the activity, that is:
$$a = \gamma \times C \quad \dots (5)$$

Where γ is called the activity coefficient of a component in the solution whose concentration is *C*.

From equation (5), we have:

$$\gamma = \frac{a}{C} \quad \dots (6)$$

Hence, the activity coefficient of any component in the solution may be defined as the ratio of the activity of that component in the solution to the concentration of the same component in the solution.

15.DUHEM-MARGULES EQUATION

Suppose a binary is having n_1 moles of A and n_2 moles of B. On applying Gibbs-Duhem relation to this solution, we have:

(or)
$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\frac{n_1}{n_1 + n_2} d\mu_1 + \frac{n_2}{n_1 + n_2} d\mu_2 = 0$$

(or)

$$x_1d\mu_1 + x_2d\mu_2 = 0$$

Where x_1 and x_2 represent mole-fractions such that $x_1 + x_2 = 1$.

But

$$d\mu = RTd(lnf)$$

$$\therefore x_1RTd(lnf_1) + x_2RTd(lnf_2) = 0$$

$$x_1d(lnf_1) + x_2d(lnf_2) = 0$$

(or)

$$\frac{x_1}{dx_1}d(lnf_1) - \frac{x_2}{dx_2}d(lnf_2) = 0$$

since $dx_1 + dx_2 = 0$

(or)

$$\frac{dlnf_1}{dlnx_1} = \frac{dlnf_2}{dlnx_2}$$

since $dlnx = \frac{dx_1}{x_1}$

Similarly, it can be proved for a solution having mole fractions x1, x2, ... of various species present in it. Hence,

$$\frac{dlnf_1}{dlnx_1} = \frac{dlnf_2}{dlnx_2} = \frac{dlnf_2}{dlnx_2} = \dots$$

This equation is known as Duhem-Margules equation.

16.THIRD LAW OF THERMODYNAMICS

Statement of Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of all perfectly crystalline solids may be taken as zero at the absolute zero temperature.

Nernst Heat Theorem

Nernst heat theorem gives the variation of enthalpy change (ΔH) and the free energy change (ΔG) of a system with decrease of temperature.

According to Gibbs-Helmholtz equation:

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

It is evident from this equation that at absolute zero, that is, when T = 0, $\Delta G = \Delta H$. However, Nernst observed that as the temperature is lowered towards absolute zero, the value of $\frac{\partial \Delta G}{\partial T}$ decreases and then approaches zero asymptotically. This means that ΔG and ΔH are not only equal to the absolute zero but the values approach each other asymptotically in the vicinity of this temperature. This result is known as Nernst heat theorem. Mathematically, it may be expressed as:

$$\lim_{T \to 0} \left(\frac{\partial \Delta G}{\partial T} \right)_P = \lim_{T \to 0} \left(\frac{\partial \Delta H}{\partial T} \right)_P$$

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REVIEW QUESTIONS

PART – A QUESTIONS

- 1. State second law of thermodynamics. Calculate the entropy change for the reversible isothermal expansion of 10 moles of an ideal gas to 50 times its original volume at 298K.
- 2. Define entropy for an ideal gas.
- 3. Define entropy.
- 4. What happens to entropy of the following? (a) A gaseous nitrogen is converted to liquid nitrogen (b) Solid iodine is sublimed to its vapour.
- 5. What is the significance of decrease in free energy?
- 6. Differentiate free energy and work function.
- 7. State third law of thermodynamics.

- 8. State Nernst heat theorem.
- 9. Define the term fugacity.
- 10. Define the term activity coefficient.
- 11. Define partial molar free energy.

PART – B QUESTIONS

- 1. Calculate the efficiency of a Carnot engine working between two temperatures T_1 and T_2 .
- 2. Derive the expression of entropy change in (i) a reversible process and (ii) an irreversible process.
- 3. Derive the expression of entropy change for an ideal gas (i) as a function of temperature and pressure and (ii) as a function of temperature and volume.
- 4. Derive the expression of the entropy change for an isothermal process.
- 5. Explain the relation between free energy and spontaneity.
- 6. Discuss the criteria for a chemical reaction to be spontaneous.
- 7. Derive Gibbs-Helmholtz equation and mention its applications.
- 8. Derive Clausius-Clapeyron equation for liquid-vapour equilibria.
- 9. Derive expressions for variation of chemical potential (i) with temperature and (ii) with pressure.
- 10. Derive Gibbs-Duhem equation.



SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – II – Electrochemistry-II – SCY1316

1. INTRODUCTION

Electrochemistry is a branch of physical chemistry, which deals with the relationship between chemical energy and electrical energy. The knowledge of electrochemistry is essential for understanding various electrochemical processes such as Batteries and Fuel cells, Corrosion and its prevention, Industrial metal finishing etc.

2. ELECTRODE POTENTIAL AND ELECTROCHEMICAL CELLS

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

Galvanic Cell

In a galvanic cell, a zinc rod is partially immersed in $1M ZnSO_4$ solution and a copper rod is partially immersed in $1M CuSO_4$ solution. The two solutions are interconnected by a salt bridge. The salt bridge is a U-tube containing saturated KCl or NH_4NO_3 in agar-agar gel. The salt bridge provides electrical contact between two compartments.



Fig. 2.1: Galvanic Cell

It also helps to maintain electrical neutrality by allowing the migration of ions. If zinc and copper rods are connected from outside, electrons flow from zinc to copper since zinc atoms are oxidised and copper atoms are reduced. The flow of electrons are indicated by ammeter placed in the circuit (Fig. 2.1).

Daniel Cell

The practical application of an electrochemical cell is Daniel cell. It consists of zinc rod dipped in ZnSO₄ solution and a copper rod dipped in CuSO₄ solution. The two solutions are separated by a porous pot. The two solutions can seep through the pot and so come into contact with each other automatically. Here the porous pot acts as salt bridge (Fig. 2.2).

The electrode reaction occurs in the Daniel cell are,

At anode (negative electrode) $Zn \rightarrow Zn^{2+} + 2e$

At cathode (positive electrode) $Cu^{2+} + 2e \rightarrow Cu$



Fig. 2.2: Daniel Cell

Representation of a cell

- (i) A cell consists of two electrodes namely anode and cathode
- (ii) The anode half cell must be represented always on the left side while the cathode half cell must be represented always on the right side.
- (iii) The anode half cell must be written by writing metal first and then electrolyte. The two must be separated by a vertical line or a semicolon

Example : M/M^{n+} or M; M^{n+}

(iv) The cathode half cell must be written by writing electrolyte first and then the metal. The two must be separated by a vertical line or a semicolon.

Example : M^{n+}/M or M^{n+} ; M

- (v) The electrolyte may be represented by whole formula or its ionic species. The concentration of the electrolyte may also be represented in bracket.
- (vi) A salt bridge is indicated by two vertical lines (||) separating the two half cells.

Applying the above rules to a galvanic cell, we can represent it as,

 $Zn / ZnSO_4 (1M) \parallel CuSO_4 (1M) / Cu.$

or $Zn / Zn^{2+} (1M) \parallel Cu^{2+} (1M) / Cu.$

or Zn; $Zn^{2+}(1M) \parallel Cu^{2+}(1M)$; Cu.

3. ORIGIN OF ELECTRODE POTENTIAL

All metals consist of positive metallic ions and their valency electrons. When a metal is placed in a solution of its own salt, the positive metal ions pass into the solution leaving behind its valency electrons on the metal itself and making it negatively charged. This tendency is known as solution pressure of metal. Different metals have different solution pressures.

The negative charge developed on the metal attracts positive metal ions from solution, and a layer forms close to the metal. The layer formed around the negatively charged metal is called as electrical double layer (edl). The edl prevents further transfer of positive metal ions from the metal and the equilibrium state is reached with some definite value of potential difference. The potential difference of edl formed at the interface of the metal and electrolyte is called electrode potential.

In certain cases, when a metal is placed in a solution on its own salt, the positive metal ions from the solution deposit over the metal and gain electrons (remove the electrons from the metal) and making it positively charged. [Metal = Positive ion + Electrons]. This tendency is known as osmotic pressure of solution.

The positive charge developed on the metal attracts negative ions from solution, and forms a layer close to the metal. This edl prevents further deposition of positive ions from the solution and an equilibrium state is reached with some definite value of potential difference (Fig. 2.3). This potential difference of edl is also known as electrode potential.



Fig. 2.3: Formation of Electrical Double Layer

Therefore, electrode potential is defined as "the measure of tendency of a metallic electrode to loose or gain electrons when in contact with a solution of its own salt."

According to Nernst's solution pressure theory, if the solution pressure of metal is greater than osmotic pressure of solution, the metal becomes negatively charged. This electrode is called anode and the potential difference of the metal and solution is called as oxidation potential. If the osmotic pressure of solution is greater than the solution pressure of metal, the metal becomes positively charged. This electrode is called as cathode and the potential difference of the metal and solution is called as reduction potential.

Single electrode potential (E)

It is defined as "the measure of tendency of a metallic electrode to loose electrons (oxidation or decomposition) or gain electrons (reduction or discharged) when in contact with a solution of its own salt is called single electrode potential of a metal".

Standard electrode potential (E°)

It is defined as "the measure of tendency of a metallic electrode to lose or gain electrons when in contact with a solution of its own salt of 1 molar concentration at 25° C".

4. REFERENCE ELECTRODES

To determine the electrode potential it is necessary to have another electrode whose single electrode potential (half cell potential) is accurately known. This electrode is called "reference electrode". The two half cells can then be combined to form a Voltaic cell, the emf (electromotive force or net cell potential) of which can be directly measured.

(i) Primary Reference Electrode

Eg: Standard Hydrogen Electrode (SHE)

The primary reference electrode is the normal or standard hydrogen electrode (NHE or SHE). This can be prepared by bubbling hydrogen gas of 1 atmospheric pressure over platinised platinum, immersed in a solution of HCl containing 1 M H^+ ions of unit activity. The electrode potential of SHE is zero at all temperatures (Fig. 2.4).

E°=0 Volt.

It is represented as

Pt, H₂ (1 atm) / H⁺ (1 M)

The cathodic reaction is

 $2H^+ + 2e \rightarrow H_2$



Fig. 2.4: Standard Hydrogen Electrode (SHE)

(ii) Secondary Reference Electrode

Eg: Saturated Calomel Electrode (SCE)

SCE is an example of secondary reference electrode. It is a glass tube containing mercury at the bottom over which mercurous chloride is placed. The rest of the vessel is filled with saturated solution of KCl. The bottom of the tube is sealed with a platinum wire. The upper end is closed with cork (Fig. 2.5). Its electrode potential at 25° C is +0.2422 V. It is represented as

Hg / Hg₂Cl₂, satd KCl $E^{\circ} = +0.2422$ Volt

The cathodic reaction is

 $Hg_2Cl_2 + 2e \rightarrow 2Hg + 2Cl^-$



Fig. 2.5: Saturated Calomel Electrode (SCE)

The potentials of three calomel electrodes are

(i) Hg/Hg_2Cl_2 , 0.1 NKCl	+ 0.3350 V
(ii) Hg / Hg ₂ Cl ₂ , 1 NKCl	+ 0.2810 V
(iii)Hg / Hg ₂ Cl ₂ , Satd KCl	+ 0.2422 V

5. DETERMINATION OF SINGLE ELECTRODE POTENTIAL

Single electrode potential of a metal is defined as "the measure of its ability to loose or gain electrons when in contact with a solution of its own salt".

Absolute value of single electrode potential cannot be determined. However, potential difference of two half cells i.e., emf of a cell can be determined by using a voltmeter. Therefore single electrode potential of any electrode is obtained by coupling the electrode with standard hydrogen electrode (SHE). Since single electrode potential of standard hydrogen electrode is zero at all temperatures, the measured emf of the cell is the single electrode potential of the other electrode.

According to IUPAC convention, the term single electrode potential is reserved exclusively for half cell reactions written as reduction direction and is generally reported as reduction potential.

According to IUPAC convention, during single electrode potential determination, reference electrode, SHE should be kept at left and hence the single electrode potential of other electrodes are reported as electrode reduction potentials.

$$E_{right} - E_{left} = \pm emf$$

or

$$E_{right} = \pm emf \qquad [:: E_{left} = 0]$$

Since $E_{left} = 0$, the measured emf is the reduction potential of the other electrode.

The positive sign of the measured emf indicates that the reaction proceeds in the forward direction with respect to standard hydrogen electrode. i.e., The reduction reaction is feasible with respect to SHE and hence the electrode acts as cathode with respect to SHE (SHE which acts as anode). The negative sign of the measured emf indicates that the reaction proceeds in the opposite direction with respect to SHE i.e., The reduction reaction is not feasible with respect to SHE, and hence the electrode acts as cathode.



Fig. 2.6a: Determination of Single Electrode Potential



Fig. 2.6b Determination of Single Electrode Potential

(i) If zinc electrode is coupled with SHE, keeping SHE in the left, emf is observed to be -0.76 V. (Fig. 2.6a).

i.e., $-0.76 V = E^{\circ}_{Zn^{2+}Zn} - E^{\circ}_{SHE}$

$$\therefore E^{\circ}_{Zn^{2+}/Zn} = -0.76 \text{ V}$$
 [:: $E^{\circ}_{SHE} = 0$]

(ii) If copper electrode is coupled with SHE, Keeping SHE in the left, emf is observed to be + 0.34 V. (Fig. 2.6b).

i.e., $+ 0.34 \text{ V} = E^{\circ}_{Cu^{2+}/Cu} - E^{\circ} \text{ SHE}$

:.
$$E^{\circ}_{Cu^{2+}/Cu} = +0.34 \text{ V}$$
 [:: $E^{\circ}_{SHE} = 0$]

6. ELECTROCHEMICAL SERIES (or) EMF SERIES

Electrochemical Series or Emf Series: The arrangement of various metals in the order of increasing values of standard reduction potentials is called as electrochemical series.

Applications of Electrochemical Series

1. Relative ease of oxidation or reduction: Higher the value of standard reduction potential, the greater is the tendency to get reduced form.

(a) The positive sign of reduction potential indicates that the electrode reaction occurs in forward direction, i.e., reduction direction. The fluoride has higher positive value of standard reduction potential (+2.65V) shows higher tendency towards reduction.

(b) The negative sign of reduction potential indicates that the electrode reaction occurs in opposite direction i.e., backward direction. It means, the reduced form has a greater tendency to loose electrons and get oxidised. Thus Lithium (-3.01 V) has highest negative reduction potential and shows higher tendency to lose electrons.

. Displacement of one species by the other

The metal with more negative reduction potential can displace those metals with less negative or positive potentials from their solution.

For example, we can know whether copper will displace zinc from solution or vice versa. We know that $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V and $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ V. Therefore Cu²⁺ has much greater tendency to get Cu-form than Zn²⁺, for getting Zn – form. In other words zinc will displace copper from its solution.

3. Calculation of standard emf of the cell

Using E° of anode half cell and cathode half cell, the standard emf can be calculated.

 E° cell or standard emf of a cell = $E^{\circ}_{Cathode} - E^{\circ}_{anode}$

4. Predicting feasibility or spontaneity of the cell

In a reversible cell, when the cell yields electrical energy, there is a fall in free energy (or) – $\Delta G = nFE$..

- (a) If ΔG = Negative; E = Positive. Then the cell reaction is feasible.
- (b) If ΔG = Positive; E = Negative. Then the cell reaction is non spontaneous (not feasible).
- (c) If $\Delta G = 0$; E = 0. Then the cell reaction has the equilibrium.

5. Determination of equilibrium constant for the reaction

Standard electrode potential can be used to determine equilibrium constant for the reaction. We know that

 $-\Delta G^{\circ} = RT In k = 2.303 RT log k$

$$\log k = \frac{-\Delta G^{\circ}}{2.303RT}$$
$$\log k = \frac{nFE^{\circ}}{2.303RT} \qquad [\because -\Delta G^{\circ} = nFE^{\circ}]$$

So, from the value of E° for a cell reaction, its equilibrium constant can be calculated.

Table 2.1: Standard Electrode Potential (Half Cell Potential) of some Metals with respect to SHE at $25^\circ C$

Half Cell Reaction	E°, Volts Vs SHE	Half cell Representa-tion	
$Li^+ + e \Leftrightarrow Li$	- 3.01	Li ⁺ / Li	Anodic
$Mg^{2+} + 2e \Leftrightarrow Mg$	- 2.37	Mg^{2+}/Mg	▲
$Al^{3+} + 3e \Leftrightarrow Al$	- 1.66	Al ³⁺ / Al	
$Pb^{2+} + 2e \iff Pb$	- 1.12	Pb ²⁺ / Pb	
$Zn^{2+} + 2e \Leftrightarrow Zn$	- 0.76	Zn^{2+} / Zn	
$Fe^{2+} + 2e \iff Fe$	- 0.44	Fe ²⁺ / Fe	
$Cd^{2+} + 2e \Leftrightarrow Cd$	- 0.40	Cd^{2+}/Cd	
$\operatorname{Sn}^{2+} + 2e \Leftrightarrow \operatorname{Sn}$	-0.13	Sn ²⁺ / Sn	
$2H^+ + 2e \iff H_2$	0.00	$2H^+ / Pt, H_2$	Reference
$Cu^{2+} + 2e \Leftrightarrow Cu$	+ 0.34	Cu ²⁺ / Cu	
$Ag^+ + 2e \iff Ag$	+ 0.80	Ag ⁺ / Ag	
$Pt^{4+} + 4e \iff Pt$	+ 0.86	Pt ⁴⁺ / Pt	
$Au^+ + e \iff Au$	+ 1.50	Au ⁺ / Au	
$\frac{1}{2}F_2 + e \Leftrightarrow F^-$	+ 2.65	$1/2 F_2 / F^-$	Cathodic
		1	

7. RELATION BETWEEN ELECTRICAL ENERGY AND FREE ENERGY CHANGE IN A CELL

A galvanic cell is a source of electrical energy, and it can be quantitatively converted into work. The electrical work or electrical energy is the product of emf of the cell and the electrical charge that flows through the external wire.

If n is the number of electrons flowing through the wire and F is the 1 Faraday of electricity, then the electrical charge flowing through the wire is equal to nF.

If E_{cell} is the emf of the cell, then the electrical work or electrical energy is given by,

 $W_{elec} = nFE_{cell}$

Since the electrical work is done by the system (ie: galvanic cell), by convention it is taken as negative.

i.e.: $-W_{elec} = nFE_{cell}$

or $W_{elec} = -nFE_{cell}$

According to thermodynamics, the free energy change (ΔG) for a process occurring at constant temperature and constant pressure is the measure of useful work. Therefore,

$$\Delta G = W_{elec}$$

where W_{elec} is the useful work produced by the system.

or
$$\Delta G = -nFE_{cell}$$

or $-\Delta G = nFE_{cell}$

8. NERNST EQUATIONS

1. Nernst Equation for Single Electrode Potential or Variation of Electrode Potential with Concentration

Consider a general redox reaction

 $M^{n+} + ne \iff M$

The electrode potential forms between the metal and the solution of its own salt of valency 'n' be E. Now the electrical energy required to transfer 1 gm equivalent of metal ion from the metal to solution of its own salt would be 'nFE' where F is 1 Faraday of electricity. That is, the decrease in free energy of a metal produces "nFE" electrical energy.

 $-\Delta G = nFE$ [ΔG is free energy change]

According to Van't Hoff's reaction isotherm, at equilibrium this free energy change in terms of concentration are inter related as

$$\Delta G = \Delta G^{\circ} + 2.303 \text{ RT} \log \frac{\text{Pr} oduct}{\text{Re} ac \tan t}$$

where ΔG° is the standard free energy change.

or
$$-nFE = -nFE^{\circ} + 2.303 \text{ RT} \log \frac{[M]}{[M^{n+}]}$$

or
$$E = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

or
$$E = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{[1]}{[M^{n+}]}$$

[:: the activity of solid metal = 1 at a given temperature]

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

When R = 8.314 J/K/Mole; F = 96,500 Coulombs; $T = 298^{\circ} \text{ K}$ then,

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$
 at 25° C

where E° is standard electrode potential and n is number of electrons transferred.

This equation is known as "Nernst equation for single electrode potential".

2. Nernst Equation for the Emf of a Complete Cell

Consider a general redox cell reaction involving the transfer of n electrons,

$$aA + bB \iff cC + dD$$
 ...(1)

The decrease in free energy change, ΔG , accompanying the process is given by a well known thermodynamic equation as

$$\Delta G = \Delta G^{\circ} + 2.303 \text{ RT} \log \frac{[\text{Pr} oducts]}{[\text{Re} ac \tan ts]}$$

or
$$\Delta G = \Delta G^{\circ} + 2.303 \text{ RT} \log \frac{[C]^{c} [D]^{d}}{[A]^{a} [B]^{b}} \qquad \dots (2)$$

Since $\Delta G = -nFE_{cell}$, equation (2) can be written as

$$- \operatorname{nFE}_{\operatorname{cell}} = -\operatorname{nFE}_{\operatorname{cell}}^{\circ} + 2.303 \operatorname{RT} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

(or)
$$E_{cell} = E_{cell}^{\circ} - \frac{2.303 RT}{nF} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \dots (3)$$

This equation is often referred to as the Nernst equation for the emf of a complete cell.

At 25° C, the equation (3) can be written as

$$\mathbf{E}_{\text{cell}} = \mathbf{E}^{\circ}_{\text{cell}} - \frac{0.0591}{n} \quad \log \quad \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

9. EMF OF A CELL

It is defined as "the difference of potential which causes the flow of current from an electrode having higher potential to another having lower potential is known as emf of the cell". It is expressed in Volts.

Emf of a cell (Ecell) is theoretically calculated by

 $E_{cell} = E_{Right side electrode} - E_{Left side electrode}$

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

1. Determination of Emf of a Cell by Poggendorff's Compensation Method (Potentiometric Method)

The accurate emf of a cell can not be determined by voltmeter directly because (i) internal resistance of cell may absorb a part of available potential difference and (ii) a part of cell current is drawn from the cell during the process of measurement itself. To get accurate emf of a cell, potentiometers are used which involves little flow of electricity.

Poggendorff's Method

Principle

In this method, the emf of the cell is compensated or balanced by an external emf so that no current flows in the circuit. At this stage, the applied emf is equal to the magnitude of emf of the test cell.

Description

The potentiometer circuit consists of a storage battery, P. The constant emf of the storage battery must be larger than that of the cell under measurement. This sends a constant current I through the uniform cross-section potentiometer wire AB. It is made of platinum-iridium and is stretched over a meter scale (Fig. 2.7).

Now the cell whose emf is to be measured is also connected to A having the positive pole in the same direction as the storage battery P and send current in the same direction. When the sliding contact C is pressed on the potentiometer wire, the test cell opposes the flow of current through the galvanometer. Adjust the sliding contact along the wire until the galvanometer G shows null deflection. This is called the null point. At this point the emf of the cell is balanced by the potential difference between the points AC of the potentiometer wire.

i.e.: Potential difference between A and $C = i \times Resistance$ of AC.



Fig. 2.7: Poggendorff's Circuit for Emf Determination

Now the test cell is replaced by a standard cell in the circuit. The point of null deflection is again determined. Now the balance length is AD.

and

i.e.: Potential difference between A and $D = i \times \text{Resistance of AD}$.

As the wire AB is uniform and its resistance is proportional to its length,

- $\therefore \quad \text{Emf of test cell} \quad \alpha \quad i \times \text{ length AC} \\ \quad \text{Emf of standard cell } \alpha \quad i \times \text{ length AD} \\ \quad \text{ } \end{aligned}$
- $\therefore \text{ Emf of test cell} = \text{Emf of std. cell} \times \frac{AC}{AD}$

Standard Cell (Example: Weston-Cadmium cell)



Fig. 2.8: Weston-Cadmium Cell

It consists of a H-shaped glass vessel. The bottom of the glass tubes are sealed with platinum wire. The positive electrode contains mercury over which mercurous sulphate is placed. The negative electrode consists of an amalgam of Hg-Cd over which some crystals of CdSO₄ 8/3 H₂O are sprinkled. The rest of the vessel is filled with saturated solution of CdSO₄. The upper end of the

arms are closed with either corks or sealing wax (Fig. 2.8). The purpose of solid crystals is to keep the electrolyte saturated at all temperatures. The emf of the cell is 1.01807 V at 25°C.

10.APPLICATIONS OF EMF MEASUREMENTS

1. Determination of pH of an Aqueous Solution

(A) The Glass Electrode

The most common standard electrode used in pH measurements is the glass electrode.



Fig. 2.9: Determination of pH by Glass Electrode

It consists of a thin glass bulb with a long neck. The glass bulb is made up of a special glass having low melting point and high electrical conductivity. The glass bulb is filled with 0.1 N HCl solution and silver wire coated with silver chloride is inserted to make the electrical contact (Fig. 2.9). This half cell glass electrode is represented as,

Ag, AgCl / HCl (0.1N) / Glass / Unknown solution

It has been observed that a potential difference exists at the interface between glass and solution containing H^+ ions. The magnitude of this difference of potential (single electrode potential) at 25°C is given by

$$E_{G} = E^{\circ}_{G} + 0.0591 \log [H^{+}]$$

$$E_{G} = E^{\circ}_{G} - 0.0591 pH \qquad [\because pH = -\log [H^{+}]]$$

where E°_{G} is constant for the given glass electrode and it depends upon the nature and composition of glass membrane

To carryout the determination of pH of a solution, the glass electrode is connected with a saturated calomel electrode. The cell is therefore represented as

Ag, AgCl / HCl (0.1N) / Glass / Unknown solution SCE

 $E_{cell} = E_{right} - E_{left}$ = 0.2422 - (E°_G - 0.0591 pH)

$$= 0.2422 - E^{\circ}_{G} + 0.0591 \text{ pH}$$

or $pH = \frac{E_{cell} - 0.2422 + E^{\circ}_{G}}{0.0591}$

Merits of Glass Electrode

- (i) It can be used in any solutions.
- (ii) A small quantity of solution is sufficient for the determination of pH.

(iii) It can be used even in the presence of metallic ions and poisons.

Demerits of Glass Electrode

(i) Since the resistance of glass membrane used in the bulb is very high, electronic potentiometers are needed for the measurement.

(ii) It can not be used in strongly alkaline solution (pH>10). In such cases, special type of glass must be used.

(B) The Quinhydrone Electrode

The quinhydrone electrode is a good example of redox electrode, used for the measurement of pH. The quinhydrone electrode consists of a platinum electrode dipped in the test solution, quinhydrone (an equimolar compound of quinone, Q and hydroquinone, QH₂). The half cell reaction of the quinhydrone electrode is written as

$$O = \underbrace{\bigcirc}_{Quinone (Q)} O + 2 H^{+} + 2e \iff HO - \underbrace{\bigcirc}_{Quinone (QH_2) (QH_2)} OH$$

This redox electrode system is represented as

Pt / Q, QH_2 / H⁺ (unknown concentration)

The potential developed on platinum electrode is given by Nernst equation as

$$E = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{[Pr oduct]}{[Re ac \tan t]}$$

$$= E^{\circ} - \frac{2.303 RT}{2F} \log \frac{[QH_2]}{[Q][H^+]^2}$$

$$= E^{\circ} + \frac{2.303 RT}{2F} \log \frac{[Q][H^+]^2}{[QH_2]}$$
$$= E^{\circ} + \frac{2.303 RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303 RT}{2F} \log [H^+]^2$$

Since the concentration of hydroquinone $[QH_2]$ is same as that of quinone [Q], the quantity $[Q] / [QH_2]$ is unity.

$$\therefore \mathbf{E} = \mathbf{E}^{\circ} + \frac{2.303 RT}{2F} \log 1 + \frac{2.303 RT}{2F} \log [H^{+}]^{2}$$

$$= \mathbf{E}^{\circ} + \frac{2.303 RT}{F} \log [H^{+}] \qquad [\because \log 1 = 0]$$

$$= \mathbf{E}^{\circ} + 0.0591 \log [H^{+}] \qquad \text{at } 25^{\circ} \text{ C.}$$

$$\mathbf{E} = \mathbf{E}^{\circ} - 0.0591 \text{ pH}$$

[where E° is the standard electrode potential of quinhydrone electrode = 0.6996V]

or E = 0.6996 - 0.0591 pH

or

To carry out the determination of pH of a solution, the quinhydrone electrode is connected with a saturated calomel electrode. This combination may be represented as

SCE || H⁺ (unknown) / Q, QH₂ / Pt. E_{cell} = E_{right}- E_{left} E_{cell} = 0.6996 - 0.0591 pH - 0.2422 pH = $\frac{0.6996 - 0.2422 - E_{cell}}{0.0591}$

Merits of Quinhydrone Electrode

- (i) It can work in the presence of oxidizing and reducing agents.
- (ii) It can be used for pH measurements in non-aqueous media.

Demerits of Quinhydrone Electrode

- (i) It cannot be used for solutions of pH more than 8.
- (ii) It cannot be used in the presence of solutes that react with hydroquinone.

2. Potentiometric Titrations

Potentiometric titration involves the measurement of the potential of a suitable indicator electrode as a function of titrant volume. It is useful with coloured and turbid solution and for detecting the presence of unsuspected species.

The electrode dipped in the test solution is called the indicator electrode, and the other electrode is called the reference electrode, whose potential remains constant. Hence the potential of the indicator electrode will change relative to that of reference electrode.

(i) Acid – Base Titration

A glass indicator electrode is used to carry out acid – base titration. The cell may be constructed as:

Pt, H₂ (1 atm) / H⁺ SCE

and its emf is given by $E_{cell} = 0.2422 - E_G^o + 0.0591 \text{ pH}$

By measuring the emf of cell after each addition of alkali, and plotting against volume of alkali added, the end point can be detected.



Fig. 2.10: Acid – Base Titration

(ii) Redox Titration

An inert electrode (platinum) is used to carry out redox titration. Both the oxidised and reduced forms are usually soluble and their ratio varies throughout the titration. The potential of the indicator electrode will vary and directly proportional to log $\frac{[reduced species]}{[oxidised species]}$ For Fe²⁺–Fe³⁺ system, the following cell may be constructed.

SCE ||
$$Fe^{3+}$$
 – Fe^{2+} / Pt

and its emf is given by

$$E_{cell} = \left[E^{\circ} + \frac{0.0591}{n} \log \left[\frac{[Fe^{3+}]}{[Fe^{2+}]} \right] - 0.2422 \right]$$

The progressive addition of $K_2Cr_2O_7$ will change in the emf of the cell. At the equivalence point a sharp change in emf is observed. This is due to sudden oxidation of all the ferrous ions into ferric ions. By plotting emf vs volume of $K_2Cr_2O_7$ added, the end point is determined.

A still better result of end point can be obtained by plotting the differential change in emf with volume $\left[\frac{\Delta E}{\Delta V}\right]$ against volume of K₂Cr₂O₇.



Fig. 2.11: Redox Titration

3. Determination of Solubility of a Sparingly Soluble Salt

The solubility and solubility product of a sparingly soluble salt can be calculated by measuring emf of suitable concentration cell.

For example, to find out the solubility of AgCl, the following cell may be constructed.

$$\begin{array}{c|c} Ag / AgCl (0.01 \text{ NKCl}) & AgNO_3 (0.01\text{ N}) / Ag\\ [Ag^+] = c & [Ag^+] = 0.01 \end{array}$$

The cell can be prepared by placing one of silver electrodes in contact with 0.01N solution of $AgNO_3$ and the other in contact with 0.01 N solution of KCl. The two half cells are connected by a salt bridge. A drop of $AgNO_3$ solution is added to KCl solution. A small amount of AgCl is produced which is sufficient to give its saturated solution. The cell so constructed is a concentration cell with respect to silver ions. The emf of such cell is given by

$$E_{cell} = \frac{2303 RT}{nF} \log \frac{0.01}{c}$$

Where c is the concentration of Ag^+ ions furnished by AgCl in KCl solution. By measuring emf of cell, the value 'c' can be calculated.

If 0.01N KCl is assumed to be completely dissociated, the activity of Cl⁻ ion is equal to 0.01.

Therefore solubility product, $K_{sp} = [Ag^+] [Cl^-]$

 $K_{SP}\!\!= c \times 0.01$

Solubility of AgCl = $\sqrt{K_{sp}} = \sqrt{c \times 0.01}$ gm.eqt. / lit

11. CONCENTRATION CELLS

In a concentration cell, electric energy is produced by transfer of matter or substance from one half cell to the other because of difference in the concentration of the species involved.

There are two types of concentration cells.

- (i) Electrode concentration cell.
- (ii) Electrolyte concentration cell

1. Electrode Concentration Cell

An electrode concentration cell consists of two identical electrodes of different composition dipped in a common electrolyte containing ions of the electrode material.

(i) A simple electrode concentration cell may be constructed by placing two hydrogen electrodes at different pressures in the same solution of hydrochloric acid.

 $\begin{array}{ll} Pt, \ H_2\ (P_1)\ /\ HCl\ (aq)\ /\ H_2\ (P_2),\ Pt & (P_2 > P_1) \\ (ii) & Another \ commonly \ employed \ electrode \ concentration \ cell \ is \ cadmium\ -\ amalgam\ cell. \ It \ consists \ of \ two \ amalgam\ electrodes \ at \ different \ activities \ in \ contact \ with \ a \ solution \ of \ an \ electrolyte \ containing \ ions \ of \ the \ metal \ dissolved \ in \ amalgam. \end{array}$

 $Cd-Hg(a_1) / CdSO_4(a_1) / Cd-Hg(a_2)$ (a₂ > a₁)

2. Electrolyte Concentration Cell

In this type, the two electrodes of the same metal are in contact with same electrolyte of different concentration.

Example: Copper ion concentration cell

$$\operatorname{Cu} / \operatorname{Cu}^{2+}(c_1) \parallel \operatorname{Cu}^{2+}(c_2) / \operatorname{Cu}$$
 (c₂ > c₁)

Determination of Emf of a Concentration Cell

According to Nernst equation, when a metal is placed in a solution of its own salt of concentration, c, the electrode potential

forms between the metal and the solution is determined by the equation

$$\mathbf{E} = \mathbf{E}^\circ + \frac{2.303 \ RT}{nF} \log \mathbf{c}$$

At 25° C, $E = E^{\circ} + \frac{0.0591}{n} \log c$

Let us consider a general electrolyte concentration cell in which two half cells are made up of similar electrodes and similar electrolytes. But the concentration of reactive ions around the electrodes are different.

It may be represented as

$$M / M^{n+}(c_1) \parallel M^{n+}(c_2) / M$$
 (c₂ > c₁)

where c_1 and c_2 are the concentration of reactive ions at the two electrodes (Fig. 2.12).



Fig. 2.12: Electrolyte Concentration Cell

Metal immersed in higher concentration acts as cathode because of high osmotic pressure of solution whereas the metal immersed in lower concentration acts as anode.

The emf of cell is generally determined by

Emf of cell $E_{cell} = E_{right} - E_{left} = E_{cathode} - E_{anode}$

where E_{cathode} and E_{anode} are half cell potential s of cathode and anode respectively.

The half cell potential can be determined by Nernst equation.

$$E_{cell} = \left[E^{\circ}_{M^{n+}/M} + \frac{0.0591}{n} \log c_2 \right] - \left[E^{\circ}_{M^{n+}/M} + \frac{0.0591}{n} \log c_1 \right] \text{at } 25^{\circ}\text{C}.$$
$$= \frac{0.0591}{n} \log c_2 - \frac{0.0591}{n} \log c_1$$
$$E_{cell} = \frac{0.0591}{n} \log \frac{c_2}{c_1} \qquad \text{at } 25^{\circ}\text{C}.$$

The reactions occurring at the two half cells are,

At cathode $M^{n+}(c_2) + ne \rightarrow M$ (reduction)

At anode $M \rightarrow M^{n+}(c_1) + ne$ (oxidation)

Overall reaction $M^{n+}(c_2) \rightarrow M^{n+}(c_1)$

It is clear from the above equation that there is no net chemical reaction. Therefore the emf developed is due to the transfer of metal ions from the solution of higher concentration to the lower concentration.

Applications of Concentration Cells

1. Determination of solubility of sparingly soluble salt

The solubility and solubility product of a sparingly soluble salt can be calculated by measuring emf of suitable concentration cell.

For example, to find out the solubility of AgCl, the following cell may be constructed.

Ag / AgCl (0.01 NKCl)
$$\|$$
 AgNO₃ (0.01N) / Ag
[Ag⁺] = c [Ag⁺] = 0.01

The cell can be prepared by placing one of silver electrodes in contact with 0.01N solution of $AgNO_3$ and the other in contact with 0.01 N solution of KCl. The two half cells are connected by a salt bridge. A drop of $AgNO_3$ solution is added to KCl solution. A small amount of AgCl is produced which is sufficient to give its saturated solution. The cell so constructed is a concentration cell with respect to silver ions. The emf of such cell is given by

$$E_{cell} = \frac{2303 RT}{nF} \log \frac{0.01}{c}$$

Where c is the concentration of Ag^+ ions furnished by AgCl in KCl solution. By measuring emf of cell, the value 'c' can be calculated.

If 0.01N KCl is assumed to be completely dissociated, the activity of Cl⁻ ion is equal to 0.01.

Therefore solubility product, $K_{sp} = [Ag^+] [Cl^-]$

 $K_{SP} = c \times 0.01$

Solubility of AgCl = $\sqrt{K_{sp}} = \sqrt{c \times 0.01}$ gm.eqt. / lit

2. Determination of Valency of an Ion

By substituting the measured value of emf of a concentration cell, the values of c_1 and c_2 in the equation.

$$\text{Emf} = \frac{0.0591}{n} \log \frac{c_2}{c_1} \qquad at \ 25^{\circ}C$$

The value of n, the number of electrons involved in the cell reaction can be calculated.

12. REVERSIBLE CELLS AND IRREVERSIBLE CELLS

1. Reversible Cells

Examples: Daniel cell, Secondary batteries

Cells which obey the conditions of thermodynamic reversibility are called as reversible cells.

Daniel cell is an example of reversible cell because it obeys the following conditions. Its emf is 1.1 volt.

 $Zn / ZnSO_4(1M) \parallel CuSO_4(1M) / Cu$

(i) If an external emf of 1.1 volt is applied in the opposite direction from an external source, the chemical reaction taking place in the cell stops i.e., no current flows.

(ii) If the external emf is slightly greater than 1.1 volt is applied, the current will begin to flow in the opposite direction and hence the chemical reaction in the cell gets reversed.

Since the secondary batteries (Lead-acid battery, Nickel-Cadmium battery) obey these conditions, they can be recharged and are called rechargeable batteries.

2. Irreversible Cells

Examples : Zinc-silver cell, Dry cell (Primary cells)

Cells which do not obey the conditions of thermodynamic reversibility are called irreversible cells.

Zinc-Silver cell is an example of an irreversible cell. It may be represented as

 $Zn / H_2SO_4 (aq) / Ag$

The cell reactions taking place at the anode and cathode are,

 $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow (At anode)$ $2 Ag^+ + 2e \rightarrow 2 Ag \qquad (At cathode)$

When two electrodes are connected from outside, zinc dissolves with the liberation of hydrogen gas.

When the external emf is slightly greater than the actual emf of the cell is applied to it, the above chemical reactions are not reversed, since one of the products, H_2 gas has already escaped. Such a cell which does not obey the conditions of reversibility is called as irreversible cell.

Similarly primary cells (Eg: dry cell) do not obey the conditions of reversibility and hence they are unchargeable.

13. LIQUID JUNCTION POTENTIAL

- A liquid junction potential is developed when a cell contains two electrolytic solutions of different concentration in contact with one another (Development of potential at the junction of the two liquids).
- The more concentrated solution possesses a tendency to diffuse into the comparatively less concentrated one.
- Large concentration difference between the liquid phases results in high liquid junction potential.
- The rate of diffusion of an ion at the junction of the two solutions is proportional to its speed.
- The rate of diffusion of each ion \propto its speed (ion mobility) in an electric field
- It may be regarded as a steady state where an effectively time-independent charge separation is developed. It is non-equilibrium potential.
- The structure of the liquid junction may hardly change as diffusion tends to be a slow process in it.
- The dilute solution always acquires the charge of faster moving ion.

If the cations (positively charged ions) move faster from concentrated solution to diluted solution than anions (negatively charged ions), the (+)ve ions will diffuse ahead of the (-)ve ions in the dilute solution. Thus the dilute solution will be (+)vely charged with respect to concentrated solution. Similarly, if the anion (negatively charged ions) moves faster, it will diffuse rapidly than (+)ve ion and the dilute solution will be (-)vely charged. In both the cases, an electrical double layer is formed at the junction of solutions resulting potential difference. This potential difference developed at the junction of two solutions is known as liquid junction potential (E_L) or diffusion potential, the magnitude which depends upon the relative speed of the ions. The electrical separation and potential difference thus arises will continue to increase until the rates of diffusion of (-)ve and (+)ve ions are equalized by electrical forces. If two ions are moving with the same speed there will be no liquid junction potential.

Expression for Liquid Junction Potential

When different concentrations of same electrolytic solutions are in contact, liquid junction potential can be measured. Let us consider the simplest case in which the junction is formed between two solutions of the same uni-univalent electrolyte at activities a_1 and a_2 .

KCl
$$(a_1)$$
 KCl (a_2)

Adopting the usual convention for a (+)ve emf, the left hand electrode is the source of electrons so that (+)ve current flows through the interior of the cell from left to right. If one Faraday of electricity is passed in the cell, n_c gram ion of cation (i.e. K⁺ ion) migrates from left to right i.e., from solution of activity a_1 to a_2 . Likely, n_a gm ion of anion (i.e., Cl⁻ ion) migrates from right to left. n_a and n_c are the transference numbers of anions and cations respectively. If transference number is assumed to be independent of concentration, then the free energy change during the passage of one faraday of electricity may be calculated.

The free energy change for (+)ve ion in the left compartment = $n_c RT \ln \frac{a_{+2}}{a_{+1}}$ 1

The free energy change for (-)ve ion in the right compartment = $n_a RT \ln \frac{a_{-1}}{a_{-2}}$ 2

Thus the total free energy change (ΔG) is:

$$\Delta G = n_c RT \ln \frac{a_{+2}}{a_{+1}} + n_a RT \ln \frac{a_{-1}}{a_{-2}} \dots 3$$

Let E_L be the liquid junction potential.

The electrical work done = $-nE_LF$

$$\Delta G = -nE_LF \qquad (n = 1) \qquad \dots \qquad 4$$

From equation (3) and (4)

$$-E_{L}F = n_{c}RT \ln \frac{a_{+2}}{a_{+1}} + n_{a}RT \ln \frac{a_{-1}}{a_{-2}}$$

$$E_{L} = -\frac{n_{c}RT}{F} \ln \frac{a_{+2}}{a_{+1}} - \frac{n_{a}RT}{F} \ln \frac{a_{-1}}{a_{-2}}$$

$$E_{L} = -\frac{n_{c}RT}{F} \ln \frac{a_{+2}}{a_{+1}} + \frac{n_{a}RT}{F} \ln \frac{a_{-2}}{a_{-1}} \dots 5$$

Here a_1 and a_2 are the mean activities of the electrolyte in the two solutions. By making further approximation of writing;

$$\frac{a_{+2}}{a_{+1}} = \frac{a_2}{a_1}$$
 and $\frac{a_{-2}}{a_{-1}} = \frac{a_2}{a_1}$

Hence, equation (5) reduces to

$$E_L = -\frac{n_c RT}{F} \ln \frac{a_2}{a_1} + \frac{n_a RT}{F} \ln \frac{a_2}{a_1}$$
$$E_L = (-n_c + n_a) \frac{RT}{F} \ln \frac{a_2}{a_1} \dots \dots 6$$
$$n_a = 1 - n_c$$

Since $n_a + n_c = 1$

Equation (6) may be written as

$$E_{L} = (-n_{c} + 1 - n_{c}) \frac{RT}{F} \ln \frac{a_{2}}{a_{1}}$$

$$E_L = (1 - 2n_c) \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \dots \dots 7$$

It is clear from equation (6) that the sign of liquid junction potential depends upon the relative values of transfernce number of anion and cation.

If the liquid function potential under consideration forms part of the concentration cell

Ag/AgCl(s), KCl (a1) / KCl (a2), AgCl(s)/Aghe emf of the cell (Et) is given by

$$\mathbf{E}_t = -2n_c \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \dots \dots 8$$

Dividing equation (7) by (8)

$$\frac{\mathrm{E}_L}{\mathrm{E}_t} = \frac{(1-2n_c)}{-2n_c}$$
$$\mathrm{E}_L = \frac{(1-2n_c)}{-2n_c} \mathrm{E}_t$$

This is the expression for liquid junction potential (diffusion potential).

14. SOLVED PROBLEMS

1. Determine the electrode potential of zinc electrode immersed in 0.1M ZnSO₄ solution at 25° C. $[E^{\circ}_{Zn^{2+}/Zn} = -0.763V]$

Given: Concentration $ZnSO_4 = 0.1M$; $E^{\circ}_{Zn^{2+}/Zn} = -0.763V$; E = ?

Since this problem has concentration term, we must use Nernst equation for calculating electrode potential

$$E = E^{\circ} + \frac{0.0591}{2} \log [Zn^{2+}] \text{ at } 25^{\circ}\text{C}.$$
$$= -0.763 + \frac{0.0591}{2} \log (0.1)$$
$$= -0.763 - 0.0295$$

E = -0.7925V

2. Calculate the standard emf of a galvanic cell. The standard reduction potential of zinc and copper are -0.76V and +0.34V respectively.

Given: $E_{z_n^{2+}/z_n}^{\circ} = -0.76V$; $E_{Cu^{2+}/Cu}^{\circ} = +0.34V$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

$$= E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn}$$

$$= +0.34 - (-0.76) = 0.34 + 0.76$$

 $E^{\circ}_{cell} = +1.1V$

3. The standard electrode potentials of lead and silver are - 0.13V and + 0.80 V respectively. Write down the cell reaction and calculate the emf of the cell.

Given: $E^{\circ}_{Ag^{+}/Ag} = +0.80V; E^{\circ}_{Pb}^{2+}/Pb = -0.13V$

We know that, $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$$= E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{Pb^{2+}/Pb}$$

= + 0.80 - (- 0.13)
= + 0.080 + 0.13
= + **0.93V**

The anode half cell reaction: $Pb \rightarrow Pb^{2+} + 2e$

The cathode half cell reaction: Ag $^+$ + e \rightarrow Ag

(or) $2Ag^+ + 2e \rightarrow 2Ag$

The net cell reaction: $Pb + 2 Ag^+ \rightarrow Pb^{2+} + 2 Ag$.

4. Calculate the emf of Daniel cell at 25°C when the concentration of ZnSO₄ and CuSO₄ are 0.01M and 0.1M respectively. Standard emf of the cell is 1.1V.

Given: Concentration of $ZnSO_4 = 0.01M$; Concentration of $CuSO_4 = 0.1M$; Std. Emf of the cell = 1.1 V

Since the problem has the concentration terms, we must use Nernst equation to calculate electrode potentials of zinc and copper.

We know that $E_{cell} = E_{cathode} - E_{anode}$

$$E_{\text{cell}} = E_{Cu^{2^+}/Cu} - E_{Zn^{2^+}/Zn} \qquad \dots (1)$$

According to Nernst equation,

$$E_{_{Cu^{2+}/Cu}} = E_{_{Cu^{2+}/Cu}}^{\circ} + \frac{0.0591}{2} \log [0.1] \text{ at } 25^{\circ}\text{C}$$

$$E_{zn^{2+}/Zn} = E_{zn^{2+}/Zn}^{\circ} + \frac{0.0591}{2} \log [0.01] \text{ at } 25^{\circ}\text{C}$$

Substituting these values in equation (1), we get

$$E_{cell} = \left[E^{\circ}_{Cu^{2+}/Cu} + \frac{0.0591}{2} \log(0.1) \right] - \left[E^{\circ}_{Zn^{2+}/Zn} + \frac{0.0591}{2} \log(0.01) \right]$$
$$= E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn} + \frac{0.0591}{2} \log(0.1) - \frac{0.0591}{2} \log(0.01) \right]$$

$$= 1.1 + \frac{0.0591}{2} \log \frac{0.1}{0.01} \qquad \left[:: E^{\circ}_{Cu^{2^+}/Cu} - E^{\circ}_{Zn^{2^+}/Zn} = 1.1V\right]$$

= 1.1 + 0.02955

= 1.12955V

5. Calculate the cell potential at 298K for the cell Zn(s)/Zn²⁺(0.1M) $\|$ Sn²⁺(0.001M)/Sn(s). Given: $E^{\circ}_{Zn^{2+}/Zn} = -0.76V$; $E^{\circ}_{Sn^{2+}/Sn} = -0.1V$

The reactions taking place in the cell are

$$Zn \rightarrow Zn^{2+} (0.1M) + 2e$$
 (Anode half cell reaction)
 $Sn^{2+} (0.001M) + 2e \rightarrow Sn$ (Cathode half cell reaction)
 $Zn + Sn^{2+} (0.001M) \rightarrow Zn^{2+} (0.1M) + Sn$

The net cell reaction involves a transfer of 2 moles of electrons ie: n = 2. The Nernst equation for a reversible complete cell is given by

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \left[\frac{Zn^{2+}}{Sn^{2+}} \right] \text{ at } 298^{\circ}\text{K}$$

$$E^{\circ}_{cell} = -0.14 - (-0.76)$$

$$= 0.62 \text{ V}$$

$$\therefore E_{cell} = 0.62 - \frac{0.0591}{2} \log \frac{0.1}{0.001}$$

$$= 0.62 - 0.0591$$

$$= 0.5609 \text{ V}.$$

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REVIEW QUESTIONS

PART – A QUESTIONS

- 1. What is a galvanic cell?
- 2. What is single electrode potential?
- 3. What is electrochemical series?
- 4. What are reference electrodes?
- 5. Give the relation between single electrode potential and standard electrode potential.
- 6. What are reversible and irreversible cells?
- 7. Define emf of a cell?
- 8. What are potentiometric titrations?
- 9. What are concentration cells?
- 10. Define liquid junction potential.
- 11. How the valency of an ion is determined by potentiometric method?

PART – B QUESTIONS

- 1. Explain the construction and working of a galvanic cell.
- 2. Explain the origin of electrode potential by Nernst pressure theory.
- 3. Write a brief account of reference electrodes.
- 4. How is single electrode potential determined by using SHE?
- 5. What is electrochemical series? Explain its significance.
- 6. Derive Nernst equation for single electrode potential.
- 7. Derive Nernst equation for the EMF of a complete cell.
- 8. Differentiate reversible and irreversible cells. Illustrate with examples.
- 9. Explain Poggendorff's method for the determination of emf of a cell.
- 10. Explain the various applications of emf measurements.
- 11. Explain how pH of an aqueous solution is determined by using glass electrode? Mention its merits and demerits.
- 12. What are potentiometric titrations? Explain with respect to ferrous/ferric system.
- 13. Explain the principle involved in potentiometric titrations. Write an experimental procedure for carrying out the titration of a redox reaction.
- 14. Discuss the electrolyte concentration cells.



SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – III– Chemical Kinetics-II – SCY1316

1. INTRODUCTION

Chemical kinetics deals with the reaction velocity and the mechanism of various chemical reaction by which they proceed. In the ideal chemical reactions, a definite number of molecules (reactants) are converted into a definite number of molecules of various products. But in most of the reactions, the above conditions are not fulfilled, and the course of the reaction is complicated. To study the mechanism of a reaction, various possible steps are written and the order of the reaction is determined experimentally. The order of reaction which indicates the slowest step in the overall reaction may be used to verify the reaction mechanisms in the complex reactions.

2. STEADY-STATE HYPOTHESIS (or) STEADY-STATE PRINCIPLE

Steady state principle can be applied only to a short-lived reactive intermediate. According to the steady state principle *"the rate of change of concentration of reaction intermediate is assumed to be zero"*.

i.e,
$$\frac{d[C_i]}{dt} = 0$$

where C_i is the concentration of reactive intermediate.

Steady-state principle can also be defined as "when a short-lived reactive intermediate exists at low concentration in a system, the rate of formation of intermediate can be considered to be equal to its rate of disappearance".

For example, the rate of decomposition of acetaldehyde can be obtained by using steady-state hypothesis.

$$CH_{3}CHO \xrightarrow{k_{1}} CH_{3} + CHO$$

$$CH_{3} + CH_{3}CHO \xrightarrow{k_{2}} CH_{4} + CO$$

$$CH_{3}CO \xrightarrow{k_{3}} CH_{3} + CO$$

$$CH_{3} + CH_{3} \xrightarrow{k_{4}} C_{2}H_{6}$$

According to steady-state principle,

Rate of formation of intermediate = Rate of its disappearance Rate of formation of intermediate = $k_1 [CH_3CHO] + k_3 [CH_3CO]$ Rate of disappearance of intermediate = $k_2 [CH_3] [CH_3CHO] + k_4 [CH_3]^2$

Or

$$k_{2}[CH_{3}][CH_{3}CHO] + k_{4}[CH_{3}]^{2} = k_{2}[CH_{3}][CH_{3}CHO] + k_{4}[CH_{3}]^{2}$$

3. ENERGY OF ACTIVATION

The concept of activation energy was developed by Arrhenius in 1888. According to Arrhenius, the reactant molecules must attain a discrete minimum energy before they react to form products. In other words, reactant molecules must be activated before reaction. *The quantity of energy required by the reactants to overcome the activated state or energy barrier is known as energy of activation.*

According to the concept of activation, the transformation of reactants into product $(A \rightarrow C)$, does not take place directly, but along the path ABC. In other words, reactant molecules must climb the energy barrier before they react to form product. (Fig. 3.1).



Fig. 3.1: Reaction Coordinate – Potential Energy Diagram

4. ARRHENIUS EQUATION (or) EFFECT OF TEMPERATURE ON RATE CONSTANT (or) TEMPERATURE DEPENDENCE OF RATE OF A REACTION

Generally rate constant increases with the increase of temperature and its value approximately doubles for every rise of 10°C. The quantitative relation between the rate constant and temperature is given by Arrhenius equation.

$$k = A e^{-E a/RT} \qquad \dots (1)$$

where k is rate constant, A is frequency factor, E_a is the activation energy, T is the temperature in Kelvin and R is gas constant.

Arrhenius equation has two solutions.

(i) Taking natural logarithm on both sides, we get

$$\log k = \log A - \frac{E_a}{2.303 RT}$$
 ...(2)

When log k is plotted against $\frac{1}{T}$, a straight line is obtained with an intercept equal to log A and slope equal to $\frac{-E_a}{2.303 R}$ (Fig. 3.2).



(ii) The reaction between the rate constant at two temperatures can be derived from the logarithmic Arrhenius equation.

If k_1 and k_2 are the rate constants of a reaction at temperature T_1 and T_2 respectively, then from equation (2), we get

$$\log k_{1} = \log A - \frac{E_{a}}{2.303 RT_{1}} \qquad ...(3)$$
$$\log k_{2} = \log A - \frac{E_{a}}{2.303 RT_{2}} \qquad ...(4)$$

On subtracting (3) from (4), we get

$$\log k_2 - \log k_1 = \frac{-E_a}{2.303 RT_2} + \frac{E_a}{2.303 RT_1}$$

or

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \qquad \dots(5)$$

or

Thus by knowing the rate constant at two different temperatures, the energy of activation E_a , can be calculated.

5. COMPLEX REACTIONS

1. Reversible or Opposing Reactions

There are certain reaction in which the products start reacting to give back the original reactants. Such reactions are called reversible or opposing or counter reactions.

Examples

1. Oxidation of nitric oxide to nitrogen dioxide

$$2 NO + O_2 \stackrel{k_1}{\underset{k_2}{\Leftrightarrow}} 2 NO_2$$

2. Hydrolysis of ethyl acetate in aqueous solution

CH₃COOC₂H₅ + H₂O
$$\rightleftharpoons_{k_2}^{k_1}$$
 CH₃COOH + C₂H₅OH

3. Conversion of ammonium cyanate into urea

NH₄CNO
$$\underset{k_2}{\overset{k_1}{\Leftrightarrow}}$$
CO(NH₂)₂

4. Mutarotation of glucose

 α - D - Glucose $\Leftrightarrow \beta$ - D - Glucose

 $(k_1 is the rate of constant for the forward reaction and k_2 is the rate constant for the backward reaction)$

In this category, the reaction proceeds on both directions and finally a state of equilibrium is set up. (i.e. at equilibrium the rate of forward direction is equal to that of reverse direction). At the point, the net speed of reaction is zero.

Kinetic Study of Reversible (or) Opposing Reactions

Case 1: Both Forward and Backward Reactions are of First Order

Consider the simple case, in which both forward and reverse reactions are of the first order (first order in both the directions)

$$A \stackrel{k_1}{\underset{k_2}{\Leftrightarrow}} B$$

where k_1 and k_2 are the first order rate constant of forward reaction and reverse reaction respectively.
Initially at t = 0, let 'a' be the concentration of A and there will be no B. After time 't' if 'x' is the amount A converted into B, then the concentration of A and B will be (a - x) and x respectively.

The rate of formation of $B = k_1 (a - x)$

The rate of disappearance of $B = -k_2 x$

The net rate of formation of B after time t = $\frac{dx}{dt} = k_1 (a - x) - k_2 x$...(1)

At equilibrium, the net rate is zero and the concentration of x is then xe

i.e.,
$$k_1 (a - x_e) - k_2 x_e = 0$$

or $k_2 x_e = k_1 (a - x_e)$

$$k_2 = \frac{k_1(a - x_e)}{x_e}$$
 ...(2)

On substituting the value of k_2 in equation (1), we get

$$\frac{dx}{dt} = k_1(a-x) - \frac{k_1(a-x_e)x}{x_e} \qquad ...(3)$$

or

or

$$= \frac{k_1 x_e(a-x) - k_1 x(a-x_e)}{x_e}$$

 $= \frac{k_1 x_e a - k_1 x_e x - k_1 x a + k_1 x x_e}{x_e}$

or

 $= \frac{k_1 x_e a - k_1 x a}{x_e}$

or

 $= \frac{k_1 a (x_e - x)}{x_e}$

On separating the variables, we have

$$\frac{dx}{(x_e - x)} = \frac{k_1 a}{x_e} dt$$

On integration,

$$\int \frac{dx}{\left(x_e - x\right)} = \frac{k_1 a}{x_e} \int dt$$

...(4)

$$-\ln(x_e - x) = \frac{k_1 a}{x_e} t + C$$
 ...(4)

where C is the integration constant. When t = 0, x=0, we get

 $-\ln x_e = C$

Substituting the value of C in equation (5), we get

$$-\ln(x_e - x) = \frac{k_1 a}{x_e} t - \ln x_e$$

or
$$\frac{k_1 a}{x_e} \quad t = \ln x_e - \ln(x_e - x)$$

or
$$\frac{k_1 \cdot a}{x_e} = \frac{1}{t} \ln \left[\frac{x_e}{(x_e - x)} \right]$$
 ...(5)

or
$$k_1 = \frac{1}{t} \cdot \frac{x_e}{a} \ln \left[\frac{x_e}{(x_e - x)} \right]$$
 ...(6)

Therefore, if x is known, the rate constant for the forward reaction can be calculated.

Further equation (2) may be rearranged as

$$k_{2}.x_{e} = k_{1} (a - x_{e})$$
or
$$k_{2} x_{e} = k_{1} a - k_{1}x_{e}$$
or
$$k_{2} x_{e} + k_{1}x_{e} = k_{1}a$$
or
$$x_{e} (k_{2}+k_{1}) = k_{1}a$$

 $k_2 + k_1 = \frac{k_1 \cdot a}{x_e}$...(7)

From equation (6) and (8),

$$k_2 + k_1 = \frac{1}{t} \ln \frac{x_e}{(x_e - x)} \qquad \dots (8)$$

Therefore, knowing $k_1 \ , \ x \ , \ x_e$ and t , the rate of constant for reverse reaction (k_2) can be calculated.

Case 2: Both Forward and Backward Reactions are of Second Order

Examples

1. Dissociation of hydrogen iodide

 $2HI \ \Leftrightarrow \ H_2+I_2$

2. Saponification of ester by an alkali

 $CH_{3}COO\ C_{2}H_{5}\ +\ NaOH\ \Leftrightarrow\ CH_{3}\ COONa\ +\ C_{2}H_{5}\ OH$

$$\mathbf{A} + \mathbf{B} \underset{k_2}{\Leftrightarrow} \overset{k_1}{\mathbf{C}} \mathbf{C} + \mathbf{D}$$

Initial concentration	а	а	0	0
Concentration at time, t	(a – x)	(a – x)	Х	Х
Equilibrium concentration	$(a - x_e)$	$(a - x_e)$	Xe	Xe

Net rate of forward reaction = Rate of forward reaction - Rate of backward reaction

i.e.,
$$\frac{dx}{dt} = k_1 (a - x)^2 - k_2 x^2$$
 ...(1)

At equilibrium, $x = x_e$ and dx/dt = 0

Hence,

 $k_1 (a-x_e)^2 - k_2 x_e^2 = 0$

 $k_1 (a-x_e)^2 = k_2 x_e^2$

or

or

$$\mathbf{k}_2 = \mathbf{k}_1 \left(\frac{a - x_e}{x_e}\right)^2 \qquad \dots (2)$$

From equations (1) and (2), we have

$$\frac{dx}{dt} = k_1 (a - x)^2 - k_1 \left[\frac{(a - x_e)}{x_e}\right]^2 \qquad ...(3)$$

Integrating equation (3)* under the condition that at t = 0 and x = 0, we get

$$k_{1} = \frac{2.303x_{e}}{2at(a - x_{e})} \log\left[\frac{x(a - 2x_{e}) + ax_{e}}{a(x_{e} - x)}\right] \qquad \dots (4)$$

Equation (4) gives k_1 in terms of easily measurable quantities. Knowing k_1 , the value of k_2 can be calculated with the help of equation (2).

2. Consecutive Reactions

Reactions proceed from reactants to products through one or more intermediate stages are called consecutive reactions or successive reactions. In these reactions, each stage has its own rate and its own velocity constant. The stage which is slowest determines the order of overall reactions.

Examples

1. Radioactive decay of polonium

 $\overset{218}{_{84}}Po \xrightarrow{3.1\min;\alpha} \overset{214}{_{82}}Pb \xrightarrow{26.8\min;\beta} \overset{214}{_{83}}Bi$

2. Decomposition of dimethyl ether

 $CH_3OCH_3 \xrightarrow{k_1} CH_4 + HCHO$

HCHO $\xrightarrow{k_2}$ H₂ + CO

3. Bacterial nitrification of ammonia

 $NH_3 \xrightarrow{O_2} NO_2 \xrightarrow{O_2} NO_3$ Nitrosomonas Nitrobacter bacteria bacteria

Mathematical Analysis (Kinetics) of Consecutive Reactions

Consider a simple consecutive reaction in which A is the original reactant and gives the product B at the rate constant k_1 . The product formed further reacts to give the substance C at the different rate constant k_2 .

 $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

The kinetics of such reaction is determined by the slowest step. In the above reaction, if first reaction is faster than the second reaction, the kinetics will be determined by the second reaction.

To show the variation of concentration of A, B and C with time, it is necessary to set up rate equations and if possible to integrate them.

- Let (i) a be the initial concentration of A.
 - (ii) x is the amount of A decomposed in time t.

(iii) y is the amount of C formed at the same time t.

(i) The rate of disappearance of A is given by

$$-\frac{dx}{dt} = k_1 x \qquad \dots (1)$$

where x is the amount of A decomposed in time 't'.

On rearranging and integrating the equation (1), we have

$$-\int \frac{dx}{x} = k_1 \int dt$$

- ln x = k_1 t + C(2)

where C is integration constant. When t = 0, x = a, then $C = -\ln a$. Substituting C in equation (2), we get

$$-\ln x = k_1 t - \ln a$$

or
$$1n x - 1n a = -k_1 t$$

or $1n\frac{x}{a} = -k_1t$

or

or

 $x = ae^{-k_1 t} \qquad \dots (3)$

Equation (3) states that concentration of A falls off continuously with time.

(ii) The rate of formation of B from $A = k_1 x$

The rate of decomposition of B into $C = k_2 y$

The rate of accumulation of B in the reaction is equal to the difference in its state of formation from A and its decomposition to C, hence

The net rate of B = Rate of formation of B - Rate of decomposition of B

i.e.,
$$\frac{dy}{dt} = k_1 x - k_2 y$$

or $\frac{dy}{dt} + k_2 y = k_1 x$

Substituting the value of x in equation (4), we get

$$\frac{dy}{dt} + k_2 y = k_1 a e^{-k_t t} \qquad ...(4)$$

This is a linear differential equation of first order of the type

$$\frac{dy}{dt} + Py = Q$$

The solution of the above equation* is given by

whose solution is given by,

$$y = \frac{ak_1}{(k_2 - k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right] \qquad \dots (5)$$

(iii) Since there is no change in the number of moles during the reaction, the sum of moles of A, B and C at time t is equal to the initial moles of A.

i.e.,
$$x + y + z = a$$

or $z = a - x - y$...(6)

Putting the values of x and y in equation (6), we have

$$z = a - ae^{-k_{1}t} - \frac{ak_{1}}{(k_{2} - k_{1})} \left[e^{-k_{1}t} - e^{-k_{2}t} \right]$$

or = $a \left[1 - e^{-k_{1}t} - \frac{k_{1}}{(k_{2} - k_{1})} \left(e^{-k_{1}t} - e^{-k_{2}t} \right) \right]$

Taking out minus symbol alone from the expression, we get

or =
$$a \left[1 - \left(e^{-k_1 t} + \frac{k_1}{(k_2 - k_1)} \left(e^{-k_1 t} - e^{-k_2 t} \right) \right) \right]$$

or = $a \left[1 - \left(\frac{k_2 e^{-k_1 t} - k_1 e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right) \right]$
 $\left[z = a \left[1 - \left(\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right) \right] \dots (7)$

3. Parallel (or) Side Reactions

In these reactions, the reacting molecules react or decompose in more than one way to yield more than one independent product. The reaction yielding the largest amount of a product is known as main reaction while the others yielding smaller amounts of products are known as side reactions. Parallel reactions are very common in organic chemistry.

1. Nitration of phenol yields para and ortho nitrophenols simultaneously,

$$OH$$

$$OH$$

$$H HNO_{3}$$

$$K_{1}$$

$$(Main reaction)$$

$$K_{2}$$

$$OH$$

$$H_{2}O$$

$$H$$

$$OH$$

$$H_{2}O$$

$$H_{$$

2. Alcohol can be dehydrated to olefin as well as dehydrogenated to aldehyde



3. Reaction of ethyl bromide with caustic potash

$$\begin{array}{c} k_1 \\ C_2H_5Br + alcoholic_KOH \\ k_2 \\ k_$$

Kinetic Study of Parallel Reaction

Let us consider a reaction of the following type



where A is the reactant and B, C are the products obtained from A.

Let a be the concentration of A at the commencement of the reaction and x is the amount of A decomposes to form B and C at time t.

The amount of A left unreacted after time, t = (a - x)

- The rate of formation of B from A $= k_1 (a x)$...(1)
- The rate of formation of C from A = $k_2 (a x)$...(2)

Hence the overall rate of the reaction = $k_1(a - x) + k_2(a - x)$...(3)

i.e.,
$$\frac{dx}{dt} = k_1 (a - x) + k_2 (a - x)$$

or
$$\frac{dx}{dt} = (a - x)(k_1 + k_2)$$
 ...(4)

On rearranging and integrating the equation (4), we have

$$\int \frac{dx}{(a-x)} = (k_1 + k_2) \int dt$$

or $-\ln(a-x) = (k_1 + k_2) t + C$...(5)

where C is the integration constant.

When t = 0, x = 0, then C = -1n a

Substituting C in equation (5), we get

 $(k_1 + k_2) = \frac{1}{t} \ln \frac{a}{a - r}$

$$-\ln(a-x) = (k_1 + k_2) t - \ln a$$

or

Therefore from the disappearance of the reactant A, the sum of the rate constant $(k_1 + k_2)$ can be calculated.

...(6)

From equations (1) and (2), we can write

$$\frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} = \frac{\text{Amount of B at time t}}{\text{Amount of C at time t}}$$

 $\frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} = \frac{k_1(a-x)}{k_2(a-x)} = \frac{k_1}{k_2}$

Hence from the rate of formation of individual products, the ratio $\frac{k_1}{k_2}$ can be calculated. Further, from the values of $(k_1 + k_2)$ and $\left(\frac{k_1}{k_2}\right)$, the individual rate constant k_1 and k_2 can be evaluated.

6. COLLISION THEORY

According to this theory, a chemical reaction takes place only by collision between the reacting molecules. But all the collisions do not lead to product formation. Only those collisions in

which the colliding molecules attain a certain minimum amount of energy called activation energy produce effective reaction. Further the reacting molecules must collide with correct orientation. If the molecules are not in proper orientation, product formation is not possible.

The mathematical statement of collision theory is given by

$$k = P Z e^{-E_a/RT}$$

where $Z = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8k_b T(m_A + m_B)}{\pi m_A m_B}}$

 σ_A and $\sigma_B\,$ are the diameter of molecules A and B with mass m_A and $m_B.$

 k_b is the Boltzmann constant E_a is the activation energy and P is the steric factor

7. ACTIVATED COMPLEX THEORY (ACT) (or) ABSOLUTE REACTION RATE THEORY (ARRT)

This theory explains the rate on the basis of thermodynamics and was developed by Henry Eyring in 1938. According to this theory, the reacting molecules must form an activated complex before undergoing reaction to form the products. Further an equilibrium exists between the activated complex and the reactant molecules.

Reactant
$$\Leftrightarrow$$
 Activated Complex \rightarrow Products

In the activated complex, the atoms are linked together with loose valence bonds. It is not stable and cannot be isolated. It breaks down either to give reactants or products depending on the experimental conditions. Thus, the stable molecules before being converted into products, must pass through an unstable, high energy, intermediate species. This highly reactive intermediate species is known as the activated complex.

Consider a simple bimolecular reaction between the molecules A and B. This reaction is represented as

$$\frac{A+B}{\text{Reactants}} \Leftrightarrow \frac{AB^*}{\text{Activated complex}} \to \text{Pr} oducts$$

The rate of the reaction is equal to the number of activated complexes which pass over the energy barrier in unit time. This, in turn, is equal to the concentration of activated complex and the frequency at which the complex dissociates into products.

i.e., Rate = $\begin{cases} Concentration of \times \\ activated complex \end{cases}$ Frequency of dissociation of complex $\begin{cases} Frequency of \\ complex \\ co$

or Rate = [AB*]
$$\times$$

Frequency at which
the complex dissociates
into products
...(1)

If [A], [B] and [AB*] represent the concentration of A, B and AB* at time t, then equilibrium constant for the formation of activated complex may be written as

$$k^{*} = \frac{[AB^{*}]}{[A][B]}$$

[AB*] = k* [A] [B](2)

The activated complex undergoes dissociation only if enough vibrational energy is supplied to the system. This vibrational energy causes the atoms to vibrate with certain critical frequency (γ), leading to bond rupture.

Now according to Planck's quantum theory

$$\mathrm{E_{vib}} = \mathrm{h} \ \gamma$$

 $\gamma = rac{E_{vib}}{h}$

where h is Planck's constant. Further, this vibration is responsible for disrupting the complex into the product. The vibration is large enough in amplitude to decompose the complex. The frequency of such vibrations will be low and the average vibrational energy (E_{vib}) at temperature T will be the order of classical vibrational energy k_bT , where k_b is called Boltzman constant. Therefore,

...(3)

The frequency at which
the complex dissociates
$$\gamma = \frac{E_{vib}}{h}$$

into products

or

or

 $\gamma = \frac{k_b T}{h}$

Substituting the values of [AB*] and γ in equation (1), we get

Rate = k* [A] [B]
$$\frac{k_b T}{h}$$
 ...(4)

If k is the velocity constant of the reaction, the experimentally obtained rate law is given by

Comparing (4) and (5), we get

k* [A] [B]
$$\frac{k_b T}{h} = k$$
 [A] [B]
k = k* $\frac{k_b T}{h}$...(6)

Expression (6) is the mathematical statement of transition state theory.

The equilibrium constant k* can be expressed in thermodynamic terms, so that it can be measured experimentally.

The expression for k^* in terms of ΔG^* , we have

$$\Delta G^* = -RT \ln k^*$$
$$\ln k^* = \frac{-\Delta G^*}{RT}$$

For the reaction at a temperature T, ΔG^* can be expressed in terms of ΔH^* and ΔS^* by the equation

$$\Delta G^* = \Delta H^* - T \Delta S^* \qquad \dots (7)$$

Substituting ΔG^* in equation (7), we get

 $\ln \mathbf{k}^* = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R}$

$$\ln \mathbf{k}^* = \frac{-\left(\Delta \mathbf{H}^* - T\Delta S^*\right)}{RT} \qquad \dots (8)$$

or

or

or

or
$$k^* = e^{-\Delta H^* / RT} e^{\Delta S^* / R}$$
 ...(9)

Substituting k^* in equation (6), we get

$$k = \frac{k_b T}{h} \cdot e^{-\Delta H^{*/RT}} \cdot e^{\Delta S^{*/R}} \qquad \dots (10)$$

where ΔH^* - Standard enthalpy change (or) standard heat of activation. ΔS^* - Standard entropy change (or) standard entropy of activation.

Equation (10) is the fundamental relation of transition state theory.

8. LINDEMANN'S THEORY OF UNIMOLECULAR REACTIONS

Postulates of Lindeman's Mechanism

- According to Lindemann's mechanism, at least two molecules must collide so that the kinetic energy of second molecule will get converted into the vibrational energy and to form an energised molecule.
- The energised molecule in turn gets deactivated with rate constant of k_{-1} or get decomposed with the rate constant of k_2 .



Derivation of Lindeman's Mechanism

$$k = \frac{-d[A^*]}{dt} = k_1[A][A] \dots (1)$$
$$k = \frac{-d[A^*]}{dt} = k_{-1}[A^*][A] \dots (2)$$
$$k = \frac{+d[P]}{dt} = \frac{-d[A^*]}{dt} = k_2[A^*] \dots (3)$$

The concentration of any intermediate species can be determined y applying steady state approximation [SSA]. According to SSA,

Rate of formation of = Rate of decomposition of intermediate species intermediate species + Rate of deactivation of intermediate species

$$k_1[A][A] = k_{-1}[A^*][A] + k_2[A^*]$$

$$k_1[A][A] = k_{-1}[A^*]\{k_{-1}[A] + k_2\}$$

$$[A^*] = \frac{k_1[A]^2}{\{k_{-1}[A] + k_2\}} \quad \dots (4)$$

$$\therefore$$
 The rate of reaction $= \frac{-d[A]}{dt} = k_2[A^*]$

(or) The rate of reaction
$$= \frac{-d[A]}{dt} = \frac{k_1 k_2 [A]^2}{\{k_{-1}[A] + k_2\}} \dots (5)$$

Limiting cases

Case 1: At high pressures, the chances of collisions between A^* and A are greater, in turn deactivation is prominent than product formation. i.e., $k_{-1}[A] >>> k_2$. Hence, k_2 can be neglected.

$$\frac{-d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A]}$$

$$\frac{-d[A]}{dt} = \frac{k_1 k_2}{k_{-1}} [A]$$

$$\frac{-d[A]}{dt} = k_{\infty}[A] \qquad \text{where } k_{\infty} = \frac{k_1 k_2}{k_{-1}}$$

$$\frac{-d[A]}{dt} \alpha [A]$$

: The rate is of first order at high pressures.

Case 2: At low pressures, the chances of collisions between A^* and A are lesser, in turn deactivation is less than product formation. i.e., $k_{.1}[A] <<< k_2$. Hence, $k_{.1}[A]$ can be neglected.

$$\frac{-d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_2}$$
$$\frac{-d[A]}{dt} = k_1 [A]^2$$
$$\frac{-d[A]}{dt} \alpha [A]^2$$

 \therefore The rate is of second order at low pressures.

Rearranging equation (5), we have:

$$-\frac{1}{[A]}\frac{d[A]}{dt} = \frac{k_1k_2[A]}{k_{-1}[A] + k_2} \quad \dots (6)$$

$$k' = \frac{k_1k_2[A]}{k_{-1}[A] + k_2}$$
where $k' = -\frac{1}{[A]}\frac{d[A]}{dt}$, is known as first order rate coefficient

At high pressures, k_{-1} [A] >>> k_2 , we have:

k'α [A]

At low pressures, k_{-1} [A] <<< k_2 , we have:

 $k'\alpha [A]^2$



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REVIEW QUESTIONS

PART – A QUESTIONS

- 1. State steady state approximation.
- 2. What is meant by energy of activation?
- 3. What are the postulates of collision theory?
- 4. What are the limitations (weakness) of collision theory?
- 5. Why does reaction rate increase with a) increase in temperature (b) increase in concentration of the reactants?
- 6. Give one example of a unimolecular reaction.
- 7. Explain how does presence of a catalyst increase the rate of a reaction.
- 8. Give the mathematical statement of transition state theory.
- 9. What are the postulates of Lindemann's theory of unimolecular reactions?
- 10. What is a consecutive reaction? Give one example.
- 11. What is a parallel reaction? Give one example.
- 12. What is a opposing reaction? Give one example.

PART – B QUESTIONS

1. Explain the term energy of activation. How is the energy of a reaction of a reaction determined?

- 2. Derive an expression for the variation of rate constant of a reaction with temperature.
- 3. What is meant by energy of activation? Explain how energy of activation is determined with the help of Arrhenius equation.
- 4. Discuss the kinetics of first order consecutive reactions, $A \rightarrow B \rightarrow C$.
- 5. Discuss the kinetics of the first order parallel reaction and explain clearly how the values of k_1 and k_2 can be determined separately.
- 6. Derive an expression for the rate of reversible reaction when the direct and reverse reactions are of first order.
- 7. Derive an expression for the kinetics of opposing reaction, second order in both the directions.
- 8. Discuss collision theory.
- 9. Explain the absolute rate theory of reaction rates.
- 10. Discuss Lindemann's theory of unimolecular reactions.



SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – IV– Surface Chemistry and Catalysis – SCY1316

88

1. INTRODUCTION

Adsorption: Adsorption is a surface phenomenon. In this process, accumulation or concentration of a substance takes place at the surface or interface of a solid or liquid.

* Examples

- \Rightarrow Adsorption of water vapours on silica gel.
- \Rightarrow Adsorption of hydrogen gas on nickel surface.

Adsorbent: The substrate (solid or liquid) on which adsorption of gas or solute takes place is called adsorbent. Most adsorbents are highly porous material and adsorption occurs on the walls of the pores.

***** Examples

 \Rightarrow Silica gel, Activated carbon, Zeolites, Alumina, Platinum, Nickel etc.

Adsorbate: The substance, which accumulates on the surface of the substrate (adsorbent), is called adsorbate.

* Examples

 \Rightarrow Various gases (ammonia gas, water vapour, CO_2 , N_2 , O_2 , etc.); Substances in solution (NaCl, a mineral poison, a bacterial toxin, a dye etc.)

Absorption: Absorption is a bulk phenomenon. In this process a substance is not only retained on the surface but it passes through the surface and distributed throughout the body of a solid or liquid.

* Examples

- \Rightarrow Absorption of water by anhydrous *CaCl*₂.
- \Rightarrow Absorption of ammonia by water.

Differences Between Adsorption and Absorption: In adsorption, molecules of one phase are present in higher concentration on the surface of the second phase. In absorption, molecules of one phase interpenetrate uniformly among those of another phase.

Sorption: When adsorption and absorption take place simultaneously, the process is known as sorption.

* Examples

✓ Ammonia can undergo adsorption and absorption when it is passed through water in contact with charcoal. Water absorbs ammonia whereas charcoal attracts and retains ammonia on its surface.

Desorption: The process of removal of an adsorbed substance from the surface on which it is adsorbed is called desorption.

Enthalpy of Adsorption: The amount of heat released for the adsorption of one mole of an adsorbate on an adsorbent surface.

Adsorption Isotherm: The variation of amount of substance adsorbed per unit mass of adsorbent with pressure at constant temperature.

2. CAUSES OF ADSORPTION

The primary driving forces for the adsorption of an adsorbate on an adsorbent surface are

1. Lyophobic (Or) Hydrophobic (Solvent Disliking) Character

Lyophobic (solvent disliking) character of the solute (adsorbate) in an aqueous solution comes out of the solvent and has high affinity for adsorption at the surface of solid adsorbent.

2. Surface Energy

Adsorption is a consequence of surface energy. In the interior of liquid, molecules (adsorbates) experience forces of attraction from all sides. However, the molecules at the surface experience a net attraction downward and tend to move towards the interior to increase attractions. On account of the unbalanced forces, the surface of a liquid or solid is in a state of strain. This indicates that the surface molecules have higher energy than those present in the interior. So, when an adsorbent is placed in the liquid, surface molecules having higher energy get attached readily to the surface of the adsorbent and lose their energy. In other words, adsorption results in decrease of surface energy.

3. Forces of Attraction

Weak molecular forces such as van der Waals forces provide the driving force for physical adsorption while a chemical reaction forms a chemical bond between the compound (adsorbate) and the surface of the solid (adsorbent) provide driving force for chemical adsorption.

4. Enthalpy (Heat) of Adsorption

The adsorption processes are exothermic in nature. Adsorption is a spontaneous process and therefore its free energy change should be negative ($\Delta G < 0$). However, the entropy change associated with adsorption is generally negative because the adsorbate molecules lose their translation freedom when they get attached to the surface of the adsorbent. Therefore, in order for ΔG to be negative, the enthalpy change (ΔH) must be sufficiently negative, such that, ($\Delta G = \Delta H - T \Delta S$)<0. This explanation accounts for exothermic adsorption processes. Enthalpy of adsorption, (the amount of heat released for the adsorbent surface), is usually in the range of 20 kcal/mole to 40 kcal/mole for physical adsorption while 40 kcal/mole to 400kcal/mole for chemical adsorption.

3. TYPES OF ADSORPTION

Depending upon the nature of attractive forces existing between the adsorbate and adsorbent, adsorption can be classified as: (i) Physical adsorption or Vander waals adsorption (Physisorption) and (ii) Chemical adsorption or Activated Adsorption (Chemisorption).

S. No.	Characteristics	Physisorption	Chemisorption
1.	Nature of forces	It is due to Van der waals	It is due to strong chemical bond
		physical forces of attraction.	forces.
2.	Heats of	Low, usually less than 20–40	Very high. Usually in the range
	adsorption	kcals/mole.	of 40-400 kcals/mole.
3.	Occurrence	It occurs at ordinary	It occurs at high temperature.
		temperature and decreases	
		with rise in temperature.	
4.	Reversibility	It is reversible in nature.	It is irreversible.
5.	Specificity	It is not specific. It is	It is highly specific. Only certain
		independent of chemical	types of molecules will be
		nature of substance being	adsorbed by a particular solid.
		adsorbed.	
6.	Effect of	The rate of adsorption	Generally, the rate of adsorption
	pressure	increases with of pressure.	decreases with increase of
			pressure.
7.	Structure of	Multilayers are formed at the	Monolayer (one molecule thick)
	adsorbed layer	surface.	is usually formed at the surface.
8.	Examples	Adsorption of various gases	Adsorption of O_2 on silver, H_2 on
		on solids.	nickel.

 Table 4.1: Differences between physisorption and chemisorption

1. Physical Adsorption

Physical adsorption occurs due to the formation of weak van der Waals forces of attraction between adsorbed molecule and the surface. These forces are characterized by low heats of adsorption (less than 40 kcals/mole).

A rise in temperature will increase the kinetic energies of adsorbed molecules and the molecules will leave the surface and thereby lowering the extent of adsorption. Since the forces of attraction are weak, the process of physisorption can be reversed by heating or by lowering the pressure of adsorbate. Physical adsorption is not very specific. It is independent of the chemical nature of the substance being adsorbed

✤ Examples

- \Rightarrow Adsorption of various gases on charcoal.
- \Rightarrow Adsorption of nitrogen on mica.

2. Chemical Adsorption

Chemical adsorption occurs due to the formation of strong chemical bonds between adsorbed molecules and the surface. Chemisorption is associated with high heats of adsorption (40–400 kcals/mole). So, it is observed only at higher temperatures.

The chemical bond formed between the adsorbate and the adsorbent cannot be broken easily and therefore chemisorption is rarely reversible. Chemisorption is highly selective since a particular solid will adsorb only certain types of molecules.

✤ Examples

- \Rightarrow Adsorption of *CO* on tungsten.
- \Rightarrow Adsorption of hydrogen on nickel.

4. ADSORPTION OF GASES ON SOLIDS

All solids adsorb gases to some measurable extent. The magnitude of adsorption of gases by solids depends on (i) the nature of adsorbent. (ii) the specific area of adsorbent, (iii) the nature of adsorbate, (iv) temperature, and (v) the pressure of gas.

Factors Influencing Adsorption of Gases on Solids

1. The Nature of Adsorbent

Even though all solids adsorb gases to some extent, porous substances like silica gel, alumina, and charcoal are very effective as adsorbents. The adsorption power of these substances can further be enhanced by a process called activation. During activation, the adsorbent is heated in steam or air atmosphere to about 1500°C. Heating drives out all impurities as gases and thereby leads to a larger free surface for adsorption.

Example: Activated charcoal at 24°C adsorbs 1.48 gm of carbon tetrachloride per gram of charcoal whereas before activation it could adsorb only 0.011gm per gram of charcoal.

2. The Specific Area of Adsorbent

Adsorption involves accumulation of a substance on the surface of adsorbent. Hence, the extent of adsorption depends upon the specific area of adsorbents. Specific area of an adsorbent is the surface area available for adsorption per gram of the adsorbent. The larger the surface area of the adsorbents, the greater is the adsorption.

Example: Finely divided metals like *Ni* and *Pt* etc. and porous substances like charcoal, fuller's earth, silica etc. provide large surface area and are the best solid adsorbents.

3. The Nature of Adsorbate (Gas Adsorbed)

The volume of gas adsorbed by solid adsorbent depends on the nature of the gas. Since physical adsorption is non-specific, every gas gets adsorbed on the surface of any solid. How much will get adsorbed depends on the nature of the gas.

Example: Under a given condition of temperature and pressure, more readily soluble and easily liquefiable gases such as NH_3 , HCl, Cl_2 , SO_2 , etc., have significant van der waal's forces of attraction and hence they are adsorbed more readily than those gases which do not liquefy easily (H_2 , O_2 and N_2).

4. Effect of Temperature

Since adsorption is an exothermic process, an increase in temperature leads to a decrease in the amount of gas adsorbed on solids and vice versa.

In the case of physical adsorption, a rise in temperature increases the kinetic energies of adsorbed molecules and hence the molecules leave the surface and thereby lowering the extent of adsorption.

In the case of chemical adsorption, the chemical bond forms between the adsorbate and the adsorbent cannot be broken easily and hence the adsorption increases initially. But, high temperature increases the activation energy of adsorbed molecules, in turn causes the desorption of adsobates (Fig. 4.1).

Example: At 600 mm pressure, one gram of charcoal adsorbs about 10 cc of nitrogen at 0° C, about 20cc of nitrogen at -30° C and about 45 cc of nitrogen at -80° C.



Fig. 4.1: Effect of temperature on adsorption of gases on solids

5. Effect of Pressure

According to Le-Chatlier's principle, the amount of gas adsorbed by a solid increases with the increase of pressure at constant temperature and vice versa.

5. THE FREUNDLICH ADSORPTION ISOTHERM

Freundlich suggested an empirical equation (which is known as Freundlich adsorption isotherm) to show the variation of the amount of gas adsorbed per unit mass of the adsorbent with pressure at constant temperature.

$$\frac{x}{m} = kP^{\frac{1}{n}} \qquad \dots (1)$$

where x is the amount of gas adsorbed, m is the mass of adsorbent; P is the equilibrium pressure and k and n are constants which depend on the nature of the adsorbate and adsorbent and on the temperature. This equation is applicable only at low pressure. In order to test equation (1), take the logarithm on both sides, we get:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P \qquad \dots (2)$$

This mathematical equation (2) is known as Freundlich adsorption isotherm.

The Freundlich adsorption isotherm is also used for the adsorption of solute from solution and has been found satisfactory. The pressure in the equation (1) is replaced by equilibrium concentration (c) of solute.

$$\frac{x}{m} = kc^{\frac{1}{n}} \qquad \dots (3)$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \qquad \dots (4)$$

Testing of Freundlich Adsorption Isotherm

Freundlich equation explains the behaviour of adsorption approximately. The value n lies between 0 and 1. Here 'k' is a measure of the capacity of the adsorbent (mass adsorbate/mass adsorbent) and 'n' is a measure of how the affinity of the adsorbate changes with changes in adsorption density.

Case 1: When n = 1, the Freundlich isotherm becomes linear isotherm and indicates that all sites on the adsorbent have equal affinity for adsorbate.

Case 2: When *n*<1 indicates that affinities decrease with increasing adsorption density.

The linearised form of Freundlich adsorption isotherm can be used to calculate k and n values, which can be written as:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

On plotting log $\frac{x}{m}$ against log *P*, a straight line is obtained with slope 1/n and intercepts log *k* (Fig. 4.2).



Limitations of Freundlich Adsorption Isotherm

- 1. Freundlich's adsorption isotherm fails if the pressure (or concentration) of adsorbate is very high. This equation is valid over a certain range of pressure or concentration only.
- 2. Freundlich equation is purely empirical. It has no theoretical basis.
- 3. The constant k and n are not temperature independent. They vary with temperatures.

6. THE LANGMUIR ADSORPTION ISOTHERM

Freundlich adsorption isotherm holds good for a certain range of pressure only. Moreover, it is a purely empirical formula without theoretical foundations. To solve these difficulties, Langmuir (1916) worked out an adsorption isotherm known as Langmuir's adsorption isotherm.

Postulates (or) Assumptions of Langmuir Adsorption Isotherm

- \Rightarrow The adsorbed gas forms only a unimolecular layer on the solid adsorbent (i.e.: adsorbed gas is unimolecular in thickness).
- \Rightarrow The adsorbed molecules on the surface do not interact with each other.
- \Rightarrow The molecules of a gas are adsorbed only on vacant sites of the adsorbent surface. Each site can hold only one molecular species of the adsorbate.
- \Rightarrow The process of adsorption is a dynamic process, which consists of two opposite processes.
 - (i) Condensation (Adsorption) Process: It involves the condensation (adsorption) of molecules of the gas on the surface of the solid
 - (ii) Evaporation (Desorption) Process: It involves evaporation (desorption) of molecules of the adsorbate from the surface of the adsorbent

Derivation of Langmuir Adsorption Isotherm

Consider an adsorbing surface of area 1 square centimeter is exposed to a gas (Fig. 4.3). Molecules of the gas will strike the surface and stick for an appreciable time due to condensation while other gas molecules will evaporate from the surface due to thermal agitation.

If θ is the fraction of surface area covered by gas molecules at any instant, then the fraction of the remaining surface available for adsorption is $(1-\theta)$.



Fig. 4.3: Equilibrium between free molecules and adsorbed molecules

If *P* is the pressure of the gas, then the rate of condensation (adsorption) molecules is expected to be the proportional to the pressure, *P* and fraction of uncovered surface, $(1-\theta)$. Hence,

The rate of adsorption $=k_1(1-\theta)P$...(1)

The rate at which gas molecules evaporates from the surface (desorption) will depend on the fraction of the surface covered by the gas molecules, (θ) . Hence,

The rate of evaporation of gas
$$= k_2 \theta$$
 ...(2)
molecules

where k_1 and k_2 are proportionality constants for a given system.

At equilibrium, the rate of adsorption and the rate of evaporation are equal, then,

$$k_{1}(1-\theta)P = k_{2}\theta$$

$$k_{1}P - k_{1}P\theta = k_{2}\theta$$

$$k_{1}P = k_{2}\theta + k_{1}P\theta$$

$$k_{1}P = \theta(k_{2} + k_{1}P)$$

$$\theta = \frac{k_{1}P}{k_{2} + k_{1}P}$$
...(3)

Dividing the numerator and denominator of the right hand side of equation (3) by k_2 , we get:

$$\theta = \frac{\binom{k_1}{k_2}P}{1 + \binom{k_1}{k_2}P}$$

$$\theta = \frac{bP}{1 + bP} \qquad \dots (4)$$

where $b = k_1/k_2$ and is called adsorption coefficient.

If x is the amount of gas adsorbed on the mass m of the adsorbent, then x/m is the amount of gas adsorbed per unit mass of the adsorbent.

Since the amount of gas adsorbed per unit mass of adsorbent (x/m) is proportional to the fraction (θ) of the surface covered, then

$$\frac{x}{m} \quad \alpha \theta$$

$$\frac{x}{m} = k \theta$$

$$\theta = \frac{x}{km} \qquad \dots (5)$$

where k is proportionality constant.

Substituting the value of θ in equation (4), we have

$$\frac{x}{km} = \frac{bP}{1+bP}$$
$$\frac{x}{m} = \frac{kbP}{1+bP}$$
$$\frac{x}{m} = \frac{aP}{1+bP}$$
...(6)

where the constant a = kb.

Equation (6) relates the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as the Langmuir adsorption isotherm.

The constant a and b depends on the nature of the system and on the temperature. In order to test this isotherm, the *equation* (6) is divided by P on both sides, we get:

$$\frac{\binom{x}{m}}{P} = \frac{1}{P} \left[\frac{aP}{1+bP} \right] \qquad \dots (7)$$

Further taking reciprocals, we get:

$$\frac{P}{\begin{pmatrix} x \\ m \end{pmatrix}} = \frac{P(1+bP)}{aP}$$

$$\frac{P}{\begin{pmatrix} x \\ m \end{pmatrix}} = \frac{(1+bP)}{a}$$

$$\frac{P}{\begin{pmatrix} x \\ m \end{pmatrix}} = \frac{1}{a} + \left(\frac{b}{a}\right)P$$
...(8)

This equation is similar to an equation for a straight line (y = mx + c). Hence if P/(x/m) is plotted against *P*, a straight line should be obtained with a slope equal to (b/a) and intercept equal to (1/a) (*Fig. 4.4*).



Fig. 4.4: Langmuir Adsorption Isotherm

Testing of Langmuir Adsorption Isotherm

We shall now consider three special cases of Langmuir isotherm.



Fig. 4.5: Testing of Langmuir Adsorption Isotherm

Case 1: At very low pressures, bP can be neglected in comparison with unity (i.e: bP <<1) and hence,

$$\frac{P}{\begin{pmatrix} x \\ m \end{pmatrix}} = \frac{1}{a}$$
$$\frac{x}{m} = a P$$

At very low pressures, the amount of gas adsorbed is directly proportional to the pressure.

Case 2: At high pressures bP >> 1, and hence 1 can be neglected in comparison with bP.

$$\frac{P}{\begin{pmatrix} x/m \end{pmatrix}} = \left(\frac{b}{a}\right)P$$
$$\frac{x}{m} = \frac{a}{b} \qquad \dots(10)$$

At very high pressures, the extent of adsorption at a given temperature is independent of pressure of the gas. This condition arises when the surface of the adsorbent is completely covered by the unimolecular layer of gas molecules.

Case 3: At intermediate pressure, Langmuir equation becomes Freundlich equation.

At very low pressure,

$$\frac{x}{m} \quad \alpha P$$

$$\frac{x}{m} = k P$$

At very high pressure,

 $\frac{x}{m} = k$

At intermediate pressure, the equation becomes:

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

where the value *n* lies between 0 and 1. This equation is known as *Freundlich equation*.

7. KINETICS OF UNIMOLECULAR SURFACE REACTIONS

Let us consider a unimolecular surface reaction between molecules of *A* and the vacant site of the surface *S*. The mechanism of unimolecular reaction may be represented as:

$$A + S \xrightarrow{k_1} AS$$
$$AS \xrightarrow{k_2} A + S$$
$$AS \xrightarrow{k_2} \Pr oducts$$

If *r* is the rate of the reaction, then according to Langmuir-Hinshelwood hypothesis, *r* is proportional to the fraction of the surface covered (θ). Hence,

$$r = k_2 \theta \qquad \dots (1)$$

Assuming steady-state approximation for the concentration of AS, we have

$$r = \frac{d[AS]}{dt} = k_1[A][S] - k_{-1}[AS] - k_2[AS] = 0 \qquad \dots (2)$$

If C_S is the total concentration of active sites on the surface, then the concentration [S] of the vacant sites on the surface is equal to the product of C_S and $(1-\theta)$, where $(1-\theta)$ is the fraction of sites remaining uncovered. Therefore,

$$[S] = C_s(1-\theta) \qquad \dots (3)$$

From the equation (2)

$$\begin{bmatrix} (2) \\ [AS] \end{bmatrix} = \frac{k_1[A][S]}{k_{-1} + k_2} \qquad \dots (4)$$

Also, the concentration of AS on the surface [AS], is given by:

$$[AS] = C_S \theta \qquad \dots (5)$$

From the above equations (3), (4), and (5), we get:

$$C_{S}\theta = \frac{k_{1}[A]C_{S}(1-\theta)}{k_{-1}+k_{2}} \dots (6)$$

$$\frac{1-\theta}{\theta} = \frac{k_{-1}+k_2}{k_1[A]} \qquad \dots (7)$$

$$\frac{1}{\theta} - 1 = \frac{k_{-1} + k_2}{k_1[A]} \qquad \dots (8)$$

$$\frac{1}{\theta} = \frac{k_{-1} + k_2}{k_1[A]} + 1 \qquad \dots (9)$$

$$\frac{1}{\theta} = \frac{k_1[A] + k_{-1} + k_2}{k_1[A]} \dots (10)$$

$$\theta = \frac{k_1[A]}{k_1[A] + k_{-1} + k_2} \qquad \dots (11)$$

Substituting the value of θ in equation (1), we get:

$$r = \frac{k_1 k_2 [A]}{k_1 [A] + k_{-1} + k_2} \qquad \dots (12)$$

Equation (11) may be rewritten in the form:

(or)

$$\frac{1}{r} = \frac{k_1[A] + k_{-1} + k_2}{k_1 k_2[A]} \dots (13)$$

$$\frac{1}{r} = \frac{1}{k_2} + \frac{k_{-1} + k_2}{k_1 k_2 [A]} \dots (14)$$

According to equation 14, a plot of 1/r versus 1/[A] would give a straight line with intercept equal to $1/k_2$ and slope equal to $(k_{-1}+k_2)/k_1k_2$.

For gaseous adsorbate, the concentration is expressed in terms of the partial pressure. Hence, the equations (12) and (14) can be written as follows:

$$r = \frac{k_1 k_2 P_A}{k_1 P_A + k_{-1} + k_2} \dots (15)$$

8. THE BET THEORY OF MULTIMOLECULAR LAYER ISOTHERM AND DETERMINATION OF SURFACE AREA OF ADSORBENTS

Postulates of Brunauer-Emett-Teller (BET) adsorption isotherm

- \Rightarrow The adsorption involves the formation of multimolecular layer of adsorbate molecules on the surface of solid adsorbent.
- \Rightarrow The multilayer adsorption takes place the following manner:

Vapour + Free surface of adsorbent	\longrightarrow	Monolayer
Vapour + Monolayer	\longrightarrow	Bimolecular layer
Vapour + Bimolecular layer	\longrightarrow	Trimolecular layer
Vapour + Trimolecular layer	>	Multimolecular layer

- \Rightarrow Langmuir assumption applies to each layer and there is sa dynamic equilibrium exits between the successive layer. Further, the rate of from the first layer is equal to the rate of condensation of preceding layer.
- \Rightarrow The heat of adsorption in each layer (except the first layer) is involved in each of the evaporation process. After the formation of first layer, the heat of adsorption is equal to the latent heat of condensation of vapours.

Mathematical Expression of Brunauer-Emett-Teller (BET) Adsorption Equation

$$V_{tot} = \begin{bmatrix} V_m c \left(\frac{P_{P_o}}{P_o} \right) \\ \hline \left(1 - \frac{P_{P_o}}{P_o} \right) \left[1 - \left(\frac{P_{P_o}}{P_o} \right) + c \left(\frac{P_{P_o}}{P_o} \right) \right] \end{bmatrix} \quad \text{where } c = \begin{pmatrix} k_1 \\ k_L \end{pmatrix} \quad \dots \dots \dots (16)$$

- \Rightarrow Equation (16) is the required equation for adsorption of gaseous molecules on adsorbent surface and it is known as BET adsorption equation for multi-molecular layer formation.
- \Rightarrow Let *P*/*P*_o as *x* and hence BET equation may be represented as:

$$V_{tot} = \left[\frac{V_m \ cx}{(1-x)\left[1-x+cx\right]}\right] \quad \dots \dots (1)$$

9. APPLICATIONS OF ADSORPTION

- 1. Charcoal, because of its porous nature, adsorbs large volumes of gases including most of the poisonous ones, and is therefore used in gas masks.
- 2. Minute particles of platinum attract and hold multitudes of hydrogen molecules on their surfaces. Its ability to adsorb other gases makes platinum very useful in the production of sulfuric acid by the contact process and in the preparation of ammonia.
- 3. Charcoal is used in industry to remove colors from solutions, since it adsorbs many coloring materials and carry these with them when separated from the solution.
- 4. Adsorption is employed in the hydrogenation of oils, in gas analysis, and in chromatography.
- 5. In electrochemistry, molecules adsorbed to the surface of an electrode donate or accept electrons from the electrode as part of oxidation or reduction reactions.
- 6. In adhesion and lubrication, the chemical and mechanical properties of adsorbed monolayer play a role in determining how solid surfaces behave when in contact with one another.
- 7. In biological systems, the adsorption of atoms and molecules onto the surface of a cell membrane is the first step in molecular recognition.
- 8. In air pollution control, activated carbon is used as adsorbent for the removal of gaseous pollutants from the exhaust gases of industrial sources such as power stations, kilns, smelters, and nitric and sulphuric acid production plants.
- 9. In water pollution control, granular activated carbon (GAC) is effective in removing a variety of volatile and non-volatile organic contaminants, taste and odour causing organic compounds, synthetic organic chemicals such as pesticides, aromatic solvents, phenols and high molecular weight hydrocarbons.

10. CATALYSTS / CATALYSIS

A catalyst is a substance which alters the rate of chemical reaction but remains chemically unchanged at the end of the reaction. This phenomenon is called catalysis.

Those catalysts which increase the reaction rate are called positive catalysts while those which slow down the reaction rate are called negative catalysts or inhibitors.

Criteria of Catalytic Reactions

The following are the general characteristics of most catalysts and catalytic reactions.

1. A catalyst remains unaltered in amount and in chemical composition at the end of the reaction; however, it may undergo physical changes.

For example, granular MnO_2 used as the catalyst in the thermal decomposition of potassium chlorate and it recovered back as a fine powder at the end of the reaction.

2. A small amount of catalyst is generally sufficient to change the rate of reaction.

For example, 10^{-3} gm. ions/litre of Cu^{2+} is sufficient to change the rate of oxidation of sodium sulphate by oxygen in an aqueous solution.

- 3. A catalyst cannot initiate a reaction. It can only accelerate or retard the speed of a chemical reaction by decreasing or increasing the energy of activation.
- 4. A catalyst does not alter the equilibrium state of a reversible reaction: It simply alters the rate of both the forward and backward reactions so that the equilibrium condition is reached more quickly.
- 5. Every catalyst has a specific action. For a particular reaction, there is a particular catalyst. Even the same reactants in presence of different catalysts give different products.

For example, hydrogen and carbon monoxide combine in presence of different catalysts to produce different products.

$$CO + 2H_2 \xrightarrow{ZnO+Cr_2O_3} CH_3OH$$

$$250^{\circ}C$$

$$CO + 3H_2 \xrightarrow{Ni_3} CH_4 + H_2O$$

6. A catalyst can be poisoned by the presence of small amount of certain substances called catalytic poison.

Examples of catalytic poisons are carbon monoxide, arseneous oxide, hydrogen cyanide, hydrogen sulphide etc.

7. The activity of a catalyst is enhanced by the presence of substances called promoters.

Examples of catalytic promoters are molybdenum, bismuth, zinc oxide, chromium oxide etc.

11. CLASSIFICATION OF CATALYSIS

Catalyzed reactions are divided into two classes namely homogeneous and heterogeneous depending on the physical state of reactants, products and catalysts.

1. Homogeneous Catalysis

In homogeneous catalysis, the catalyst is present in the same phase as the reactants. It can occur in gas or liquid phase.

(i) Homogeneous Catalysis in Gas Phase

(a) Oxidation of sulphur dioxide in lead chamber for the manufacture of sulphuric acid is catalyzed by gaseous nitric oxide.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3$$

(b) Decomposition of acetaldehyde is catalyzed by iodine vapour. $CH_3CHO(g) \xrightarrow{I_2 \text{ vapour}} CH_4 + CO$

(ii) Homogeneous Catalysis in Liquid Phase: Acid-Base Catalysis

Homogeneous catalyzed reactions in a solution are mostly catalyzed by acids or bases. These are often referred to as acid-base catalysis. The most common acid catalyst in water solution is the hydronium ion; the most common base is hydroxyl ion.

If any acid catalyses the reaction, it is referred to as general acid catalysis. Similarly if any base catalyses the reaction, it is referred to as general base catalysis. If only certain acids or hydroxyl ions are effective, the phenomenon is called specific acid or specific base catalysis.

a. GENERAL ACID CATALYSIS

Under general acid catalysis, not only H^+ ions catalyse the reactions but also all Bronsted acids (proton donors) can catalyze the reaction. *Examples:* H^+ ions; undissociated acid (*CH*₃*COOH*); cations of weak base (*NH*₄⁺) etc.

In general acid catalysis, the H^+ ion or a Bronsted acid transfers a proton to the reactant to form an intermediate complex which then decomposes and gives back the proton.

Examples: The mechanism of keto-enol tautomerism of acetone.



b. General Base Catalysis

Under general base catalysts, not only OH ions catalyse the reactions but also all Bronsted bases (proton acceptors) can catalyse the reaction. *Examples:* OH^- ions; anions of weak acid (*CH*₃*COO*⁻); undissociated base.

In general base catalysis, the OH^- ion or a Bronsted base accepts a proton to form an intermediate complex which then decomposes to regenerate OH^- or Bronsted base.

Examples: Decomposition of nitramide by OH⁻ ions.

 $\begin{array}{ccc} NH_4NO_2 & \xrightarrow{OH^-} NH_4NO_2^- + H_2O \\ \text{Nitramide} & \text{Intermediate complex} \\ NH_4NO_2^- & \rightarrow N_2O + OH^- \end{array}$

c. Specific Acid Catalysis

Inversion of cane-sugar and hydrolysis of ester are the typical examples of specific acid catalysis.

 $\begin{array}{ccc} C_{12}H_{22}O_{11}+H_2O & \xrightarrow{H_3O^+} & C_6H_{12}O_6+C_6H_{12}O_6\\ \text{Cane sugar} & \text{Glucose Fructose} \end{array}$

$CH_3COOC_2H_5 + H_2O$	$\xrightarrow{H_3O^+} CH_3COOH$	$U + C_2 H_5 OH$
Ethyl aceate	Acetic acid	Ethanol

The reactions are catalysed by certain acids or H_3O^+ ions only. However, different acids have different activities.

For example, HCl has a greater activity than CH_3COOH . It is evident that the actual catalysts are H^+ or H_3O^+ ions. The rate of reaction is found to be proportional to the concentrations of H_3O^+ ions and the concentration of the reacting molecules or ions.

d. Specific Base Catalysis

Conversion of acetone to diacetonyl alcohol is an example of specific base catalysis. This reaction is catalysed by OH^- ions only.

 $\begin{array}{ccc} CH_{3}COCH_{3} + CH_{3}COCH_{3} & \xrightarrow{OH^{-}} CH_{3}COCH_{2}C(CH_{3})_{2}OH \\ \text{Acetone} & \text{Acetone} & \text{Diacetonylalcohol} \end{array}$

2. Heterogeneous Catalysis

In heterogeneous catalyzed reactions, the catalyst is present in a different phase from that of the reactants. In most of the cases, gaseous reactants are catalyzed by solid catalysts and the reactions proceed at the surface of the solid catalysts. This type of process is referred to as *contact catalysis*.

Some important examples of heterogeneous catalysis are given below.

(i) Combination of SO_2 and oxygen in the presence of finely divided platinum or V_2O_5 (Contact process for sulphuric acid).

$$2SO_2(g) + O_2(g) \xrightarrow{Pt \text{ or } V_2 O_5(S)^{+}} 2SO_3$$

(ii) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron (Haber process for ammonia).

$$N_2(g) + 3H_2(g) \xrightarrow{Fei(S)} 2NH_3$$

(iii)Hydrogenation of unsaturated organic compounds is catalyzed by finely divided nickel.

$$H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3$$

12. ENZYME CATALYSIS

Characteristics of Enzyme Catalysts

 \Rightarrow Enzymes are extremely specific in their catalytic function. For example, the enzyme *urease* will catalyze the hydrolysis of urea and no other reactions.

- \Rightarrow The activity of enzyme depends on the temperature. All enzymes are effective at room temperature. Since many of them are so sensitive, they become inactive at about 50°C.
- \Rightarrow The enzyme activity also depends on the pH.

Some important examples are:

1. Maltase, an enzyme converts maltose into glucose

 $C_{12}H_{22}O_{11} + H_2O \xrightarrow{Maltase} 2 C_6H_{12}O_6$

- 2. Urease, an enzyme converts urea into ammonia. $NH_2CONH_2 + H_2O \xrightarrow{Urease} 2 NH_3 + CO_2$
- 3. *Zymase*, an enzyme converts glucose into ethanol.

 $C_6H_{12}O_6 + H_2O \xrightarrow{Zymase} 2 C_2H_5OH + 2 CO_2$

4. Diastase, an enzyme converts starch into maltose sugar

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} n C_{12}H_{22}O_{11}$$

Kinetics of Enzyme Catalysis (Michaelis – Menten Equation)

The general mechanism for the kinetics of enzyme-catalysed reaction was first proposed by L.Michaelis and Mary Menten in 1913.

The mode of action of an enzyme in Michaelis-Menten mechanism is as follows:

(i) Formation of the Enzyme-substrate complex.

$$E+S \quad \stackrel{k_1}{\Leftrightarrow} ES$$

(ii) Decomposition of the complex.

$$ES \longrightarrow P + E$$

where E is the enzyme, S is the substrate, ES is the enzyme-substrate complex, (intermediate activated complex) and P is the end product.

The rate of formation of the product is given by

$$\frac{d[P]}{dt} = r = k_3[ES] \qquad \dots (1)$$

In order to solve the equation (1), it is necessary to know the concentration of *ES*. This can be calculated through steady-state principle. According to this "when a short-lived reaction intermediate exists at low concentration in a system, the rate of formation of intermediate can be considered to be equal to its rate of disappearance.".

Applying steady-state principle,

$$k_{1}[E][S] = k_{2}[ES] + k_{3}[ES]$$

$$k_{1}[E][S] = [ES](k_{2} + k_{3})$$

$$[ES] = \frac{k_{1}[E][S]}{(k_{2} + k_{3})} \dots (2)$$

Since the enzyme exists either in free form E, or the combined form ES, the total concentration of the enzyme, E_o originally added can be obtained from the material balance equation.

$$\begin{bmatrix} E_0 \end{bmatrix} = \begin{bmatrix} E \end{bmatrix} + \begin{bmatrix} ES \end{bmatrix}$$
$$\begin{bmatrix} E \end{bmatrix} = \begin{bmatrix} E_0 \end{bmatrix} - \begin{bmatrix} ES \end{bmatrix} \qquad \dots (3)$$

Inserting the value [E] in equation (2), we get

$$[ES] = \frac{k_1 \{ [E_0] - [ES] \} [S]}{(k_2 + k_3)}$$

$$(k_2 + k_3) [ES] = k_1 [E_0] [S] - k_1 [ES] [S]$$

$$(k_2 + k_3) [ES] + k_1 [ES] [S] = k_1 [E_0] [S]$$

$$[ES] \{ (k_2 + k_3) + k_1 [S] \} = k_1 [E_0] [S]$$

$$[ES] = \frac{k_1 [E_0] [S]}{k_1 [S] + (k_2 + k_3)} \qquad \dots (4)$$

Substituting [*ES*] in equation (1), we get:

$$\frac{d[P]}{dt} = r = \frac{k_3 k_1 [E_0] [S]}{k_1 [S] + (k_2 + k_3)} \qquad \dots (5)$$

Dividing the numerator and denominator of equation (5) by k_1 gives,

$$\frac{d[P]}{dt} = r = \frac{k_3[E_0][S]}{[S] + \left(\frac{k_2 + k_3}{k_1}\right)}$$

$$r = \frac{k_3[E_0][S]}{[S] + k_m} \qquad \dots (6)$$
where $k_m = \left(\frac{k_2 + k_3}{k_1}\right)$

 k_m is called Michaelis constant and equation (6) is known as *Michaelis-Menten equation*.

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REVIEW QUATIONS

PART – A QUESTIONS

- 1. Distinguish between adsorption and absorption?
- 2. Distinguish between adsorbent and adsorbate.
- 3. Distinguish between physical adsorption and chemical adsorption?
- 4. Mention any three factors that influence the adsorption of gases on solids.
- 5. What is the effect of temperature on the adsorption of gases on solids?
- 6. How does pressure influence adsorption of gas on solids?
- 7. What is meant by adsorption isotherm?
- 8. State Freundlich adsorption isotherm.
- 9. Mention the limitations of Freundlich adsorption isotherm.
- 10. Outline the postulates of BET adsorption theory.
- 11. Mention any two applications of adsorption.
- 12. Outline the characteristics of catalyst.
- 13. Differentiate homogeneous catalysis and heterogeneous catalysis.
- 14. Differentiate catalytic promoters and catalytic poisons.
- 15. What are the characteristics of enzyme catalysts?

PART – B QUESTIONS

- 1. Distinguish between physisorption and chemisorption.
- 2. Discuss the factors which affect the adsorption of a gas on a solid adsorbent?
- 3. Explain Freundlich adsorption isotherm? Give the conditions in which it fails.
- 4. Derive Langmuir's adsorption isotherm stating the assumptions on which it is based? Show that at normal pressure, Langmuir's adsorption isotherm becomes identical with Freundlich's adsorption isotherm.
- 5. Explain the kinetics of unimolecular surface reaction.
- 6. Define the term adsorption and list its applications.
- 7. What is meant by catalysis? Discuss the general characteristics of a catalyst?
- 8. What is meant by acid-base catalysis? Give an example for general acid-base catalysis and specific acid-base catalysis.
- 9. Derive Michaelis-Menten equation for enzyme catalysis?


SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – V– Physical Photochemistry – SCY1316

1. INTRODUCTION

Photochemistry deals with the study of the rate and mechanism of various chemical reactions which take place by absorbing radiations of visible/ultraviolet regions of wavelength 200 to 800 nm. Such reactions are termed as photochemical reactions. A valid application of photochemistry is photophysical phenomena such as fluorescence and phosphorescence. The fluorescent and phosphorescent materials are used in fluorescent tube lights, x-rays, TV screen etc. The study of photochemical reactions is utilized for the manufacture of solar cells which are replacing traditional sources of fuels. If suitable photochemical reactions and devices are discovered with proper utilization of these sources of light energy, we would be able to solve half of the world's energy problem.

2. DARK AND PHOTOCHEMICAL REACTIONS

1. Dark Reactions

Reactions which are induced by temperature, concentration of reactants and products or by the presence of catalysts etc. except light radiations are known as dark reactions or thermal reactions.

✓ Examples:

 $N_2 + 3H_2 \iff 2NH_3$

$$PCl_5 \iff PCl_3 + Cl_2$$

2. Photochemical Reactions

- Reactions which occur by the absorption of visible and ultraviolet light of wave lengths 200 to 800 nm are known as photochemical reactions.
- ✓ Examples

2HBr	\rightarrow	$H_2 + Br_2$	(Dissociation)
$H_2 + Cl_2$	\rightarrow	2HCl	(Combination)
$2O_3$	\rightarrow	30_{2}	(Decomposition)

Table 5.1: Differences between Dark (Thermal) and Photochemical Reactions

S.No.	Photochemical Reactions	Dark or Thermal Reactions
1.	The activation energy is provided by	The activation energy is provided by
	light radiations of visible or ultraviolet	the collision of reactant molecules.
	of electromagnetic spectrum.	
2.	Only a few molecules succeeding in	Significant raises in temperature
	absorbing photons are strongly excited	increases the average energy of all
	and undergo photochemical reactions.	the molecules and undergo thermal
		reactions.

3.	For spontaneous photochemical	For spontaneous thermal reactions,
	reactions, ΔG may be positive or	ΔG must be always negative.
	negative.	
3.	Examples: Ozonisation of oxygen;	Examples: Formation of ammonia;
	Photosynthesis occurring in plants	Dissociation of PCl ₅ .

3. LAWS OF ABSORPTION

- > The absorption of light by any absorbing material is given by:
 - ✓ Lambert's law (First law of absorption)
 - ✓ Beer's law (Second law of absorption)

Statement of Lambert's Law

- When a beam of monochromatic light passes through a transparent absorbing medium, the rate of decrease of intensity of radiation with thickness of the absorbing medium is proportional to the intensity of incident radiation.
- ➤ Mathematically it is expressed as:

$$\frac{-dI}{dx} \quad \alpha \quad I$$

$$\frac{-dI}{dx} = kI \qquad \dots \dots (1)$$

Where,

- \checkmark *I* is the intensity of incident light
- \checkmark x is the thickness of the absorbing substance and
- \checkmark *k* is the absorption coefficient.

Mathematical Derivation of Lambert's Law

> If I_o is the intensity of radiation before entering the solution and I is the intensity of radiation after passing through any thickness (say, x = 0 to x), the equation (1) can be rearranged and integrated as:

$$\int_{I_o}^{I} \frac{dI}{I} = -\int_{0}^{x} k \, dx$$
$$\left[\ln I\right]_{I_o}^{I} = -k[x]_{0}^{x}$$
$$\left[\ln I - \ln I_o\right] = -k[x-0]$$
$$\frac{\ln \frac{I}{I_o}}{I_o} = -kx$$

Taking exponential on both the sides:

$$e^{\ln\left(\frac{I}{I_{o}}\right)} = e^{-kx}$$

$$\frac{I}{I_{o}} = e^{-kx} \qquad \left[\because e^{\ln x} = x \right]$$

$$I = I_{o} e^{-kx} \qquad \dots (2)$$

> The equation (2) is known as the mathematical derivation of Lambert's law.

✤ Statement of Beer's Law

- When a beam of monochromatic radiation passes through an absorbing solution, the rate of decrease of intensity of radiation with the thickness of the absorbing solution is proportional to (i) the concentration of solution and (ii) the intensity of incident radiation.
- ➤ Mathematically, it is expressed as:

$$\frac{-dI}{dx} \quad \alpha \quad cI$$

$$\frac{-dI}{dx} = k'cI \qquad \dots (3)$$

Where,

- \checkmark *I* is the intensity of incident light
- \checkmark x is the thickness of the absorbing solution
- \checkmark *c* is the concentration of the solution and
- \checkmark *k*' is molar absorption coefficient.

Mathematical Derivation of Beer's Law (Beer – Lambert's Law)

> If I_o is the intensity of radiation before entering the absorbing solution and I is the intensity of radiation after passing through any thickness of the solution (say, l), then the Beer's law can be derived by rearranging and integrating the equation (3) as:

$$\int_{I_o}^{I} \frac{dI}{I} = -k'c \int_{x=0}^{x=l} dx$$

$$\left[\ln I\right]_{I_o}^I = -k'c\left[x\right]_0^l$$

$$\left[\ln I - \ln I_o\right] = -k'c[l-0]$$

$$\ln \frac{I}{I_o} = -k'cl \qquad \dots (4)$$

Taking exponential on both the sides:

е

$$e^{\ln\left(\frac{I}{I_{o}}\right)} = e^{-k'cl}$$

$$\frac{I}{I_{o}} = e^{-k'cl} \qquad [\because \ln x = e^{x}]$$

$$I = I_{o} e^{-k'cl} \qquad \dots (5)$$

- > The equation (5) is known as the mathematical derivation of **Beer's law**.
- > By taking natural logarithm on equation (4), we have

$$2.303 \log \frac{I}{I_o} = -k'cl$$

$$-\log \frac{I}{I_o} = \frac{k'cl}{2.303}$$

$$\log \frac{I_o}{I} = \varepsilon cl \qquad \left[\because \varepsilon = \frac{k'}{2.303}\right]$$

$$A = \varepsilon cl \qquad \dots (6)$$

Where,

 $\checkmark \log \frac{I_o}{I}$ is known as absorbance (A) or optical density

- \checkmark *l* is thickness or path length of the cell
- \checkmark c is the molar concentration of the solution and
- \checkmark ϵ is the molar absorptivity.
- > The equation (6) is the mathematical derivation of *Beer-Lambert's law*. It states that, "when a beam of monochromatic radiation passes through a transparent absorbing solution, the amount of light absorbed (A) is proportional to the concentration of the solution (c) and the thickness (l, path)length) of the solution."

♦ LIMITATIONS OF BEER-LAMBERT'S LAW

- Discrepancies or Deviations from Beer-Lambert law have been observed:
 - \checkmark When the absorbing solute dissociates or associates in solution.
 - ✓ At higher concentrations on an absorbance versus concentration plot, where the curve bends towards the concentration axis.
 - \checkmark In scattering of light due to particulates in the sample.
 - \checkmark In changes of refractive index of the medium with concentration.

4. LAWS OF PHOTOCHEMISTRY

The photochemical reactions are governed by two basic laws, the Grotthus-Drapper law and Stark-Einstein law of photo-chemical equivalence.

***** Grotthus-Drapper Law

Grotthus – Drapper law states that "when the light falls on any substance, only the fraction of light that is absorbed by a substance can bring a chemical change; the reflected or transmitted light does not produce any such effect".

Stark–Einstein's Law of Photochemical Equivalence

- Stark-Einstein law states that "When an atom or molecule absorbs light of a given frequency, it absorbs photon of one quantum only".
- > The term one photon (or one quantum) means energy equal to $h\gamma$, where h is the Planck's constant and v is the frequency of radiation.

 $\begin{array}{rccc} AB &+& h\gamma &\rightarrow & AB^* \\ One & One & & Activated molecule \\ Photon & & \end{array}$

The law is concerned with the primary step of activation of molecule.

- Thus, in the primary process, the number of molecules that are activated is equal to the number of quanta absorbed.
- > Therefore, amount of energy (E) for activation of 1 gram mole will be:

$$E = N \times h\gamma$$

Where, N is the Avogadro's number and is equal to 1 gm mole.

> This quantity of energy (E) absorbed per mole of the substance is called an *Einstein*.

Illustration of Einstein's Law



One Photon, $h\gamma$



Fig. 5.1: Absorption of One Photon Decomposes One Molecule

5. QUANTUM YIELD (or) QUANTUM EFFICIENCY

Quantum efficiency (or quantum yield) is defined as "the ratio of number of molecules decomposed or formed to the number of quanta absorbed".

 $\phi = \frac{\text{number of molecules decomposed(or) formed}}{\text{number of quanta (photons) absorbed}}$

- > The photochemical equivalence law applies to primary photochemical process.
- As a result of primary absorption of one quantum, only one molecule undergoes dissociation and the products enter no further reaction. In such cases, the value of quantum yield will be unity.

$$\phi = \frac{\text{number of molecules dissociated}}{\text{number of photons absorbed}} = \frac{1}{1} = 1$$

If the yield is less than one, it is called a low quantum yield. If it is greater than one, it is called a high quantum yield.

Deviations in The Law of Photochemical Equivalence

* Case 1: Reasons for High Quantum Yield

The following are the reasons for high quantum yield:

> The primary process may produce free radicals, which may start a series of chain reactions.

- > Due to these secondary reactions many reactant molecules undergo chemical changes by absorbing one quantum only. In such cases, the value of ϕ will be greater than one.
- The reaction may be exothermic and the heat so evolved causes the collision and activates the other molecules to react without absorption of any additional quantum of radiations.
- The primary reactions may form an intermediate product which may acts as a catalyst for a series of reactions to occur without absorption of any additional quantum of radiations.

* Examples of High Quantum Yield Reactions

✓ The quantum yield of combination of CO and Cl_2 by a light of wavelength ranging from 400 to 436 nm is 10^3 .

$$CO + Cl_2 \rightarrow COCl_2 \qquad \Phi = 10^3$$

✓ The quantum yield of combination of H_2 and Cl_2 by a wavelength less than 450 nm varies from 10^4 to 10^{6} .

$$H_2 + Cl_2 \rightarrow 2HCl \qquad \varphi = 10^4 \text{ to } 10^6$$

Case 2: Reasons for Low Quantum Yield

The following are the reasons for low quantum yield:

- Excited molecules may lose their energy by collision with non-excited molecules. In such cases, the value of ϕ will be less than one
- Some of the excited molecules may re-radiate their energy before they have an opportunity for reacting. They will give low quantum yield.
- The excited molecules produced in the primary reaction may recombine to form the reactants so as to give low quantum yield.

Examples of Low Quantum Yield Reactions

 \checkmark The quantum yield of combination of H₂ and Br₂ to form HBr is about 0.01.

$$H_2 + Br_2 \rightarrow 2 HBr \qquad \phi = 0.01$$

 \checkmark The quantum yield of photolysis of ammonia by a light of wavelength 210 nm is 0.1.

$$2NH_3 \rightarrow N_2 + 3H_2$$
 $\phi = 0.1$

Experimental Determination of Quantum Yield

> The basic expression which defines the quantum yield (ϕ) of a photochemical reaction is given by:

- Hence, in order to determine the value of quantum yield of a photochemical reaction it is essential to know:
 - \checkmark The number of molecules decomposed or formed in a given time.
 - \checkmark The number of quanta absorbed during that time.

* Measurement of Number of Molecules Decomposed or Formed

The rate of reaction is measured by the usual methods. Small quantities of samples are periodically removed from the reaction mixture and its concentration is determined by monitoring various physical properties like absorption, refractive index or optical rotation.

* Measurement of Total Number of Einstein Absorbed

- An experimental arrangement for the study of a photochemical reaction is shown in Fig. 5.2.
- ➤ A is a source of light. Since visible and uv radiations are photo chemically active, a suitable source is necessary to get these radiations.
- ➢ For a quantitative type of work, mercury vapour lamp and tungsten lamp are used as *uv* radiations and visible radiations respectively.
- > To select radiation of only a single wavelength, the light is passed through the lens (B) into a monochromator (C).
- From C, the light enters the cell (D) immersed in a thermostat containing the reaction mixture.
- Finally, the light transmitted through D, falls on some suitable detector (E), where its intensity is determined.



Fig. 5.2: Apparatus for Study of Photochemical Reaction

- > The actinometer is used for determining the intensity of light coming out from the reaction vessel.
- The intensity of light is measured with the reaction cell when it is empty and then with a reaction mixture.

The difference between the two readings will give the amount of energy absorbed by the reaction system under examination. The intensity of light can be measured by using a chemical actinometer.

* Chemical Actinometers

- A chemical actinometer consists of a solution which is sensitive to light. When light is incident upon it, a chemical reaction will take place. The extent of reaction is a direct measure of energy absorbed by the reaction system.
- There are two main types of chemical actinometers: (i) Uranyl oxalate actinometer (ii) Ferrioxalate actinometer.

(i) Uranyl Oxalate Actinometer

- This actinometer is applicable to radiations lying between 200 and 500 nm with an average quantum yield of about 0.5.
- Uranyl oxalate actinometer consists of a solution of 0.05M oxalic acid and 0.01M uranyl sulphate in water.
- When light is incident upon it, oxalic acid undergoes dissociation to form CO, H₂O and CO₂.
- > The extent of decomposition of oxalic acid is a measure of intensity of light absorbed.
- > The progress of the reaction is determined by titrating with KMnO₄ before and after the exposure.

$$UO_2^{2+} + H_2C_2O_4 + h\gamma \rightarrow CO + CO_2 + H_2O + UO_2^{2+}$$

(ii) Ferrioxalate actinometer

- > In this actinometer, potassium ferrioxalate solution is used.
- > When the solution is irradiated, the reduction of Fe^{3+} to Fe^{2+} takes place.
- ▶ It is estimated colorimetrically by using O-phenanthroline as complexing agent.
- ➢ For wavelengths up to 400 nm, a solution of 0.006M K₃Fe(OX)₃ is employed. For longer wave lengths, a 0.15M solution is employed. Quantum yields vary from 1.2 to 1.1.

6. PHOTOPHYSICAL PROCESSES

1. Fluorescence

Definition

When a beam of light is incident on certain substances, they emit visible light and they stop emitting light as soon as the incident light is cut off. This phenomenon is known as *fluorescence*. Substances that exhibit fluorescence are called *fluorescent substances*.

✤ Explanation

➤ When a molecule of a substance absorbs light radiation, it gets excited to a higher energy state. In order to come back to ground state, it emits the excess energy at a greater wavelength within a short time ($\approx 10^{-8}$ seconds).

* Examples

- ✓ Minerals Fluorite, Petroleum, Vapours of sodium.
- ✓ Organic dyes Fluorescein, Eosin.
- ✓ Compounds Chlorophyll, Ultramarine, Riboflavin.

✤ Applications

- \checkmark The fluorescent materials are used in fluorescent tubes.
- \checkmark The difference in fluorescence caused by uv rays in different types of inks enables to detect forged documents.
- \checkmark When *uv* light is incident on newly laid eggs, they exhibit fluorescence with rosy colour while bad eggs appear blue.

*** TYPES OF FLUORESCENCE**

➤ There are two types of fluorescence.

(i) Resonance Fluorescence

- When an incident light falls on a substance and it emits light of same frequency as that of incident light, the phenomenon is known as *resonance fluorescence*.
- For example, when mercury vapours are exposed to light radiations of wave length 253.7 nm, it will get excited to higher states.

$$Hg + h\gamma(253.7nm) \rightarrow Hg^*$$

> If the excited atom returns to ground state, it emits radiations of same wavelength, 253.7 nm.

$$Hg^* \rightarrow Hg + h\gamma(253.7nm)$$

(ii) Sensitized Fluorescence

- A substance which is normally non-fluorescent, may be made fluorescent in the presence of other fluorescent substances. This phenomenon is known as *sensitized fluorescence*.
- For example, if the vapour of thallium is added to mercury vapour and exposed to radiations of wave length 253.7 nm, the vapour of thallium fluoresces.

Thus, the thallium which is non-fluorescent substance can be made fluorescent by adding mercury vapour.

 $Hg (normal) + h\gamma (Absorbed radiation) \rightarrow Hg^{*}(excited)$ $Hg^{*} + Tl (normal) \rightarrow Hg (normal) + Tl^{*} (excited)$ $Tl^{*} \rightarrow Tl + h\gamma (emitted radiation)$

2. Phosphorescence

Definition

When light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This type of delayed fluorescence is called *phosphorescence*. Substances that exhibit phosphorescence are called *phosphorescent substances*.

✤ Explanation

When a molecule of a substance absorbs light radiation of, it gets excited to a higher energy state. In order to return back to ground state, it emits the light of longer wavelength. In doing so, the excited molecules travel from one series of electronic state to another and get trapped. This shows the emission of light, which persists even after the removal of light source.

✤ Examples

- ✓ Minerals Ruby, Emerald.
- \checkmark Dyes when dissolved in boric acid or glycerol and cooled to form a glassy solid.
- ✓ Compounds: Cadmium sulphide, Barium sulphide.

* Applications

- ✓ Phosphorescent materials are used widely for dials on clocks and watches because they glow in the dark.
- ✓ The luminous paints contain 2.5% alkali chlorides and traces of heavy metal sulphide. Such a mixture is generally used for painting watch dials, electric switches etc.,

3. The Jablonski Diagram (Mechanism of Photophyscial Processes)

- The Jablonski diagram helps very much to understand the theory of non-radiative transitions (internal conversion and inter-system crossing) and radiative transitions (fluorescence and phosphorescence).
- In order to understand this diagram, one has to understand the meaning of singlet and triplet states. These terms arise from spin multiplicity. It defines the number of unpaired electrons in molecules in the absence of magnetic field.

✤ Ground Singlet State

In a molecule, always the electrons in the ground state are paired with opposite spin (\u03c4) (Fig. 5.3a).



Fig. 5.3a: Electrons in Ground Singlet State

- Such molecules will not have any unpaired electron in it (i.e. S = 0).
- Therefore the molecule will have spin multiplicity one. [S+1 (or) 0+1=1]. Such a state is called ground singlet state.
- Excited Singlet State
- If a molecule absorbs ultraviolet and visible radiation of the proper wavelength, one of the paired electrons gets raised to an excited state.
- In this excited state, the spin of the electron does not undergo any change and the net spin is still zero (Fig. 5.3b). Such a state is called excited singlet state.



Fig. 5.3b: Electrons in Excited Singlet State

***** EXCITED TRIPLET STATE

When a molecule absorbs ultraviolet and visible radiation of the proper wavelength, one of the paired electrons gets raised to an excited state with the opposite spin (Fig. 5.3c).



Fig. 5.3c: Electrons in Excited Triplet State

Such a system will have two unpaired electrons (S=2) and hence the system has the spin multiplicity 3. [S+1 (or) 2+1=3]. Such a state is called as *excited triplet state*. The excited molecules may lose their energy and come to ground state either without emitting radiation (called non-radiative transitions) or by emitting radiations (called radiative transitions). In the case of non-radiative transitions, the energy is lost as heat.

1. Non-Radiative Transitions

(i) Internal conversion

- ▶ When the activated molecule returns from the higher excited states (S_3 or S_2 , T_3 , T_2) to the first excited state (S_1 or T_1), the energy of the activated molecules are lost in the form of heat by molecular collisions.
- > This process is known as internal conversion (IC). All the internal conversions occur in less than about 10^{-11} second.

(ii) Inter-system conversion (ISC)

- > This process involves transition between states of different spins (From $S_1 \rightarrow T_1$ or $S_2 \rightarrow T_2$).
- Such a transition is known as non-radiative transition (or) inter-system crossing (ISC). Spectroscopically, such transitions are said to be "forbidden". However, they do take place, at relatively slow rates.

2. Radiative Transitions

> These transitions give rise to two phenomena: fluorescence and phosphorescence.

(i) Fluorescence

- It is the emission of light when the molecule returns to the ground state from an excited state of the same multiplicity.
- ➤ For most molecules in their ground state are singlet and corresponds to transitions $S_1 \rightarrow S_o$. Spectroscopically, the transition from $S_1 \rightarrow S_o$ state is an "allowed" transition and occurs in about 10^{-8} second. The emission of radiation in this transition is fluorescence.

(ii) Phosphorescence

- It is the emission of light when the molecule returns to the ground state from an excited state of different multiplicity (spin inversion).
- > For most molecules, phosphorescence corresponds to transitions $T_1 \rightarrow S_o$.
- > The transition from T_1 to the ground state S_o is rather slow because it is forbidden transition. The emission of radiation in this transition is called phosphorescence.
- > The lifetime of a triplet state is much longer and, hence phosphorescence emission can be observed over a time span of 10^{-3} to 10 seconds even after the removal of the excitation source.

3. Quenching Of Fluorescence

When an excited state of molecule undergoes collision with another molecule before it has a chance to radiate as fluorescence, the process may be stopped. This phenomenon is known as *quenching*.



Fig. 5.4: The Jablonski Diagram (Electron Energy Level Diagram) Showing Various Photophysical Processes

(i) Internal quenching

➢ If the change of singlet excited state to triplet excited state occurs before it fluoresces, the phenomenon is known as internal quenching.

(ii) External quenching

➢ If a foreign substance is used to take up the energy from the excited species and not to allow the reactant to fluorescence, then the phenomenon is known as external quenching.

7. ENERGY TRANSFER IN PHOTOCHEMICAL REACTIONS

Photosensitization

Definition

- Reactions in which the molecules absorbing light do not react themselves but can induce other molecules to react are called *photosensitized reactions*.
- Substances which when added to a reaction mixture helps to induce the photochemical reaction but do not react themselves are called *photo sensitizers* and the process is called *photosensitization*.

✤ Mechanism of Photosensitization

When a sensitizer (donor, D) absorbs the incident photon, singlet state of sensitizer is produced.

$$D(\text{donor, sensitiser}) + h\gamma \rightarrow D_S^*$$

By intersystem crossing (non-radiative) transition, the singlet excited state becomes triplet excited state.

$$D_{S}^{*} \xrightarrow{ISC} D_{T}^{*}$$

> The triplet excited state of substrate collides with reactant molecule (A, acceptor), to give triplet excited state of reactant (A*) and the ground state of the sensitizer $(D_{S_o}^*)$. When a product is obtained by the triplet excited state of the reactant (A_T^*) , the process is called photosensitization.

$$D_T^* + A(acceptor) \rightarrow D_{S_0}^* + A_T^*$$

 $A_T^* \rightarrow Product (Photosensitization)$

* Examples

(i) Photosynthesis of carbohydrates in plants

- > This process occurring in plants everyday during the sunlight.
- Chlorophyll a green pigment) in plants acts a photosensitizer in photosynthesis process. It absorbs strongly the visible light region between 600 and 700 nm and passes on its energy to CO₂ and water molecules to form glucose along with the evolution of oxygen.

 $Chlorophyll + h\gamma(680nm)) \longrightarrow Chlorophyll^{*}$ $6CO_{2} + 6 H_{2}O + Chlorophyll^{*} \longrightarrow C_{6}H_{12}O_{6} + 6O_{2} + Chlorophyll$

(ii) Applications in Photography

Cyanine, a red dye acts as photosensitizer in photographic plates. When silver halides in photographic plates are exposed to the light of wavelength 750 – 820 nm, cyanine dye absorbs the photon which reduces silver ion to produce silver grain.

 $\begin{array}{rcl} Cyanine + h\gamma & \longrightarrow & Cyanine^* \\ AgBr + Cyanine^* & \longrightarrow & Ag^+ + Br^- + e^- + Cyanine \\ & Ag^+ + e^- & \longrightarrow & Ag \end{array}$

(iii)Combination of CO and H₂ sensitized by mercury vapour

When a mixture of CO and H_2 containing traces of mercury vapours are exposed to *uv* light of 253.7 nm, the mercury atoms are excited. These excited mercury atoms then transfer their energy by collisions to hydrogen molecules and dissociate them into hydrogen atoms. This initiates a radical reaction

8. KINETICS OF SOME TYPICAL PHOTOCHEMICAL REACTIONS

1. Decomposition of HI

The photochemical decomposition of HI was studied by Warburg in 1918 at room temperature and at a pressure of 80-250mm in uv light of wavelengths 207, 253 and 282 nm. He reported that the quantum yield varies slightly with change in temperature.

Wave length, nm	Quantum yield
207	1.98
253	2.08
283	2.10

Warburg postulated the following mechanism for the decomposition of HI as follows:

(i)
$$HI + h\gamma \xrightarrow{I_{abs}} H + I$$
 Rate = I_{abs}
(ii) $H + HI \xrightarrow{k_2} H + I$ Rate = $k_2[H][HI]$
(iii) $I + I \xrightarrow{k_3} I_2$ Rate = $k_3[I]^2$

In the above mechanism, hydrogen iodide is consumed in steps (i) and (ii). Hence its rate of decomposition is given by:

$$-d \frac{[HI]}{dt} = I_{abs} + k_2[H][HI] \qquad \dots \dots (1)$$

Also, the rate of formation of hydrogen atoms is given by:

$$d \frac{[H]}{dt} = I_{abs} - k_2[H][HI]$$
(2)

As [H] atom is short lived, the steady state treatment, therefore, can be applied to it. Hence, the equation (2) becomes:

$$d \frac{[HI]}{dt} = 0 \equiv I_{abs} + k_2[H][HI]$$

(or) $I_{abs} = k_2 [H] [HI]$ (3)

Substituting this value in equation (1) we get,

$$\frac{-d[HI]}{dt} = 2 I_{abs} \qquad \dots (4)$$

By definition, the quantum yield is given by

$$\phi = \frac{-d[HI]/dt}{I_{abs}}$$
$$= \frac{2I_{abs}}{I_{abs}}$$
$$= 2$$

This means that the absorption of one quantum of radiation causes the decomposition of two moles of HI which is in agreement with experimental value.

$$\mathbf{H} + \mathbf{I}_2 \xrightarrow{k_4} \mathbf{H} \mathbf{I} + \mathbf{I} \qquad \text{rate} = \mathbf{k}_4 [\mathbf{H}] [\mathbf{I}_2]$$

The value of quantum yield decreases as the reaction proceeds according to reaction

With the inclusion of this reaction, the steady-state treatment when applied to hydrogen atoms is given by:

$$\frac{d[H]}{dt} = 0 = \mathbf{I}_{abs} - \mathbf{k}_2 [\mathbf{H}][\mathbf{H}\mathbf{I}] - \mathbf{k}_4 [\mathbf{H}] [\mathbf{I}_2]$$

or)
$$I_{ab} = K_2 [H] [HI] + K_4 [H] [I_2]$$

or)
$$I_{ab} = [H] \{K_2 [HI] + K_4 [I_2]\}$$

$$[H] = \frac{I_{abs}}{k_2[HI] + k_4[I_2]} \qquad \dots (5)$$

Substituting this in equation (1), we get

By definition, the quantum yield is given by

$$\Phi = \frac{-d[HI]/dt}{I_{abs}}$$

$$= \frac{I_{abs}[1 + \frac{1}{1 + k_4[I_2] + k_2[HI]}]}{I_{abs}}$$

$$= 1 + \frac{1}{1 + k_4[I_2]/k_2[HI]} \qquad \dots (7)$$

With time, the concentration of I_2 increases and that of HI decreases. Further the equation (7) reveals that the accumulation of molecular iodine retards the quantum yield.

2. Dissociation of HBr

The quantum yield for the dissociation of HBr is also two. Spectroscopic studies reveals that the mechanism followed by this reaction is the same as represented above for the dissociation of hydrogen iodide.

1. Primary process: $HBr + h\nu \rightarrow H + Br$

2. Secondary process:

a) Chain propagation H + HBr → H₂ + Br
b) Chain termination

 $Br + Br \rightarrow Br_2$

Therefore, over all reaction is: $2HBr + hv \rightarrow H_2 + Br_2$

Quantum yield = 2

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REVIEW QUESTIONS

PART – A QUESTIONS

- 2. What is photochemistry?
- 3. Distinguish dark reactions and photochemical reactions.
- 4. Stark-Einstein law of photochemistry.
- 5. State Beer-Lambert's law.
- 6. State Grotthus-Drapper's law.
- 7. Define quantum efficiency.
- 8. Mention any two reasons for low quantum yield.
- 9. Mention any two reasons for high quantum yield.
- 10. Distinguish fluorescence and phosphorescence?
- 11. What is photosensitization?

PART – B QUESTIONS

- 1. Derive the mathematical expression of Beer-Lambert's law.
- 2. Compare photochemical and dark reactions.
- 3. State and explain Einstein law of photochemical equivalence.
- 4. Define quantum efficiency. How would you explain high and low quantum efficiency of photochemical reactions?
- 5. Define quantum yield. How can it be experimentally determined?
- 6. Sketch a Jablonski diagram and show the terms absorption, fluorescence, phosphorescence, internal conversion and inter-system crossing with it.
- 7. Explain the photosensitization with mechanism.
- 8. Describe the photochemical kinetics of dissociation of hydrogen iodide reaction.