



Internal energy (U/E)

Enthalpy (H)

Heat capacity (C) C_p - Heat capacity at constant pressure

Entropy (S)

Free energy Gibbs free energy (G)

Helmholtz free energy (A)

Fundamental parameters

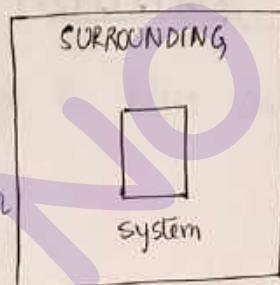
→ Temp (T), Pressure (P), Vol^m (V), Heat (q), no. of moles.

1st Law of thermodynamics :-

Statement of 1st law

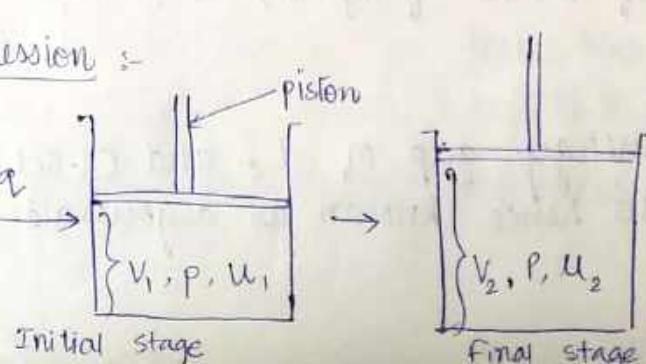
It may be stated in many

1) Energy can neither be created nor destroyed in a process, however it can be converted from one form to another form.



- 2) Whenever certain quantity of one form of energy disappears, exactly equivalent quantity of some other form of energy must appear.
- 3) The sum of total forms of energy in an isolated system remains constant.
- 4) The sum of total forms of energy in the universe i.e. energy of system plus energy of surrounding taken together, is constant.

Mathematical expression :-



$$\Rightarrow q = (u_2 - u_1) + p(v_2 - v_1)$$

$$\Rightarrow q = \Delta u + p\Delta v$$

$$\Rightarrow \boxed{q = \Delta u + w} \quad \text{--- (1)}$$

where, u_1 is the initial internal energy.

u_2 is the final internal energy

v_1 is the initial vol^m.

v_2 is the final vol^m.

$\Delta u = u_2 - u_1$ is change in internal energy.

$\Delta v = v_2 - v_1$ is change in volume.

Internal Energy (U/E)

The energy possessed by a system by virtue of its existence is known as internal energy and it is represented by the letter U or E.

It originates from individual particles which aggregates to form the whole system.

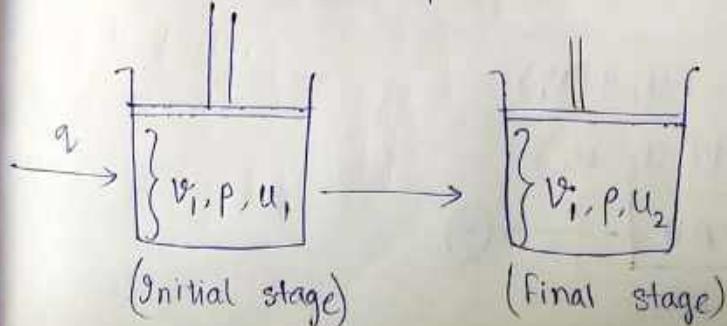
$$\begin{array}{c} A \\ B \\ C \\ D \\ E \\ F \end{array} \Rightarrow U = E_A + E_B + E_C + E_D + E_E + E_F$$

It is contributed by different molecular motions, such as translational, vibrational, rotational, nuclear etc.

The following aspects are important in reference to internal energy:

- 1) It is an extensive property. (Mass dependent)
- 2) Its absolute value can not be measured, therefore, Δu is given more importance than absolute U.
- 3) Physical significance

Let us consider a process that occur at constant volume



According to first law

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

$$q = \Delta U$$

$$\boxed{q_v = \Delta U} \quad \text{--- (2)}$$

where q_v is the heat of a process at constant volume.

Enthalpy (H)

If a process occurs at constant pressure, then the total energy content includes the energy due to work done by /on the system in addition to the internal energy of the system.

OR

Heat content in a system at constant pressure is known as enthalpy (H).

Mathematically,

$$\boxed{H = U + PV}$$

H → Enthalpy

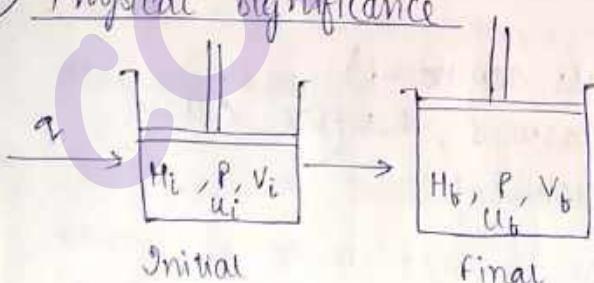
U → Int. energy

P → pressure

V → Vol^m

The following points are imp. in reference to enthalpy

- 1) It is an extensive property
- 2) The absolute value of enthalpy can't be measured, hence ΔH is given more importance than H.
- 3) Physical significance



∴ $\Delta H = H_f - H_i$

$$\Delta H = (U_f + PV_f) - (U_i + PV_i)$$

$$\Delta H = (V_f - V_i) + P(U_f - U_i)$$

$$\boxed{\Delta H = \Delta U + P\Delta V} \quad \text{--- (3)}$$

$$\Rightarrow \Delta H = \Delta U + W \quad \text{where } PAV = W$$

(4)

From 1st law, we know that,

$$q = \Delta U + W$$

By comparing this eqⁿ w.r.t eqⁿ(4),

$$\Rightarrow \Delta H = q$$

$$\Rightarrow \boxed{\Delta H = q_p}, \text{ where } q_p \text{ is the heat of a process at constant pressure.}$$

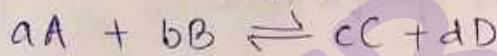
Relation betⁿ q_p and q_v :-

$$\text{We know, } \Delta H = \Delta U + P\Delta V$$

$$\boxed{q_p = q_v + P\Delta V} (\because \Delta H = q_p \text{ and } \Delta U = q_v)$$

(6)

Now, let us consider a hypothetical chemical reaction



$$\begin{aligned} \text{here, } \Delta n &= (c+d) - (a+b) \\ &= \text{change in no. of moles.} \end{aligned}$$

Let, V is the vol^m occupied by 1 mole of a gas.

The vol^m occupied by Δn mole of a gas

$$\text{i.e. } \Delta V = \Delta n \times V$$

Substituting the value of ΔV in eqⁿ(6),

$$\Rightarrow q = q_v + P\Delta nV$$

$$\Rightarrow \boxed{q_p = q_v + \Delta n PV}$$

$$\Rightarrow \boxed{q_p = q_v + \Delta n RT} - (7) \quad (\because PV = RT \text{ from ideal gas eq²})$$

Heat capacity (c)

The amt. of heat req'd to raise the temp. of a system by 1°C is called heat capacity (C).

S

$$C = \frac{q}{\Delta T}$$

i.e. q amount of heat req'd to raise the temp. ΔT for 1°C

Specific heat

The heat req'd to raise the temp. of a unit system having unit mass by 1°C is called specific heat.

$$\text{Specific heat} = \frac{q}{m \cdot \Delta T}$$

Molar specific heat

When $m = 1$ mole,

Specific heat is known as molar specific heat

$$\text{Molar specific heat} = \frac{q}{\Delta T} \quad (\because m = 1 \text{ mole})$$

For a small change,

$$\text{Specific heat}, \quad C = \frac{dq}{dT}$$

Case 1 :- Specific heat at constant vol^m (C_V)

Here no work is done as the vol^m is constant. Thus, according to first law, it can be written as,

$$dq = dU + PdV$$

$$\Rightarrow dq = dU$$

Again, we know,

$$\Rightarrow C_V = \frac{dq}{dT}$$

$$\Rightarrow C_V = \frac{dU}{dT} \quad (\because dq = dU)$$

$$\Rightarrow dU = C_V dT \quad \xrightarrow{\textcircled{8}}$$

Case 2 :- Specific heat at constant pressure (C_p) :-

Here heat is utilized in 2 ways, both in raising the temp. and doing some useful work.

Thus, heat capacity in constant pressure can be written as

$$dH = dU + PdV \quad \text{--- (a)}$$

again, from 1st law

$$dq = dU + PdV \quad \text{--- (b)}$$

From (a) and (b)

$$\boxed{dH = dq}$$

So, the specific heat at constant pressure,

$$C_p = \left(\frac{dH}{dT} \right)_P \Rightarrow \boxed{dH = C_p \cdot dT} \quad \text{--- (c)}$$

Relation betⁿ C_p and C_v

$$\boxed{C_p - C_v = R} \quad \text{--- (d)}$$

Entropy (S) :-

Entropy is the measure of randomness / disorderness at the molecular level of a system.

It is represented by the letter 'S'.

It is an extensive property (mass dependent).

Mathematically,

$$S = \frac{\alpha}{T}$$

For a small change,

$$\boxed{ds = \frac{da}{T}}$$

also,

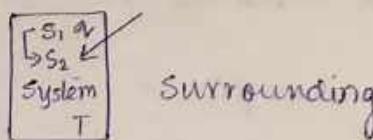
$$\boxed{\Delta S = \frac{\alpha}{T}}$$

Entropy calculation :-

→ Entropy change in a reversible process :-

Let us consider a reversible isothermal process in

- Which the system absorbs 'q' amount of heat from surrounding. At temp 'T', it is given as.



S_1' - before giving 'q' amount of heat to the system.

S_2' → entropy of the surrounding after giving 'q' amount of heat to the system.

$$S_1' > S_2'$$

E.g. → Ice and water

Change in entropy of system,

$$\Delta S_{\text{sys}} = S_2 - S_1 = \frac{+q}{T}$$

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

Change in entropy of surrounding

$$\Delta S_{\text{sur}} = S_2 - S_1 = \frac{-q}{T}$$

$$\Rightarrow \boxed{\Delta S_{\text{sur}} = \frac{-q}{T}}$$

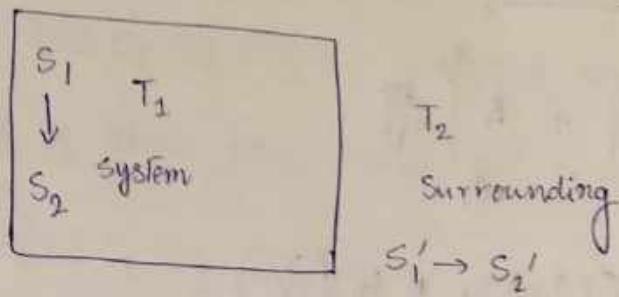
$$\begin{aligned} \text{Total change in entropy} &= \Delta S_{\text{sys}} + \Delta S_{\text{sur}} \\ &= \frac{q}{T} - \frac{q}{T} \\ &= 0 \end{aligned}$$

In a reversible process, the ^{total} change in entropy is zero.

→ Entropy change in an irreversible process :

Let us consider an irreversible process in which the system is at lower temp 'T₁' absorbs 'q' amount of heat from the surrounding which is at higher temp 'T₂'.

E.g. → Sun and earth
 (T_2) or planets
 (T_1)



Here, $T_2 > T_1$

$$\Delta S_{sys} = \frac{+q}{T_1} \quad \text{and} \quad \Delta S_{surv} = \frac{-q}{T_2}$$

Total change in entropy

$$\Delta S_{sys} + \Delta S_{surv} = \frac{q}{T_1} - \frac{q}{T_2}$$

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

$$\Rightarrow \Delta S = q \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

As $T_2 > T_1$,

$$\Delta S \rightarrow +ve$$

→ Entropy change accompanying different process involving ideal gases

a) Temperature and volume as variable :-

$$\text{For small change } ds = \frac{dq}{T}$$

$$\text{From 1st law, } dq = du + PdV$$

$$\text{So, the above eqn will be } \Rightarrow ds = \frac{du + PdV}{T}$$

$$\Rightarrow ds = \frac{C_V dT + PdV}{T} \quad (\text{from eqn 8})$$

From ideal gas eqn,

For 1 mole of ideal gas,

$$\Rightarrow PV = RT \quad \text{and} \quad P = \frac{RT}{V}$$

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

$$du = C_V dT$$

Integrating both the sides,

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

$$\Rightarrow (S_2 - S_1) = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \boxed{\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)} \quad \text{--- (11)}$$

for 'n' mole of ideal gas eqn (11) can be written as

$$\Rightarrow \Delta S = n C_V \ln\left(\frac{T_2}{T_1}\right) + n R \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \boxed{\Delta S = 2.303 n C_V \log\left(\frac{T_2}{T_1}\right) + 2.303 \cdot n R \log\left(\frac{V_2}{V_1}\right)} \quad \text{--- (12)}$$

b) Temperature and pressure as variables:

From ideal gas law,

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

$$\Rightarrow \left(\frac{T_2}{T_1}\right) = \frac{P_2 V_2}{P_1 V_1} \quad \text{also, } \left(\frac{V_2}{V_1}\right) = \frac{P_1 T_2}{P_2 T_1}$$

Substituting these values in eqn (11),

$$\Rightarrow \Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{T_2}{T_1} \cdot \frac{P_1}{P_2}\right)$$

$$\Rightarrow \Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{P_1}{P_2}\right)$$

$$\Rightarrow \Delta S = \ln\left(\frac{T_2}{T_1}\right) (C_V + R) + R \ln\left(\frac{P_1}{P_2}\right)$$

We know,

$$C_P - C_V = R$$

$$\Rightarrow C_V + R = C_P$$

$$\Rightarrow \boxed{\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{P_1}{P_2}\right)} \quad \text{--- (13)}$$

For 'n' mole of ideal gas, eqⁿ (13) will be,

$$\Rightarrow \Delta S = 2.303 C_p \log \left(\frac{T_2}{T_1} \right) + 2.303 R \log \left(\frac{P_1}{P_2} \right)$$

for 'n' mole of ideal gas, above eqⁿ becomes,

$$[\Delta S = n \cdot 2.303 C_p \log \left(\frac{T_2}{T_1} \right) + n \cdot 2.303 R \log \left(\frac{P_1}{P_2} \right)] \quad \text{--- (14)}$$

Case 1 : for isothermal process ($T_1 = T_2$)

Eqⁿ (12) will be,

$$\Rightarrow [\Delta S = 2.303 n R \log \left(\frac{V_2}{V_1} \right)] \quad \text{--- (15)}$$

Eqⁿ (14) will be,

$$\Rightarrow [\Delta S = n R \cdot 2.303 \log \left(\frac{P_1}{P_2} \right)] \quad \text{--- (16)}$$

Case 2 : for isobaric process ($P_1 = P_2$)

Eqⁿ (14) will be,

$$[\Delta S = n \cdot 2.303 C_p \log \left(\frac{T_2}{T_1} \right)] \quad \text{--- (17)}$$

Case 3 : for isochoric process ($V_1 = V_2$)

Eqⁿ (12) will be,

$$[\Delta S = 2.303 n C_V \log \left(\frac{T_2}{T_1} \right)] \quad \text{--- (18)}$$

Entropy change during mixing of ideal gases :

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Let us consider 1 mole of an ideal gas. The entropy change can be expressed as,

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

$$\Rightarrow dS = (C_P - R) \frac{dT}{T} + R \cdot \frac{dV}{V} \quad [\because C_P - C_V = R]$$

$$\Rightarrow C_V = C_P - R$$

On integrating both sides,

$$\Rightarrow \int dS = (C_P - R) \int \frac{dT}{T} + R \int \frac{dV}{V}$$

$$\Rightarrow S = (C_P - R) \ln T + R \ln V + S^{\circ} \quad (\text{where } S^{\circ} \text{ is the integration constant})$$

$$\Rightarrow S = C_P \ln T - R \ln T + R \ln \left(\frac{RT}{P} \right) + S^{\circ}$$

$$\Rightarrow S = C_P \ln T - R \ln T + R \ln R + R \ln T - R \ln P + S^{\circ}$$

$$PV = RT \quad V = \frac{RT}{P}$$

$$\Rightarrow S = C_P \ln T - R \ln P + R \ln R + S^{\circ}$$

$$\Rightarrow S = C_P \ln T - R \ln P + S' \quad [\text{where } S' = S^{\circ} + R \ln R \text{ is constant}]$$

Let us consider a no. of ideal gases in a mixture i.e. n_1 moles of a gas 1, n_2 moles of gas 2 and so on.

Let their partial pressures be p_1, p_2, \dots respectively.

S_1 can be written as

$$S_1 = C_P \ln T - R \ln p_1 + S'^{\circ} \quad (S_1 \text{ is the entropy of component 1})$$

$$S_2 = C_P \ln T - R \ln p_2 + S'^{\circ} \quad (S_2 \text{ is the entropy of component 2})$$

Now,

$$\text{Total entropy } S_T = \sum n_i (C_P \ln T - R \ln p_i - S'^{\circ})$$

If each gas is taken under pressure 'P', then total entropy will be,

$$S_T' = \sum n_i (C_p \ln T - R \ln P + S^\circ')$$

Entropy of mixing is the diff bet^n the entropy of mixture of gases and the sum of the entropies of the separate gases.

Thus,

$$\Delta S_{\text{mix}} = S_T' - S_T = \sum n_i (C_p \ln T - R \ln P + S^\circ') - \sum n_i (C_p \ln T - R \ln p_i + S_0')$$

$$\Rightarrow \Delta S_{\text{mix}} = \sum n_i (C_p \ln T - R \ln P + S^\circ' - C_p \ln T + R \ln p_i - S_0')$$

$$\Rightarrow \boxed{\Delta S_{\text{mix}} = \sum n_i (-R \ln P + R \ln p_i)}$$

Let the mole fraction of i^{th} component is ' χ_i ' and

$$\boxed{p_i = \chi_i P}$$

$$\frac{n_a}{N} = \frac{n_a}{n_a + n_b + n_c + \dots}$$

$$\frac{p_i}{P} = \chi_i \text{ (mole fraction)}$$

Substituting the value of p_i ,

$$\Rightarrow \Delta S_{\text{mix}} = \sum n_i (-R \ln P + R \ln (\chi_i P))$$

$$\Rightarrow \Delta S_{\text{mix}} = \sum n_i (-R \ln P + R \ln \chi_i + R \ln P)$$

$$\Rightarrow \boxed{\Delta S_{\text{mix}} = \sum n_i (R \ln \chi_i)}$$

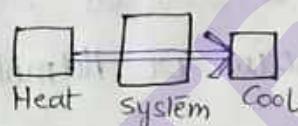
Limitations of first law

The 1st law of thermodynamics has the following limitations.

- 1) It fails to explain the extent of convertibility of energy from one form to another form.
- 2) It fails to explain the feasibility of the chemical process.

Second Law of Thermodynamics

Like 1st law, 2nd law of thermodynamics can also be stated in different ways-



1. Kelvin statement

It is impossible to take heat from a hot reservoir and convert it absolutely into work by a cyclic process without transferring a part of heat to a cooler reservoir.

2. Clausius statement

It is impossible for a cyclic process to transfer heat from a body at lower temperature to a body at higher temperature, without help of an external agent.

3. Entropy

Entropy of system and surrounding taken together remains constant during a reversible change while the same tends to increase during an irreversible change.

4. The entropy of universe tends to increase always.

E.g. → Sun and planets.

$$\Delta S \rightarrow +ve (\Delta T)$$

Concept of Free Energy :

Neither energy nor randomness alone decides the feasibility of the process. Therefore they should be considered together for convenient measure of the driving force for a process.

The thermodynamic funct' which considers both energy & randomness together are known as Free Energy Funct's.

They are of 2 types :-

- ① Helmholtz free energy.
- ② Gibb's free energy.

Helmholtz-free energy (A)

The max. amount of energy available isothermally to a system that can be converted into useful work is known as Work function or Helmholtz function.

It is denoted by 'A', it is an extensive property (mass independent)

Mathematically,

$$A = U - TS$$

where U = internal energy

T = temp. at which experiment is going on.

S = entropy of the system.

$TS \rightarrow$ loss part, $U - TS \rightarrow$ effective work.

Physical significance of A :-

Let us consider an isothermal process involving change from state 1 to state 2, then the relation can be written as

$$A_1 = U_1 - TS_1$$

$$A_2 = U_2 - TS_2$$

Then, $A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1)$

$$\Delta A = \Delta U - T\Delta S$$

$$\Delta U = \Delta A + T\Delta S$$

$$\Rightarrow \Delta A = \Delta U - T \frac{\partial q}{\partial T} \quad [\because \Delta S = \frac{\partial q}{\partial T}]$$

$$\Rightarrow \boxed{\Delta A = \Delta U - q} \quad \text{--- (20)}$$

Again from 1st law, we know that,

$$q = \Delta U + P\Delta V \quad \text{or} \quad q = \Delta U + W$$

$$\Rightarrow \Delta U = q - W$$

so eqⁿ (20) becomes,

$$\Delta A = q - W - q$$

$$\boxed{\Delta A = -W} \quad \text{--- (21)}$$

$$\boxed{W = -\Delta A}$$

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Gibb's Free Energy (G)

It is the max amount of energy isothermally available to a system that can be converted into useful work.

Represented by 'G' and is an extensive property.

Mathematically,

$$\boxed{G = H - TS}$$

TS → Amount of energy or disorderliness lost by the system / process at temp 'T'.

H - TS → Amount of energy isothermally available for effective work.

Physical significance

Let us consider a reversible change of a system.



$$G_1 = H_1 - TS_1$$

$$G_2 = H_2 - TS_2$$

$$\Delta G = G_2 - G_1$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

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

We know, $\Delta H = \Delta U + P\Delta V$ (1st Law of thermodynamics)

$$\Rightarrow \Delta G = \Delta U + P\Delta V - T\Delta S$$

$$\Rightarrow \Delta G = \Delta U - T\Delta S + P\Delta V$$

$$\Rightarrow \boxed{\Delta G = \Delta A + P\Delta V} \quad [\because \Delta A = \Delta U - T\Delta S]$$

$$\Rightarrow \boxed{-\Delta G = W - P\Delta V} \quad \text{as } -\Delta G = -\Delta A - P\Delta V$$

$$(\because -\Delta A = W)$$

(22)

Therefore, decrease in free energy is maximum work obtainable from a system.

Other than that due to change in volume i.e net work.

Variation of Free Energy (G_f) with temperature and pressure.

We know,

$$G_f = H - TS$$

$$G_f = U + PV - TS \quad (\because H = U + PV)$$

So, for a small change, the above relation can be written as-

$$\Rightarrow dG = \underbrace{dU + PdV}_{dQ} + VdP - TdS - SdT$$

$$\Rightarrow dG = dq + VdP - TdS - SdT \quad [\because dq = dU + PdV]$$

$$dS = \frac{dq}{T}$$

$$\Rightarrow dq = TdS$$

$$\Rightarrow dG = TdS + VdP - TdS - SdT$$

$$\Rightarrow \boxed{dG = VdP - SdT} \quad (23)$$

As temperature is constant, eqⁿ (23) will be

$$dG = VdP \quad \text{--- (24)}$$

At constant pressure, eqⁿ (23) will be

$$dG = -SdT \quad \text{--- (25)}$$

Eqⁿ (24) \rightarrow Variation of free energy (dG) w.r.t pressure.

Eqⁿ (25) \rightarrow Variation of free energy (dG) w.r.t temperature

Variation of free energy of an ideal gas w.r.t pressure :-

From eqⁿ (24), $dG = VdP$

Integrating both sides,

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP.$$

$$\Rightarrow (G_2 - G_1) = \int_{P_1}^{P_2} \frac{nRT}{P} . dP \quad \left[\because PV = nRT \quad V = \frac{nRT}{P} \right]$$

$$\Rightarrow \Delta G = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Rightarrow \boxed{\Delta G = nRT \ln \left(\frac{P_2}{P_1} \right)} \quad \text{--- (26)}$$

$$\Rightarrow \boxed{\Delta G = nRT \ln \left(\frac{V_1}{V_2} \right)} \quad \text{--- (27)}$$

\rightarrow Boyle's Law
 $P_1 V_1 = P_2 V_2$
 $\frac{P_2}{P_1} = \frac{V_1}{V_2}$

Q. 5 moles of an ideal gas expands isothermally from $1L$ to $10L$ at $300K$ temp. Calculate the change in free energy.

Given

$$n = 5$$

$$V_1 = 1L, V_2 = 10L$$

$$T = 300K$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta G &= nRT \ln \left(\frac{V_1}{V_2} \right) = 5 \times 8.314 \times 300 \ln \left(\frac{1}{10} \right) \\ &= -28.72 \text{ kJ} \end{aligned}$$

Gibb's Helmholtz Eqⁿ (amp)

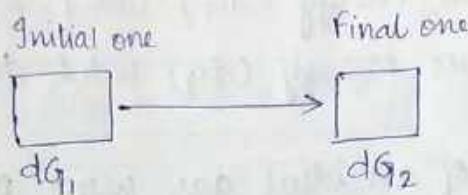


This eqⁿ provides the temperature dependence of free energy change.

We know, $dG = VdP - SdT$

At constant pressure

$$dG = -SdT \quad \text{--- (a)}$$



Let us consider an isobaric change in which the initial state is characterized by - (S_1, G_1, T_1) and final state is characterized by - (S_2, G_2, T_2) .

Now, with change in temp., initial and final free energy change by the amount dG_1 and dG_2 respectively.

from (a), $dG_1 = -S_1 dT$

$$dG_2 = -S_2 dT$$

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

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

$$\Rightarrow d(\Delta G) = -(\Delta S) dT$$

$$\Rightarrow \boxed{\left[\frac{d(\Delta G)}{dT} \right]_P = -\Delta S} \quad \text{--- (28)}$$

But we know that,

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

Substituting the value of ΔS from eqⁿ (28), we get

$$\Rightarrow \boxed{\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT} \right]_P} \quad \text{--- (29)}$$

Eqⁿ (29) is known as Gibb's Helmholtz Equation.

Alternative form of Gibb's Helmholtz Equation :-

From eqⁿ ②9, it can be written as -

$$\Rightarrow \Delta H = \Delta G - T \left[\frac{d(\Delta G)}{dT} \right]_P$$

Dividing T^2 in both sides,

$$\Rightarrow \frac{\Delta H}{T^2} = \frac{\Delta G}{T^2} -$$

$$\Rightarrow \frac{\Delta H}{T^2} = \frac{\Delta G - T \left[\frac{d(\Delta G)}{dT} \right]_P}{T^2} \quad - \textcircled{30}$$

Right side of eqⁿ ③0 can be obtained by differentiating

$\frac{\Delta G}{T}$ w.r.t T at constant pressure.

$$\Rightarrow \left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT} \right]_P = \frac{T \left[\frac{d(\Delta G)}{dT} \right]_P - \Delta G \left(\frac{dT}{dT} \right)}{T^2}$$

$$\Rightarrow \left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT} \right]_P = \frac{T \left[\frac{d(\Delta G)}{dT} \right]_P - \Delta G}{T^2}$$

$$\Rightarrow - \left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT} \right]_P = \frac{\Delta G - T \left[\frac{d(\Delta G)}{dT} \right]_P}{T^2} \quad - \textcircled{31}$$

from eqⁿ ③0 and eqⁿ ③1,

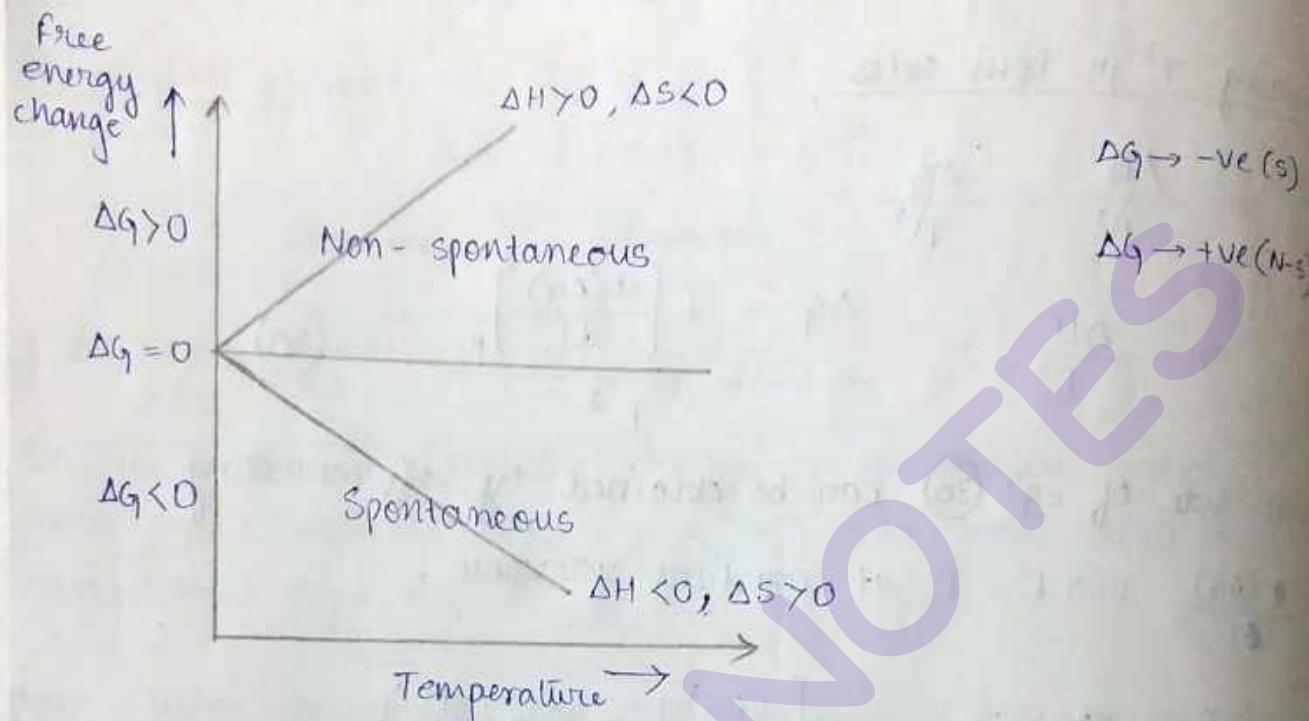
$$\Rightarrow - \left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT} \right]_P = \frac{\Delta H}{T^2} \quad \rightarrow \text{Alternate form of Gibb's Helmholtz Equation}$$

32

Criteria for Spontaneity of a Reaction :-

We know, $\Delta G = \Delta H - T\Delta S$ can be utilized for the prediction of spontaneity of a reaction under different conditions. (process)

Under constant pressure, chemical reaction is spontaneous in the direction of decrease in free energy i.e ΔG at constant T and P is less than 0.



Q2. For a reaction, $M_2O(g) \rightarrow 2M(g) + \frac{1}{2}O_2(g)$:

$\Delta H = 30 \text{ KJ mol}^{-1}$, $\Delta S = 0.07 \text{ KJ mol}^{-1}$ at 1 atm.

Calculate upto which temperature, the reaction wouldn't be spontaneous.

for non-spontaneous reactⁿ $\Rightarrow \Delta G > 0$

$$\Delta G = \Delta H - T\Delta S > 0$$

$$\Rightarrow \Delta H > T\Delta S$$

$$\Rightarrow \frac{\Delta H}{\Delta S} > T \quad \text{or} \quad T < \frac{\Delta H}{\Delta S}$$

$$\Rightarrow T < \frac{30}{0.07}$$

$$\Rightarrow T < 428.57 \text{ K}$$

When temp. is more than 428.57 \rightarrow reaction \rightarrow spontaneous
 " " " less " " \rightarrow " \rightarrow non - "

Vant Hoff Isotherm

This eqⁿ provides a quantitative relation for free energy change accompanying a chemical reaction.

The expression for change in free energy in constant temp.

$$dG = VdP - SdT$$

$$dG = VdP \quad (\text{at constant } T)$$

$$\Rightarrow dG = \frac{RT}{P} dP \quad [\because PV = RT \text{ for 1 mole of ideal gas}]$$

Integrating both sides

$$\Rightarrow \int dG = RT \int \frac{dP}{P}$$

$$\Rightarrow G_f = RT \ln P + G_f^{\circ} \quad \text{--- (33)}$$

Where $G_f^{\circ} \rightarrow g_f$ is the integration constant known as
Standard Gibbs Free Energy

22/02/2018

Now let's consider a hypothetical chemical reaction



$$\text{So, for the above reaction, } G_A = G_A^{\circ} + RT \ln P_A$$

$$G_B = G_B^{\circ} + RT \ln P_B$$

$$G_L = G_L^{\circ} + RT \ln P_L$$

$$G_M = G_M^{\circ} + RT \ln P_M$$

where $G_A^{\circ}, G_B^{\circ}, G_L^{\circ}, G_M^{\circ}$ are the free energies of A, B, L and M in their standard state. P_A, P_B, P_L, P_M are the partial pressures of A, B, L and M respectively.

Change in free energy = $\Delta G =$

$$= \Sigma \text{free energy of product} - \Sigma \text{free energy of reactant}$$

$$\Delta G = \underbrace{(cG_L + mG_M)}_{\text{free energy of product}} - \underbrace{(aG_A + bG_B)}_{\text{free energy of reactant}}$$

Substituting the value of G_L° , G_M° , G_A° and G_B° ,

$$\Rightarrow \Delta G = \{ l(G_L^\circ + RT \ln P_L) + m(G_M^\circ + RT \ln P_M) \} - \\ \{ a(G_A^\circ + RT \ln P_A) + b(G_B^\circ + RT \ln P_B) \}$$

$$\Rightarrow \Delta G = (lG_L^\circ + mG_M^\circ) - (aG_A^\circ + bG_B^\circ) + (lRT \ln P_L + mRT \ln P_M) \\ - (aRT \ln P_A + bRT \ln P_B)$$

$$\Rightarrow \Delta G = \Delta G^\circ + (RT \ln P_L^l + RT \ln P_M^m) - (RT \ln P_A^a + RT \ln P_B^b)$$

$$\Rightarrow \Delta G = \Delta G^\circ + RT \ln (P_L^l \cdot P_M^m) - RT \ln (P_A^a \cdot P_B^b)$$

$$\Rightarrow \boxed{\Delta G = \Delta G^\circ + RT \ln \frac{P_L^l \cdot P_M^m}{P_A^a \cdot P_B^b}} \quad \text{--- (34)}$$

where $\Delta G^\circ = (lG_L^\circ + mG_M^\circ) - (aG_A^\circ + bG_B^\circ) \rightarrow \underline{\text{Change in standard free energy.}}$

$$\Rightarrow \boxed{\Delta G = \Delta G^\circ + RT \ln Q_p} \quad \text{--- (35)}$$

where $Q_p = \frac{P_L^l \cdot P_M^m}{P_A^a \cdot P_B^b}$ known as reaction coefficient.

At equilibrium,

$Q_p = K_p$ (known as equilibrium constant and $\Delta G = 0$)

Eqⁿ (35) becomes,

$$\Rightarrow 0 = \Delta G^\circ + RT \ln K_p$$

$$\Rightarrow \boxed{\Delta G^\circ = -RT \ln K_p} \quad \text{--- (36)}$$

Substituting the value of ΔG° in eqⁿ (35),

$$\boxed{\Delta G = -RT \ln K_p + RT \ln Q_p} \quad \text{--- (37)}$$

Eqⁿ (37) is known as Van't Hoff Isotherm.

Van't Hoff Isochore

Temperature dependence of equilibrium constant can be obtained by combining Gibb's Helmholtz Equation with Van't Hoff Isotherm.

The relation is known as Van't Hoff reaction of isochore.

from Gibb's Helmholtz Eqⁿ,

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

$$\Rightarrow \frac{-\Delta H}{T^2} = T \left(\frac{\partial (\Delta G)}{\partial T} \right)_P - \Delta G \quad \text{--- (38)}$$

(Dividing T^2 on both sides)

The right side of eqⁿ (38) can also be obtained by differentiating $\left(\frac{\Delta G}{T} \right)$ wrt t .

Dividing T^2 both sides

$$\Rightarrow \left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_P = \frac{T \left(\frac{\partial (\Delta G)}{\partial T} \right)_P - \Delta G \cdot \left(\frac{\partial T}{\partial T} \right)}{T^2}$$

Divide

$$\Rightarrow \left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_P = \frac{T \left(\frac{\partial (\Delta G)}{\partial T} \right)_P - \Delta G}{T^2} \quad \text{--- (39)}$$

From eqⁿ (38) and (39), on comparing,

$$\Rightarrow -\Delta H = \left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_P \quad \text{--- (40)}$$

At standard condition, eqⁿ (40) will be, ΔG will be replaced by ΔG°

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

From eqⁿ (36) we know that,

$$\Delta G^\circ = -RT \ln K_P$$

Substituting the value of ΔG°

$$\Rightarrow -\frac{\Delta H}{T^2} = \frac{\partial (-RT \ln K_p)}{\partial T}$$

$$\Rightarrow \frac{\Delta H}{RT^2} = \left(\frac{\partial \ln K_p}{\partial T} \right)_P$$

$$\Rightarrow \frac{\Delta H}{R} \cdot \frac{1}{T^2} = \frac{\partial \ln K_p}{\partial T}$$

Integrating both sides with appropriate limit,

$$\Rightarrow \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{\partial T}{T^2} = \int_{K_{P_1}}^{K_{P_2}} \partial \ln K_p$$

$$\Rightarrow \ln K_{P_2} - \ln K_{P_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Rightarrow \boxed{\ln \left(\frac{K_{P_2}}{K_{P_1}} \right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)} \quad \text{--- (41)}$$

Eqn (41) is known as Vant Hoff Isochore.

Q3. ΔG for a given reaction $\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$ is -16.5 kJ/mol at 300K . find K_p and K_c .

We know, $\Delta G^\circ = -RT \ln K_p$

$$\Rightarrow \ln K_p = -\frac{\Delta G^\circ}{RT} = \frac{-(-16.5 \times 10^3)}{8.314 \times 300}$$

$$\Rightarrow K_p = 774.9 \text{ atm}^{-1}$$

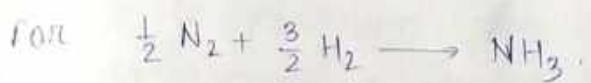
$$\Rightarrow K_p = K_c (RT)^{\Delta n}$$

$$\Rightarrow K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{774.9}{(8.314 \times 300)^{-1}}$$

$$\Delta n = 1 - 2 = -1 \quad (\text{Pro no. of moles} - \text{Reactant no. of moles}) = \Delta n$$

$$\begin{aligned} \text{Reactant} &= \frac{1}{2} + \frac{3}{2} = 2 \\ \text{no. of moles} &\qquad \qquad \qquad \text{Product} = 1 \\ &\qquad \qquad \qquad \text{no. of moles} \end{aligned}$$

$$\Rightarrow \boxed{K_c = 19.2 \text{ mol}^{-1}}$$



$$K_p = \frac{P_{NH_3}}{(P_{N_2})^{\frac{1}{2}} (P_{H_2})^{\frac{3}{2}}} = \frac{atm}{(atm)^2} = (atm)^{-1} \quad (\text{# no of product} = \text{"no of reactant})$$

$$K_c = \frac{x \text{ mol}}{y (\text{mol})^{\frac{1}{2}} z (\text{mol})^{\frac{3}{2}}} = \frac{\text{mol}}{(\text{mol})^2} = (\text{mol})^{-1}$$

Q2. Equilibrium constant K_p for a reaction at $327^\circ C$ is 10^{-12} and $427^\circ C$ is 10^{-7} . Calculate the enthalpy of the reaction.

Given $T_1 = 327^\circ C = 327 + 273 = 600 K$, $K_{P_1} = 10^{-12}$

$$T_2 = 427^\circ C + 273 = 700 K \quad K_{P_2} = 10^{-7}$$

$$\Rightarrow \ln \left(\frac{K_{P_2}}{K_{P_1}} \right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \ln \left(\frac{10^{-7}}{10^{-12}} \right) = \frac{\Delta H}{8.314} \left(\frac{700 - 600}{700 \times 600} \right)$$

$$\Rightarrow \boxed{\Delta H = 402.09 \text{ KJ}}$$

Q3. K_p for a reaction is $1.6 \times 10^{-4} \text{ atm}^{-2}$ at $400^\circ C$. What will be the K_p at $500^\circ C$ given heat of reaction at this temperature range of -25.0 K cal .

$$K_{P_1} = 1.6 \times 10^{-4} \text{ atm}^{-2}, T_1 = 400^\circ C + 273 = 673 K$$

$$K_{P_2} = ? \quad T_2 = 500 + 273 = 773 K$$

$$\Delta H = -25.0 \text{ K cal}$$

$$\Rightarrow \ln \left(\frac{K_{P_2}}{K_{P_1}} \right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \ln \left(\frac{K_{P_2}}{1.6 \times 10^{-4}} \right) = \frac{-25 \times 10^3}{1.98} \left(\frac{773 - 673}{773 \times 673} \right)$$

$$\Rightarrow \boxed{K_{P_2} = 1.46 \times 10^{-3} \text{ atm}^{-2}}$$

Q) The free energy change for a given reactⁿ is -90 KJ at 25°C and -85 KJ at 35°C. Calculate the change of enthalpy for the reactⁿ at 30°C.

Ans)

$$T_1 = 25 + 273 = 298 \text{ K}, \Delta G_1 = -90 \text{ KJ}$$

$$T_2 = 35 + 273 = 308, \Delta G_2 = -85 \text{ KJ}$$

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

$$\Delta H_{\text{at } 30^\circ\text{C}} = \Delta G - T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P \quad \text{--- (1)}$$

$$\frac{\partial(\Delta G)}{\partial T} = \frac{\Delta G_2 - \Delta G_1}{T_2 - T_1} = \frac{-85 + 90}{308 - 298} = \frac{5}{10} = 0.5 \text{ KJ K}^{-1}$$

$$\Delta G_{\text{at } 30^\circ\text{C}} = \frac{\Delta G_1 + \Delta G_2}{2} = \frac{-90 - 85}{2} = \frac{-175}{2} = -87.5 \text{ KJ}$$

As $\frac{T_1 + T_2}{2} = \frac{35 + 25}{2} = 30^\circ\text{C}$.

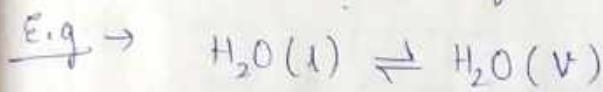
from (1), $\Delta H_{\text{at } 30^\circ\text{C}} = \Delta G_{\text{at } 30^\circ\text{C}} + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P$

$$= -87.5 - 303 \times 0.5$$

$$= -239 \text{ KJ}$$

Clapeyron - Clausius Equation

It finds its application where 2 phases of a particular substance remain in equilibrium.



Let us consider a system where 2 phases, say phase 1 and phase 2 of a particular substance



Let G_1 and G_2 be their free energies per mole at temperature 'T' and pressure 'P'. As the 2 phases are in equilibrium,

$$\text{so, } G_1 = G_2$$

Let the temperature increases changes from

$$T \text{ to } T + dT$$

and pressure, P to $P + dP$

so that the new free energies of phase-1 and phase-2 becomes $G_1 + dG_1$ and $G_2 + dG_2$ respectively.

As the phases are in equilibrium, therefore,

$$G_1 + dG_1 = G_2 + dG_2$$

$$\Rightarrow dG_1 = dG_2 \quad (\because G_1 = G_2)$$

We know, $dG = VdP - SdT$

So the above eqⁿ can be written as,

$$dG_1 = (V_1 dP - S_1 dT)$$

$$dG_1 = dG_2 = (V_2 dP - S_2 dT)$$

$$\Rightarrow V_1 dP \cdot S_1 dT = V_2 dP - S_2 dT$$

$$\Rightarrow (S_2 - S_1) dT = (V_2 - V_1) dP$$

$$\Rightarrow \Delta S \cdot dT = (V_2 - V_1) dP$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{\Delta S}{V_2 - V_1}} \quad \text{--- (42)}$$

where V_1 and V_2 are the molar volumes of the substance in phase-1 and phase-2 respectively.

Similarly, S_1 and S_2 are the molar entropies of the phases 1 and 2 respectively.

We know,

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

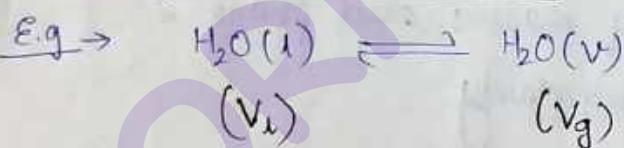
So, eqⁿ (42) will be,

$$\boxed{\frac{dP}{dT} = \frac{q}{T(V_2 - V_1)}} \quad \text{--- (43)}$$

Eqⁿ (43) is known as Clapeyron-Clausius Equation

Case-1 :-

For liquid \rightleftharpoons vapour



$$V_g \gg V_l$$

$$\Rightarrow V_g - V_l \approx V_g$$

Applying Clapeyron-Clausius Eqⁿ to this eqⁿ,

$$\Rightarrow \frac{dP}{dT} = \frac{q}{T(V_g - V_l)}$$

We know,

$$\boxed{q = \Delta H}$$

So, the above relation becomes,

$$\Rightarrow \frac{dp}{dT} = -\frac{\Delta H}{T(V_g - V_l)}$$

$$\Rightarrow \boxed{\frac{dp}{dT} = -\frac{\Delta H}{TV_g}} \quad (44)$$

We know,

$$PV_g = RT \text{ for 1 mole of an ideal gas.}$$

$$\Rightarrow V_g = \frac{RT}{P}$$

Substituting the value of V_g in eqⁿ(44),

$$\Rightarrow \frac{dp}{dT} = -\frac{\Delta H}{T \cdot \frac{RT}{P}}$$

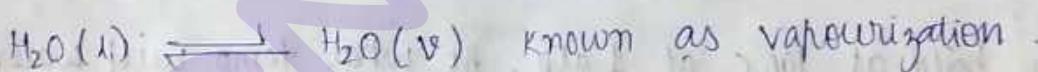
$$\Rightarrow \frac{dp}{P} = \frac{\Delta H}{R} \frac{dT}{T^2}$$

On integrating both sides with appropriate limit,

$$\Rightarrow \int_{P_1}^{P_2} \frac{dp}{P} = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\Rightarrow \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

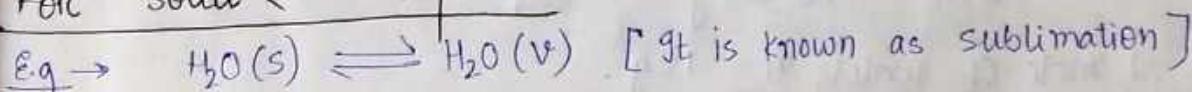
$$\Rightarrow \boxed{\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)} \quad (45)$$



so, here ΔH will be represented by ΔH_v and is known as molar heat of vapourization or latent heat of vapourization.

Case 2 :-

For solid \rightleftharpoons vapour



Here ΔH_s is known as molar heat of sublimation and the above eqⁿ becomes,

$$\boxed{\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_s}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$

Applications of Clapeyron - Clausius Equation

1. To find out the heat of vaporization.

Example :

1. The vapour pressure of H_2O at $95^\circ C$ and $100^\circ C$ are 634 and 760 mm of Hg respectively. Calculate the latent heat of vaporization or molar heat of vaporization.

Ans) Here, $T_1 = 95 + 273 = 368\text{K}$

$$P_1 = 634 \text{ mm}$$

$$T_2 = 100 + 273 = 373\text{K}$$

$$P_2 = 760 \text{ mm}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_s}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\ln\left(\frac{760}{634}\right) = \frac{\Delta H_s}{1.98} \left(\frac{373 - 368}{373 \cdot 368} \right)$$

$$\Rightarrow \Delta H_s = 9.89 \text{ K Cal/mol}$$

$$R = 1.98 \text{ (in Cal)}$$

$$R = 8.314 \text{ (in J/mole K)}$$

2. To find the boiling point or freezing point.

Example :

1. Water boils at $100^\circ C$ at 1 atm. At what temp. will water boil at a pressure of 2 atm given latent heat of vaporization of water is $\Delta H_v = 536 \text{ cal/g}^{-1}$.

Ans) Here, $P_1 = 1 \text{ atm}, T_1 = 100 + 273 = 373\text{K}$

$$P_2 = 2 \text{ atm}, T_2 = ?$$

$$\Delta H_v = 536 \text{ cal/g}^{-1}$$

For 1 mole of water, $n = 18\text{g}$.

$\therefore \Delta H_v \text{ for } 18\text{ g or 1 mole of water} = 536 \times 18 \text{ cal/mol}$

Substituting all values in eqn,

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{536}{1.98} \left(\frac{T_2 - 373}{T_2 \times 373} \right)$$

$$\Rightarrow T_2 = 277.66 \text{ K}$$

$$T_2 = 277.66 - 273$$

$$T_2 = 4.66^\circ\text{C}$$

if pressure changes from 1 atm
↓
2 atm

Water will boil at 4.66°C .

3. To find out the vapour pressure.

Example :-

Knowing the vapour pressure at a particular temp.,
are same at some other temp. can be calculated.

The vapour pressure of water at 95°C is 634 mm of Hg.
What will be the vapour pressure at 150°C given

$$\Delta H = 41.27 \text{ kJ/mol}$$

$$T_1 = 95 + 273 = 368 \text{ K}, P_1 = 634 \text{ mm}$$

$$T_2 = 150 + 273 = 423 \text{ K}, P_2 = ?$$

$$\Delta H_v = 41.27 \times 10^3 \text{ J/mol}$$

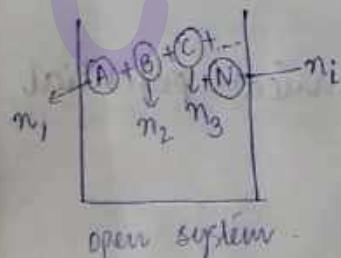
$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\ln\left(\frac{P_2}{634}\right) = \frac{41.27 \times 10^3}{8.314} \left(\frac{423 - 368}{423 \cdot 368} \right)$$

$$\Rightarrow P_2 = 3663 \text{ mm of Hg}$$

Partial Molar Properties :-

Consider an open system, there is every possibility of change
let in composition



Therefore, in such a case the state
must involve composition along with
temperature and pressure.

Now, any extensive thermodynamic property 'Z' can be
expressed as

$$[Z = f(P, T, n_1, n_2, \dots, n_i)]$$

So, dz can be represented as.

$$\cancel{dz} = \cancel{\left(\frac{dz}{dp}\right) dp} + \cancel{\left(\frac{dz}{dT}\right) dT}$$

T, n_1, n_2, \dots, n_i

$$dz = \left(\frac{\partial z}{\partial p}\right)_{T, n_1, n_2, \dots, n_i} dp + \left(\frac{\partial z}{\partial T}\right)_{p, n_1, n_2, \dots, n_i} dT + \left(\frac{\partial z}{\partial n_1}\right)_{T, p, n_2, \dots, n_i} \partial n_1 + \left(\frac{\partial z}{\partial n_2}\right)_{T, p, n_1, \dots, n_i} \partial n_2 + \dots + \left(\frac{\partial z}{\partial n_i}\right)_{T, p, n_1, n_2, \dots, n_{i-1}} \partial n_i$$

$\therefore \frac{\partial z}{\partial n_i}$ at constant $T, p, n_1, n_2, \dots, n_{i-1}$,

is known as Partial Molar Quantity of i^{th} component and may be defined as the change in property with the change in amount of i^{th} component when Temperature, Pressure and amount of ^{other} i^{th} components remains constant

It is represented by \bar{z}_i .

when, $\boxed{z = H}$

$$\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T, p, n_1, n_2, \dots, n_{i-1}} \rightarrow \begin{matrix} \text{Partial Molar} \\ \text{enthalpy} \end{matrix}$$

when $\boxed{z = S}$

$$\bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T, p, n_1, n_2, \dots, n_{i-1}} \rightarrow \text{Partial molar entropy}$$

when $\boxed{z = G}$

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_1, n_2, \dots, n_{i-1}} = \mu_i = \text{Chemical potential}$$

For a multi-component system, the free energy is a function of temperature, pressure and composition.

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

dG can be expressed as,

$$\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots, n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2, \dots, n_i} dn_1 + \dots + \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2, \dots, n_{i-1}} dn_i$$

$$\Rightarrow dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2, \dots, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2, \dots, n_i} dP + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \quad (46)$$

At constant temperature and pressure, eqⁿ (46) will be,

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \quad (47)$$

For a system with definite composition, having n_1, n_2, \dots, n_i composition moles of constituents of 1, 2, ..., i^{th} no. constituents respectively, the integration relation of eqⁿ (47) will be,

$$\Rightarrow \int dG = \int \mu_1 dn_1 + \int \mu_2 dn_2 + \dots + \int \mu_i dn_i$$

$$\Rightarrow \boxed{G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots + \mu_i n_i} \quad (48)$$

The complete differential form of eqⁿ (48) will be.

$$dG = (\underline{\mu_1 dn_1} + n_1 \underline{d\mu_1}) + (\underline{\mu_2 dn_2} + n_2 \underline{d\mu_2}) + (\underline{\mu_3 dn_3} + n_3 \underline{d\mu_3}) + \dots + (\underline{\mu_i dn_i} + n_i \underline{d\mu_i})$$

$$dG = (\mu_1 d\eta_1 + \mu_2 d\eta_2 + \mu_3 d\eta_3 + \dots + \mu_i d\eta_i) + (n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i) \quad (49)$$

On comparing eqⁿ (49) and eqⁿ (47),

$$dG = dG + (n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots + n_i d\mu_i)$$

$$\therefore n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots + n_i d\mu_i = 0.$$

$$\Rightarrow \boxed{\sum_{i=1}^i n_i d\mu_i = 0}$$

This is known as Gibbs Duhem equation.

(50)

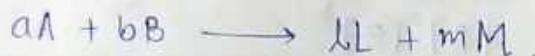
Chemical Equilibrium

26/02/2018

Law of Mass Action :-

As per this law, the rate of a reaction is directly proportional to the product of the active masses of the reactants with each term raised to the power equal to its stoichiometric coefficient.

Let us consider a hypothetical chemical reactⁿ.



According to the law of mass action law,

$$\text{Rate} \propto [A]^a [B]^b$$

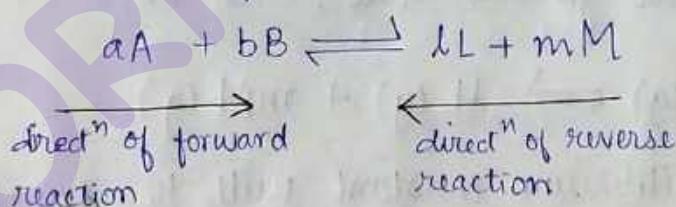
$\Rightarrow \text{Rate} = K [A]^a [B]^b$, where, $K \rightarrow$ proportionality constant or rate constant

$[A]^a \rightarrow$ Active mass of reactant A.

$[B]^b \rightarrow$ Active mass of reactant B.

Law of Chemical Equilibrium :-

Let us consider a hypothetical reversible chemical reaction



Applying law of mass action to the forward reaction,

$$\text{Rate } (r_f) = K_f [A]^a [B]^b \quad \dots \quad (1)$$

Similarly, for reverse reaction, it can be written as,

$$\text{Rate } (r_r) = K_r [L]^c [M]^d \quad \dots \quad (2)$$

At equilibrium,

$$\textcircled{1} \quad K_b = K_n$$

$$\text{So, } K_b [A]^a [B]^b = K_n [L]^l [M]^m$$

$$\Rightarrow \frac{K_b}{K_n} = \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

$$\Rightarrow K \text{ or } K_c = \frac{[L]^l [M]^m}{[A]^a [B]^b} \quad \textcircled{3}$$

where K or K_c is known as equilibrium constant in terms of molar concentrations.

$[A]^a$ = molar conc. of A / active mass of A

$[B]^b$ = molar conc. of B / active mass of B

$[L]^l$ = molar conc. of L / active mass of L

$[M]^m$ = molar conc. of M / active mass of M.

Equilibrium constant in terms of partial pressure :

When all the reactants and products in a reversible reaction are in their gaseous state, such as,



Then, this time equilibrium constant will be expressed as,

$$K_p = \frac{P_L^l \cdot P_M^m}{P_A^a \cdot P_B^b} \quad \textcircled{4}$$

where P_A, P_B, P_L, P_M are partial pressures of A, B, L and M respectively.

As we know, pressure \propto no. of moles, then,
from ideal gas eqn,

$$PV = nRT$$

similarly,

$$P_L V = n_L RT$$

$$P_L = \left(\frac{n_L}{V}\right) RT \Rightarrow P_L = [L] \cdot RT$$

similarly,

$$P_M V = n_M RT$$

$$P_M = \left(\frac{n_M}{V}\right) RT \Rightarrow P_M = [M] \cdot RT$$

similarly,

$$P_A V = n_a RT$$

$$P_A = \left(\frac{n_a}{V}\right) RT \Rightarrow P_A = [A] \cdot RT$$

Also

$$P_B V = n_b RT$$

$$P_B = \left(\frac{n_b}{V}\right) RT \Rightarrow P_B = [B] \cdot RT$$

Since, $\frac{n}{V}$ = molar concentration.

→ Substituting the value of P_L , P_M , P_B and P_A in eqn ⑦,

$$\Rightarrow K_p = \frac{([L] \cdot RT)^l \cdot ([M] \cdot RT)^m}{([A] \cdot RT)^a \cdot ([B] \cdot RT)^b}$$

$$\Rightarrow K_p = \frac{[L]^l [M]^m (RT)^{l+m-(a+b)}}{[A]^a [B]^b}$$

$$\Rightarrow K_p = K_c RT^{\Delta n} \quad \textcircled{5}$$

$$\text{where } \Delta n = (l+m) - (a+b)$$

$$= (\text{no. of moles of product}) - (\text{no. of moles of reactant})$$

Case 1 : when $\Delta n = 0$,

$$K_p = K_c$$

Case 2 : when $\Delta n > 0$

$$K_p > K_c$$

Case 3 : when $\Delta n < 0$

$$K_p < K_c$$

Q1. At 500K temperature, the equilibrium constant K_c for the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ is $4 \times 10^2 \text{ mol/lit}$. find K_p for the reaction.

$$\Delta n = 2 - 1 = 1$$

$$K_p = K_c (RT)^{\Delta n}$$

$$K_p = K_c (RT)^1$$

$$\Rightarrow K_p = (4 \times 10^2) (8.314 \times 500)$$

$$\Rightarrow K_p = 1.64$$

1.64

→ When other quantity having unit

① J or KJ, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

② Cal or Kcal, $R = 1.98 \text{ cal K}^{-1}$

When pressure is to be calculated in,

③ atm, $R = 0.0831 \text{ L atm mol}^{-1} \text{ K}^{-1}$

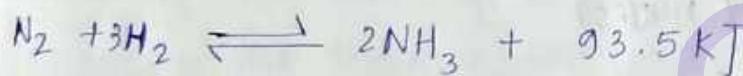
Le - Chatelier's principle

It predicts the effect of stress (conc., pressure, catalyst, temp., noble gas) on a system in equilibrium.

It states that,

If a system is in equilibrium is subjected to some external stress, the system adjusts itself so as to undo the stress i.e. the system shifts in a direction so as to reduce the outside stress.

The external stress can be in the form of change of conc., pressure, use of noble gas, use of catalyst.



Q1. Explain Le - Chatelier's principle with reference to the Haber's process for the manufacturing of NH_3 .



① Effect. of concentration

By increasing the conc. of Nitrogen and Hydrogen, the equilibrium will move in forward direction by decreasing the conc. of NH_3 , the equilibrium will move in forward direct".

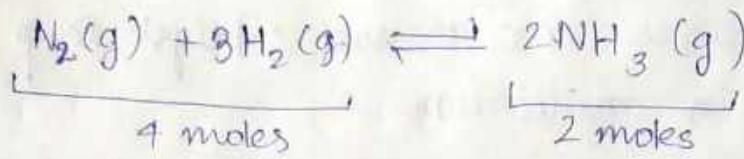
By increasing the conc. of NH_3 , the equilibrium will move in reverse or backward direct".

② Effect of temperature

By decreasing the temp., the equilibrium will move in forward direct".

→ By increasing the temp., the equilibrium will move in backward direct".

③ Effect of pressure



Pressure \propto No. of moles

Therefore, a hike in pressure shifts the equilibrium in the directⁿ in which there is a decrease in no. of moles or less no. of moles.

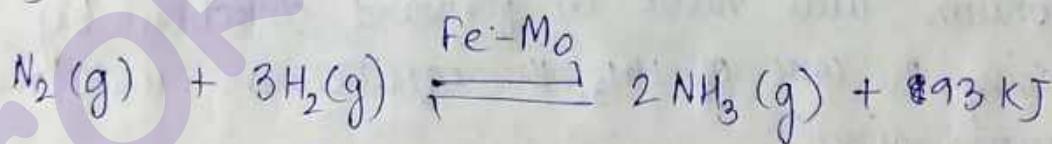
For the present case, by increasing the pressure or by addition of N and H shifts the equilibrium in forward directⁿ as the product involves less no. of moles (2 moles) than the reactant (4 moles)

④ Effect of catalyst

The use of catalyst increases the rate of forward reaction as well as the reverse reactⁿ to the same extent.

Therefore, its use doesn't alter the equilibrium rather quickens the approach of equilibrium.

In Haber's process, for manufacturing of NH₃ is catalysed by finely divided iron and Molybdenum (Mo)



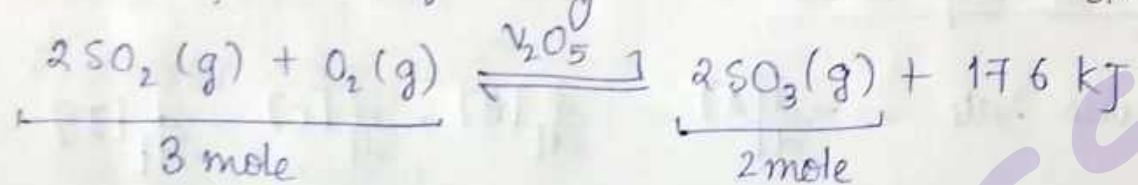
⑤ Effect of addition of Noble gas :-

Due to addition of Noble gas (He, Ar, Zn, etc) the pressure will increase, hence the equilibrium will shift to manage the pressure, hence the equilibrium will shift in forward directⁿ as less no. of moles are there (2 moles)

Q2. Apply Le Chatelier's principle so as to predict the optimum conditions for the max. yield of H_2SO_4 in contact process. and HNO_3 in Birkeland - Eyde process.

Ans) a) Contact process

Basic reactⁿ involved here is the oxidation of sulphur dioxide as per the following reaction:-



Optimum conditions for max. yield of sulphuric acid

1. By increasing the conc. of SO_2 and O_2 .
2. By decreasing the temp of the process.
3. By increasing the pressure.
4. By using Catalyst V_2O_5 .

b) Birkeland - Eyde process

Basic reactⁿ here is :-



Optimum conditions for max yield of nitric acid

1. By increasing the conc. of N_2 and O_2 .
2. As the forward reactⁿ is endothermic reactⁿ, increase in temp. results more product.
3. Pressure has no effect as both reactant and product has same moles.
4. Use of suitable catalyst such as $Cu(NO_3)_2$.

CHEMICAL KINETICS

8/3/2018

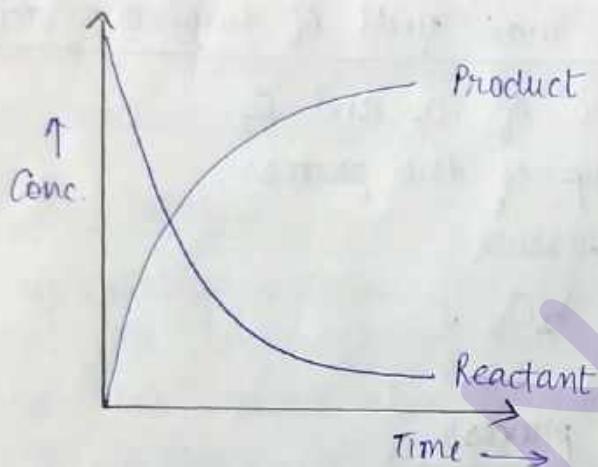


$$\text{Rate} = -\frac{\Delta A}{\Delta t} = -\frac{\Delta B}{\Delta t} = \frac{\Delta C}{\Delta t} = \frac{\Delta D}{\Delta t}$$

When Δt is very small,

$$\text{Instantaneous rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Graph



* According to the Law of Mass Action,



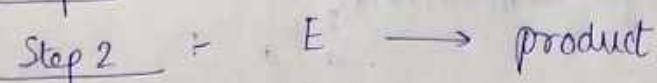
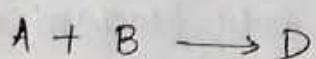
$$\text{Rate} \propto [A]^a [B]^b$$

Rate = $K [A]^a [B]^b$, where $K \rightarrow$ proportionality constant or rate constant.

$$\text{Order} = (a+b)$$

for a simple reaction, order and molecularity is same.

For a reactⁿ,



$$\boxed{\text{Rate} = K[A][B]}$$

Molecularity is no of molecules taking part in each and every elementary step of a complex reaction.

However, the rate is determined by the slowest step of a complex reaction.

Based on order, the reactions are :-

- ① Zero order reaction
- ② First - order reaction
- ③ Second - order reactⁿ.
- ④ Fractional order reactⁿ.

If $A \rightarrow$ product,

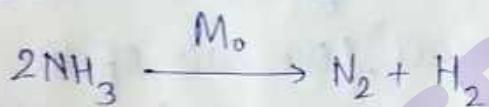
$$\text{Rate} = K [A]^0$$

Zero - Order Reaction

If order is independent on the conc. of the reactant,

E.g. →

① Decomposition of NH_3 in the surface of Mo is zero order reactⁿ.



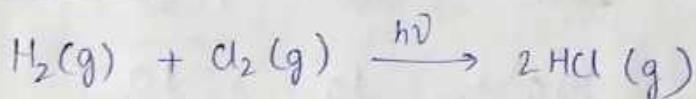
$$\text{Rate} = K [\text{NH}_3]^0 = \frac{dx}{dt}$$

If $A \rightarrow$ product

$$\text{Rate} = \frac{dx}{dt} \propto [A]^0$$

$$= \frac{dx}{dt} = K[A]^0$$

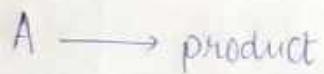
② Photochemical combination of $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$



$$\text{Rate} = \frac{dx}{dt} = K [\text{H}_2]^0 [\text{Cl}_2]^0$$

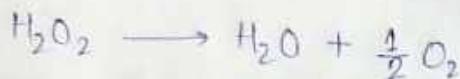
First order reaction

If the rate of the reactⁿ depends on the concentration of one reactant only.



$$\Rightarrow \text{Rate} = \frac{dx}{dt} = K[A]$$

E.g. → ① Decomposition of H₂O₂



$$\text{Rate} = K[H_2O_2]$$

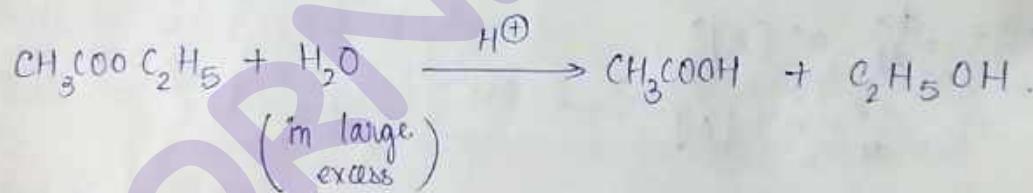
Pseudo first-order Reaction



$$\text{Rate} = K[A]^{\alpha}[B]^{\beta}$$

When there are 2 reactants in a reactⁿ, but the rate of the reactⁿ depends upon the change in conc. of only one reactant it is called pseudo first order reaction.

E.g. → ① Acid catalysed hydrolysis of ester



Time (t)	0	10	1000	0	0
t	∞	0	990	10	10

$$\text{Rate} = \frac{dx}{dt} = K [CH_3COOC_2H_5]$$

Second order reaction

If the rate of the reactⁿ directly depends on the change in concentration of 2 reactants.



$$\text{Rate} = \frac{dx}{dt} = k[A]^1[B]^1$$

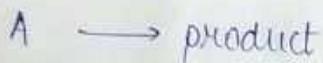


$$\text{Rate} = \frac{dx}{dt} = k[A]^2$$

Integrated Rate Law :-

Zero Order Rate Law →

Let us consider a hypothetical zero order reaction,



At time, $t=0$, $a \rightarrow 0$.

At time, $t=t$, $(a-x) \rightarrow x$

So, the rate, i.e., $\frac{dx}{dt} = k[A]^0$, where $k \rightarrow$ zero order rate constant

$$\Rightarrow \frac{dx}{dt} = k$$

$$\Rightarrow dx = kdt$$

Integrating both sides with proper limit,

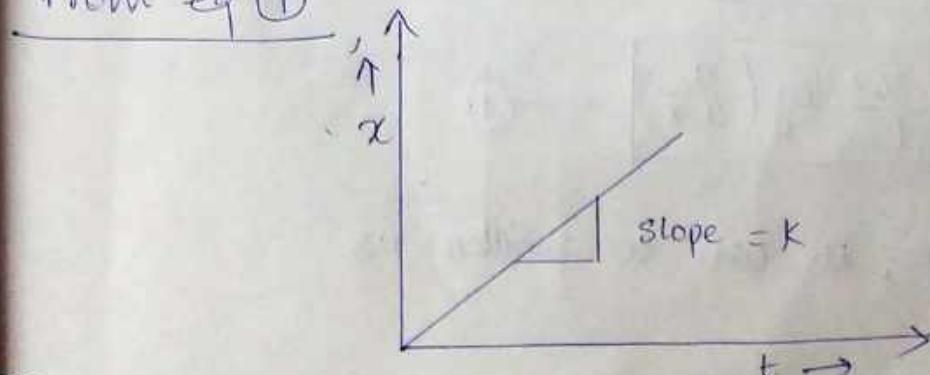
$$\Rightarrow \int_0^x dx = \int_0^t k dt$$

$$\Rightarrow (x-0) = k(t-0)$$

$$\Rightarrow \boxed{x = kt} \quad \text{--- (1)}$$

$$\Rightarrow \boxed{k = \frac{x}{t}} \quad \text{--- (2)}$$

From eqⁿ (1)



From eqⁿ ②,

The unit of zero-order rate constant,

$$K = \frac{\text{mol/litre}}{\text{time}} = \text{mol lit}^{-1} \text{time}^{-1}$$
$$= \text{mol lit}^{-1} \text{min}^{-1}$$
$$= \text{mol lit}^{-1} \text{sec}^{-1}$$

First order rate expression →

Let us consider a hypothetical first order reaction.



$$\text{At } t=0 \quad a \longrightarrow 0$$

$$\text{At } t=t \quad (a-x) \longrightarrow x$$

$$\text{So, the rate } \geq \frac{dx}{dt} \propto [A]$$

$$\Rightarrow \frac{dx}{dt} = k(a-x)$$

So, here, $k \rightarrow$ first order rate constant.

$$\Rightarrow \frac{dx}{(a-x)} = k dt$$

Integrating both sides with appropriate limit.

$$\Rightarrow \int_{a-x}^a \frac{dx}{a-x} = \int_0^t k dt$$

$$\Rightarrow [-\ln(a-x)]_a^{a-x} = k(t-0)$$

$$\Rightarrow (-\ln(a-x)^a - (-\ln a)) = kt$$

$$\Rightarrow \boxed{k = \frac{1}{t} \ln \left(\frac{a}{a-x} \right)} \quad \text{--- ③}$$

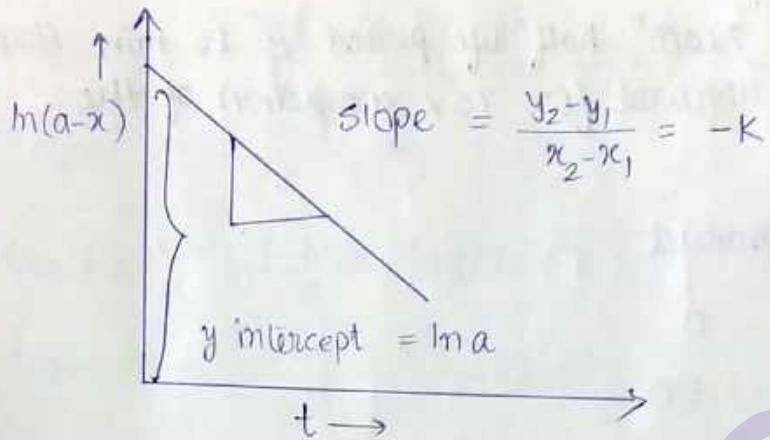
$$\Rightarrow \boxed{k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)} \quad \text{--- ④}$$

From eqⁿ ③, it can be written as

$$kt = \ln a - \ln(a-x)$$

$$\Rightarrow \ln(a-x) = -kt + \ln a \quad \text{--- (5)}$$

$$(y) = (mx) + (c)$$



Unit of 1st order rate eqⁿ sec⁻¹ or min⁻¹

$$k = \frac{1}{t} \ln \left(\frac{a}{a-x} \right) = \frac{1}{\text{sec}} \ln \frac{\text{mol/lit}}{\text{mol/lit}}$$

Half Life Period

Time required for 50% completion of the reaction or the time reqd for 50% consumption of reactant to product is called half life period.

It is denoted by $(t_{1/2})$



$$t=0 \quad a \quad 0$$

$$t=t \quad (a-x) \quad x$$

$$t=t_{1/2} \quad (a-\alpha_{1/2}) \quad \alpha_{1/2}$$

so, from eqⁿ (4), it can be written as

$$k = \frac{2.303}{t_{1/2}} \log \left(\frac{a}{a-\alpha_{1/2}} \right)$$

$$t_{1/2} = \frac{2.303}{k} \log \left(\frac{a}{\alpha_{1/2}} \right)$$

$$t_{1/2} = \frac{2.303}{K} \log 2$$

$$t_{1/2} = \frac{2.303}{K} \times 0.3010$$

$$\Rightarrow \boxed{t_{1/2} = \frac{0.693}{K}} \quad \textcircled{6}$$

Q1. for a first order reactⁿ, half life period is 15 min. How much time will be required for 75% completion of the reaction. (4 mark)



At, time, $t = 0$, 100 0

At, $t = 15 \text{ min}$, 50 50

At, $t_{75\%} = ?$ (100-75) 75

We know,

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{15}$$

$$K = \frac{2.303}{t_{75\%}} \log \left(\frac{100}{100-75} \right)$$

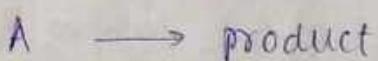
$$\Rightarrow \frac{0.693}{15} = \frac{2.303}{t_{75\%}} \log 4$$

$$\Rightarrow \frac{0.693}{15} = \frac{2.303}{t_{75\%}} \times 2 \times 0.3010$$

$$\Rightarrow t_{75\%} = \frac{2.303 \times 2 \times 0.3010 \times 15}{0.693}$$

$$\Rightarrow t_{75\%} = 30 \text{ min.}$$

Q2. Show that, in case of a first order reactⁿ, the time reqd for 99.9% completion of the reactⁿ is about 10 times than that reqd for half completion of reaction.



At $t = 0$ 100 % 0

$t = t_{1/2}$	(100 - 50)	50
$t = 99.9\%$	(100 - 99.9)	99.9

Now know, $t_{1/2} = \frac{0.693}{K}$

$$t_{99.9\%} = \frac{2.303}{K} \log \left(\frac{100}{100-99.9} \right)$$

$$t_{99.9\%} = \frac{2.303}{K} \log \left(\frac{100}{0.1} \right)$$

$$t_{99.9\%} = \frac{2.303}{K} \log(10)^3$$

$$t_{99.9\%} = \frac{2.303 \times 3 \log(10)}{K}$$

$$t_{99.9\%} = \frac{6.909}{K}$$

Now, $\frac{t_{99.9\%}}{t_{1/2}} = \frac{6.909}{K} \times \frac{K}{0.693} = 10$

$$\boxed{t_{99.9\%} = 10 t_{1/2}}$$

Second Order Rate Expression

Case 1 : $2A \rightarrow \text{product}$

Case 2 : $A + B \rightarrow \text{product}$

So,

Rate expression for case 1

$2A \rightarrow \text{product}$

$t=0 \quad a \quad 0$

$t=t \quad (a-x) \quad x$

So, the rate i.e., $= \frac{dx}{dt} \propto [A]^2$

$$\Rightarrow \frac{dx}{dt} = k(a-x)^2$$

where $k \rightarrow \text{second order rate constant}$.

$$\frac{dx}{(a-x)^2} = k \cdot dt$$

On integrating both the sides

$$\int \frac{dx}{(a-x)^2} = \int k \cdot dt$$

$$\Rightarrow -\left(\frac{(a-x)^{-2+1}}{-2+1}\right) = kt + c, \text{ where } c \rightarrow \text{integration constant}$$

$$\Rightarrow -\left(\frac{(a-x)^{-1}}{-1}\right) = kt + c$$

$$\Rightarrow \boxed{\frac{1}{a-x} = kt + c} \quad \text{--- (7)}$$

At $t=0$, $a-x \approx a$

so eqn (7) will be

$$\Rightarrow \frac{1}{a} = c + k \cdot 0$$

$$\Rightarrow c = \frac{1}{a}$$

Substituting the value of c in eqn (7)

$$\Rightarrow \frac{1}{a-x} = kt + \frac{1}{a}$$

$$\Rightarrow \frac{1}{a-x} - \frac{1}{a} = kt$$

$$\Rightarrow kt = \frac{a-a+x}{a(a-x)}$$

$$\Rightarrow kt = \frac{x}{a(a-x)}$$

$$\Rightarrow \boxed{K = \frac{1}{t} \frac{x}{a(a-x)}} \quad \text{--- (8)}$$

Half life period for second order reaction

$$K = \frac{1}{t_{1/2}} \cdot \frac{a_2}{a(a-a_2)}$$

$$K = \frac{1}{a t_{1/2}} \Rightarrow \boxed{t_{1/2} = \frac{1}{a K}}$$

Steady State Approximation

10/3/2018

Let us consider a hypothetical chemical reaction where



Mechanism:



$$\text{Rate} = k_2 [B][C] \quad \textcircled{1}$$

Rate is generally determined from the slowest step of the reaction mechanism.

→ In this reaction scheme, C is the intermediate.

Intermediate

It is such an entity which is formed *in-situ* in one step and consumed in subsequent steps so that it doesn't appear as an end product.

Rate of its formation = Rate of its utilisation or decomposition.

$$\Rightarrow k_1[A] = k_2[B][C]$$

$$\Rightarrow k_1[A] - k_2[B][C] = 0$$

$$\Rightarrow [C] = \frac{k_1[A]}{k_2[B]}$$

$$\text{Rate} = k_2[B] \times \frac{k_1[A]}{k_2[B]}$$

$$\Rightarrow \boxed{\text{Rate} = k_1[A]}$$

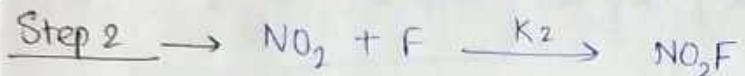
Type-1

The first step is the slow and rate controlling step followed by a rapid step.

Let us consider the reaction betⁿ $\text{NO}_2(g)$ and $\text{F}_2(g)$.



Proposed mechanism :-



Show that the rate of decomposition of NO_2

$$-\frac{d[\text{NO}_2]}{dt} = 2K_1[\text{NO}_2][\text{F}_2]$$

Here, F → intermediate

Applying steady state approximation of to the intermediate

$$\Rightarrow K_1[\text{NO}_2][\text{F}_2] - K_2[\text{NO}_2][\text{F}] = 0$$

$$\Rightarrow [\text{F}] = \frac{K_1[\text{NO}_2][\text{F}_2]}{K_2[\text{NO}_2]}$$

$$\Rightarrow [\text{F}] = \frac{K_1}{K_2}[\text{F}_2] \quad \text{--- (1)}$$

$$\text{Rate of decomposition of } \text{NO}_2 = -\frac{d[\text{NO}_2]}{dt}$$

$$\Rightarrow -\frac{d[\text{NO}_2]}{dt} = K_1[\text{NO}_2][\text{F}_2] + K_2[\text{NO}_2][\text{F}]$$

Substituting the value of [F] in above eqⁿ,

$$-\frac{d[\text{NO}_2]}{dt} = K_1[\text{NO}_2][\text{F}_2] + \frac{K_1}{K_2}[\text{F}_2]K_2[\text{NO}_2]$$

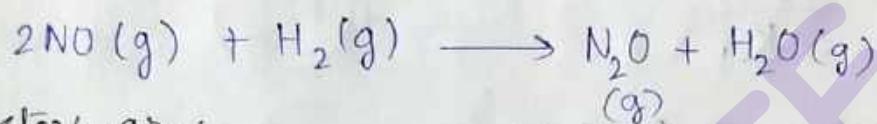
$$\Rightarrow \boxed{-\frac{d[\text{NO}_2]}{dt} = 2K_1[\text{NO}_2][\text{F}_2]} \quad (\text{proved})$$

Type - 2

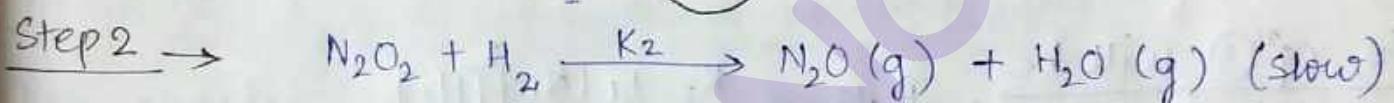
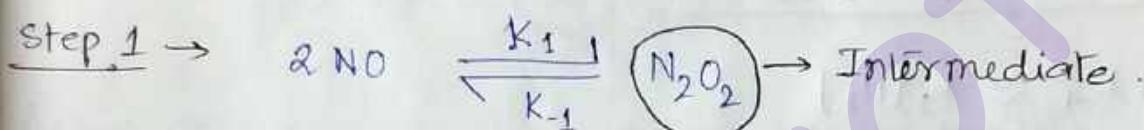
Intermediate formed in the first step remains in equilibrium with the reactants which subsequently slowly reacts in the second step.

Example :

Let us consider the reactⁿ betⁿ nitric oxide (NO) and hydrogen gas.



Mechanistic steps are :-



Here N_2O_2 is the intermediate.

Applying steady state approximation to the intermediate :-

$$\Rightarrow \text{K}_1[\text{NO}]^2 - \text{K}_{-1}[\text{N}_2\text{O}_2] + \text{K}_2[\text{N}_2\text{O}_2][\text{H}_2] = 0$$

$$\Rightarrow \text{K}_1[\text{NO}]^2 = \text{K}_{-1}[\text{N}_2\text{O}_2] + \text{K}_2[\text{N}_2\text{O}_2][\text{H}_2]$$

$$\Rightarrow [\text{N}_2\text{O}_2] = \frac{\text{K}_1[\text{NO}]^2}{\text{K}_{-1} + \text{K}_2[\text{H}_2]} \quad \text{--- } ①$$

Rate of overall reactⁿ scheme, i.e

$$\text{Rate} = \text{K}_2[\text{N}_2\text{O}_2][\text{H}_2] \quad \text{--- } ②$$

Substituting the value of eqⁿ ① in eqⁿ ②,

$$\text{Rate} = \frac{\text{K}_2 \cdot \text{K}_1[\text{NO}]^2 [\text{H}_2]}{\text{K}_{-1} + \text{K}_2[\text{H}_2]} \quad \text{--- } ③$$

Case 1 : when $K_1 \gg K_2[H_2]$

$$K_1 + K_2[H_2] \approx K_1$$

So eqⁿ ③ will be, Rate = $\frac{K_2 \cdot K_1 [NO]^2 [H_2]}{K_1}$

$$\Rightarrow \boxed{\text{Rate} = K [NO]^2 [H_2]}$$

The rate is first order
in respect to $[H_2]$ and

where, $K = \frac{K_2 \cdot K_1}{K_1}$ second order w.r.t $[NO]^2$.

Case 2 : when $K_2[H_2] \gg K_1$

$$K_2[H_2] + K_1 \approx K_2[H_2]$$

So, eqⁿ ③ will be -

$$\text{Rate} = \frac{K_2 \cdot K_1 [NO]^2 [H_2]}{K_2[H_2]}$$

$$\boxed{\text{Rate} = K_1 [NO]^2}$$

The rate is second order w.r.t $[NO]^2$.

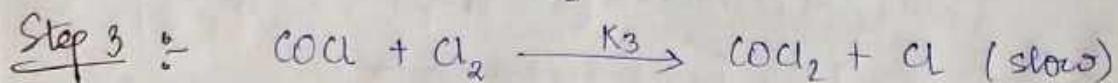
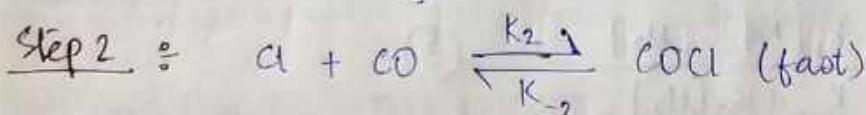
Type-3

The reaction with more than 2 elementary step with atleast one slow step.

E.g. → Reaction for formation of Phosgene



Mechanism steps are :-



$$\text{Show that} \rightarrow \frac{d}{dt}[COCl_2] = K[CO][Cl_2]^{3/2}$$

According

The rate of formation of product i.e. COCl_2

Proof :-

$$\text{Rate} = \frac{d}{dt} [\text{COCl}_2] = K_3 [\text{COCl}] [\text{Cl}_2] \quad \text{--- (1)}$$

As the step 1 is in equilibrium

The rate of forward reaction = Rate of reverse reaction.

Hence,

$$\Rightarrow K_1 [\text{Cl}_2] = K_{-1} [\text{Cl}]^2$$

$$\Rightarrow [\text{Cl}] = \left(\frac{K_1 [\text{Cl}_2]}{K_{-1}} \right)^{\frac{1}{2}} \quad \text{--- (2)}$$

Again step-2 is in equilibrium also, hence,

Rate of F.R = Rate of Reverse Reaction.

$$\Rightarrow K_2 [\text{Cl}] [\text{CO}] = K_{-2} [\text{COCl}]$$

$$\Rightarrow [\text{COCl}] = \frac{K_2 [\text{Cl}] [\text{CO}]}{K_{-2}} \quad \text{--- (3)}$$

Now, Substituting the value of Cl from eqⁿ(2) in eqⁿ(3),

$$\Rightarrow \boxed{[\text{COCl}]} = \frac{K_2}{K_{-2}} \left(\frac{K_1}{K_{-1}} \right)^{\frac{1}{2}} [\text{Cl}_2]^{\frac{1}{2}} [\text{CO}] \quad \text{--- (4)}$$

Substituting the value of $[\text{COCl}]$ from eqⁿ(4) in eqⁿ(1),

$$\frac{d}{dt} [\text{COCl}_2] = K_3 \cdot \frac{K_2}{K_{-2}} \left(\frac{K_1}{K_{-1}} \right)^{\frac{1}{2}} [\text{Cl}_2]^{\frac{1}{2}} [\text{CO}] [\text{Cl}_2]$$

$$\boxed{\frac{d}{dt} [\text{COCl}_2] = K [\text{CO}] [\text{Cl}_2]^{\frac{3}{2}}} \quad (\text{proved})$$

$$\text{Where, } K = \frac{K_3 K_2}{K_{-2}} \left(\frac{K_1}{K_{-1}} \right)^{\frac{1}{2}}$$

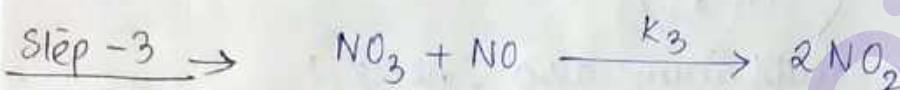
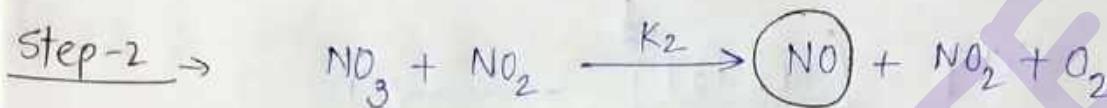
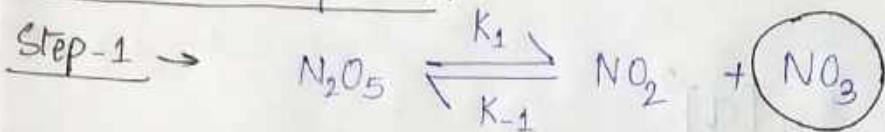
Type - 4

The reaction with more than one step and with more than one intermediate with comparable rate constant.

Eg → Decomposition reaction of N_2O_5 which is -



Mechanistic steps are :-



Show that, $\frac{d}{dt}[O_2] = K[N_2O_5]$, where $K = \frac{K_1 K_2}{K_{-1} + 2K_2}$

Here there are 2 intermediates.

$$I_2 = NO_3$$

$$I_1 = NO$$

Let us apply steady state approximation to NO

$$\Rightarrow K_2[NO_3][NO_2] - K_3[NO_3][NO] = 0.$$

$$\Rightarrow K_2[NO_3][NO_2] = K_3[NO_3][NO]$$

$$\Rightarrow [NO] = \frac{K_2[NO_2]}{K_3} \quad \text{--- (1)}$$

Applying steady state approximation to second intermediate NO_3

$$\Rightarrow K_1[N_2O_5] - K_{-1}[NO_2][NO_3] - K_2[NO_3][NO_2] - K_3[NO_3][NO] = 0$$

$$\Rightarrow [NO_3] = \frac{K_1[N_2O_5]}{K_{-1}[NO_2] + K_2[NO_2] + K_3[NO]} \quad \text{--- (2)}$$

Substituting the value of $[NO_3]$ from eqⁿ(1) to eqⁿ(2)

$$\Rightarrow [NO_3] = \frac{K_1[N_2O_5]}{K_{-1}[NO_2] + K_2[NO_2] + \frac{K_3 \cdot K_2}{K_3} [NO_2]}$$

$$\Rightarrow [NO_3] = \frac{K_1[N_2O_5]}{K_{-1}[NO_2] + 2K_2[NO_2]}$$

$$\Rightarrow [NO_3] = \frac{K_1[N_2O_5]}{[NO_2](K_{-1} + 2K_2)}$$

Finally substituting the value of $[NO_3]$, the rate eqⁿ becomes

$$\frac{d}{dt}[O_2] = K_2[NO_3][NO_2]$$

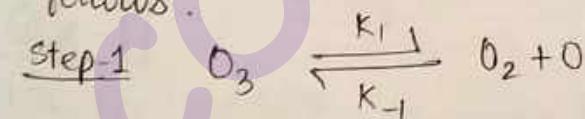
$$\frac{d}{dt}[O_2] = K_2 \cdot \frac{K_1[N_2O_5]}{[NO_2](K_{-1} + 2K_2)} \cdot [NO_2]$$

$$\frac{d}{dt}[O_2] = \frac{K_2 K_1 [N_2O_5]}{(K_{-1} + 2K_2)}$$

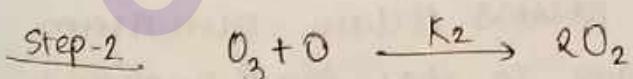
$$\boxed{\frac{d}{dt}[O_2] = K[N_2O_5]}, \text{ where } K = \frac{K_2 K_1}{(K_{-1} + 2K_2)}$$

H.W.

1. For the decomposition of O_3 the mechanistic steps are as follows.



(iii)



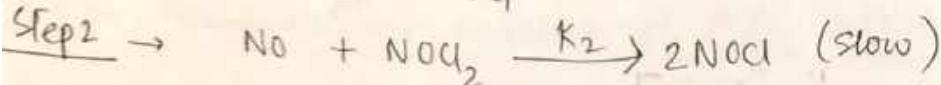
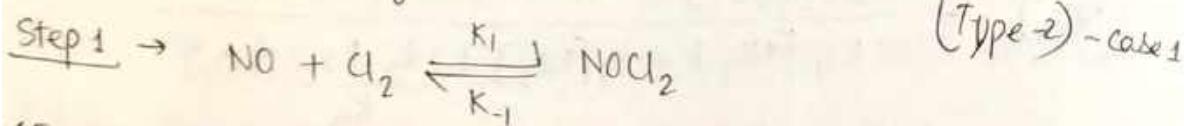
Show that the decomposition of O_3 i.e.

$$-\frac{d}{dt}[O_3] = \frac{K[O_3]^2}{[O_2]}, \text{ where, } K = \frac{2K_1 K_2}{K_{-1}}$$

Assuming,

$$K_{-1}[O_2] \gg K_2[O_3]$$

Q2. For the reactⁿ $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$, the proposed mechanism is as follows :



Show that the overall rate = $K[\text{NO}]^2[\text{Cl}_2]$. where,

$$K = \frac{K_1 K_2}{K_{-1}}, \text{ assume } K_2[\text{NO}] \ll K_{-1}$$

Theories Of Reaction Rate :-

① Collision Theory

According to the Arrhenius and Vant-Hoff, the salient features of collision theory are as follows :-

- 1) Collision among the reacting particles is the essential requirement of a reaction.
- 2) Though collision frequency is usually very high, all the collisions don't give rise to the change / product.
- 3) An effective collision is that which leads to the formation of product. This is possible when following requirements are satisfied :-

i) Energy requirement

The colliding particles must possess certain minimum energy called threshold energy so that bond rupture is possible.

ii) Orientation requirement

The reacting particles must be properly oriented, i.e. the atom taking part in bond breaking and bond making must come in contact with each other.

Mathematically, as per collision theory,

$$\text{Rate} = Z \cdot f \cdot p$$

where, $Z \rightarrow \text{collision frequency}$ (no. of collision per unit vol^m per unit time)

thus,

$$Z = \frac{1}{\sqrt{2}} \pi \sigma^2 n^2 \bar{v}$$

where, $\sigma \rightarrow \text{collision diameter}$

$n \rightarrow \text{no. of molecules taking part in react}^n$
per unit vol^m per unit time.

$\bar{v} \rightarrow \text{average velocity}$

$$f = \frac{n'}{n} = e^{-E_a/RT}$$

where, $n' \rightarrow \text{no. of molecule having threshold energy}$

$n \rightarrow \text{total no. of molecules}$

$e^{-E_a/RT} \rightarrow \text{Boltzmann's factor}$

$E_a \rightarrow \text{activation energy}$

'p' \rightarrow steric steric factor / probability factor

Now Rate = $Z f \cdot p$

$$= \frac{1}{\sqrt{2}} \pi \sigma^2 n^2 \bar{v} \cdot e^{-E_a/RT} \cdot p$$

Case-1

For the reaction, A \rightarrow product



$$\text{collision diameter} = \frac{\sigma + \sigma}{2} = \sigma$$

$$\text{The average velocity} = \bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

Substituting the value of \bar{v} in eqn ②,

$$\text{Rate} = \frac{1}{\sqrt{2}} \pi \sigma^2 n^2 \sqrt{\frac{8RT}{\pi M}} e^{-E_a/RT} \cdot P$$

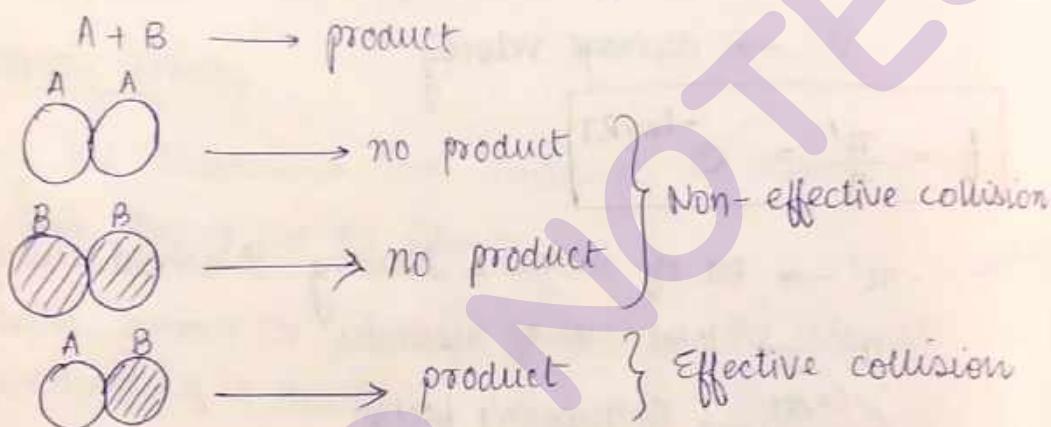
$$\text{Rate} = 2 \sigma^2 n^2 \sqrt{\frac{RT}{M}} e^{-E_a/RT} \cdot P$$

M → molecular weight of A

→ when A is the only reactant.

Case 2 : Collision among different particles

When 2 types of reactants are taking part in the reaction



So, let ' n_A ' → no. of A

' n_B ' → no. of B molecules present per unit vol^m per unit time in reactⁿ vessel.

So, the collision frequency

$$Z = \frac{1}{\sqrt{2}} \pi \sigma^2 (n_A + n_B)^2 \bar{v}$$

Subtracting the no. of collisions in A-A molecules and B-B molecules, the effective collision will be

$$Z = \frac{1}{\sqrt{2}} \pi \sigma^2 (n_A + n_B)^2 \bar{v} - \frac{1}{\sqrt{2}} \pi \sigma^2 n_A^2 \bar{v} - \frac{1}{\sqrt{2}} \pi \sigma^2 n_B^2 \bar{v}$$

$$\Rightarrow Z = \frac{1}{\sqrt{2}} \pi \sigma^2 n_A^2 \bar{v} + \frac{1}{\sqrt{2}} \pi \sigma^2 n_B^2 \bar{v} + \frac{1}{\sqrt{2}} \pi \sigma^2 2 n_A n_B \bar{v} - \frac{1}{\sqrt{2}} \pi \sigma^2 n_A^2 \bar{v} - \frac{1}{\sqrt{2}} \pi \sigma^2 n_B^2 \bar{v}$$

$$\Rightarrow Z = \sqrt{2} \pi \sigma^2 n_A n_B V$$

for this case, $V = \sqrt{\frac{8RT}{2\pi\mu}}$,

where μ is the reduced mass,

$$\mu = \frac{M_A M_B}{M_A + M_B}, \quad M_A \rightarrow \text{molecular wt. of A}$$

$$M_B \rightarrow \text{molecular wt. of B.}$$

Collision diameter (σ)

$$\sigma = \frac{\sigma_A + \sigma_B}{2}$$

$$\text{so, } Z = \sqrt{2} \pi \left(\frac{\sigma_A + \sigma_B}{2} \right)^2 n_A \cdot n_B \sqrt{\frac{8RT}{2\pi\mu}}$$

$$\Rightarrow Z = \sqrt{2} \pi \frac{(\sigma_A + \sigma_B)^2}{4} n_A n_B 2 \sqrt{\frac{RT}{\pi\mu}}$$

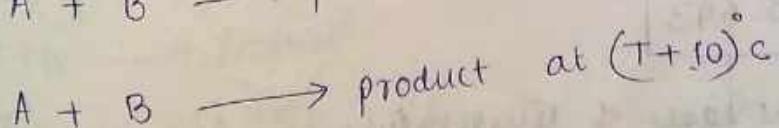
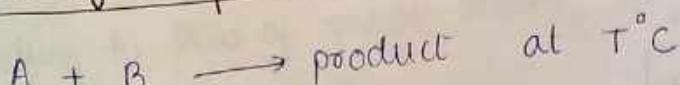
$$\Rightarrow Z = \frac{1}{\sqrt{2}} (\sigma_A + \sigma_B)^2 n_A \cdot n_B \sqrt{\frac{\pi RT}{\mu}}$$

$$\text{Rate} = Z f P$$

$$f = \alpha e^{-E_a/RT}$$

$$\boxed{\text{Rate} = \frac{1}{\sqrt{2}} (\sigma_A + \sigma_B)^2 n_A n_B \sqrt{\frac{\pi RT}{\mu}} e^{-E_a/RT} \cdot P}.$$

Effect of Temperature on Rate of Reactⁿ: Endothermic reactⁿ



$$\frac{\text{Rate (at } T+10^\circ C)}{\text{Rate (at } T^\circ C)} \approx 2 \times 10^3$$

From collision theory

$$\text{Rate} \propto \sqrt{T}$$

$$\text{Rate} \propto e^{-E_a/RT}$$

Suppose,

$$T_1 = 300\text{K}, T_2 = 310\text{K} \quad (\text{For rate} \propto \sqrt{T})$$

Then,

$$\frac{\text{Rate at } 310\text{K}}{\text{Rate at } 300\text{K}} = \frac{r_2}{r_1} = \sqrt{\frac{310}{300}} = 1.015$$

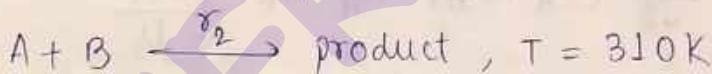
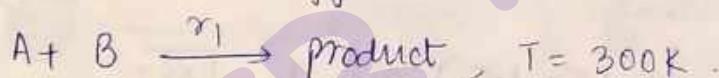
$$\Rightarrow r_1 \approx r_2$$

From this case, it is observed that there is no effect of temperature on the rate of the reaction.

Also, for (rate $\propto e^{-E_a/RT}$)

Let the activation energy, $E_a = 100\text{ kJ/mol}$

for,



$$r_2 \propto e^{-E_a/R \times 310}$$

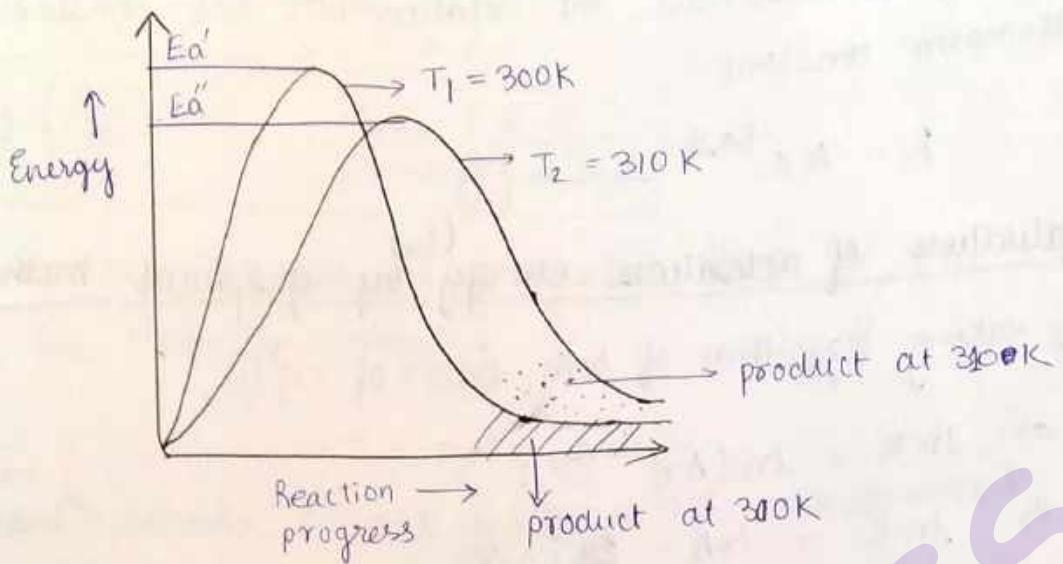
$$r_1 \propto e^{-E_a/R \times 300}$$

$$\frac{r_2}{r_1} = \frac{e^{-100 \times 10^3 / R \times 310}}{e^{-100 \times 10^3 / R \times 300}}$$

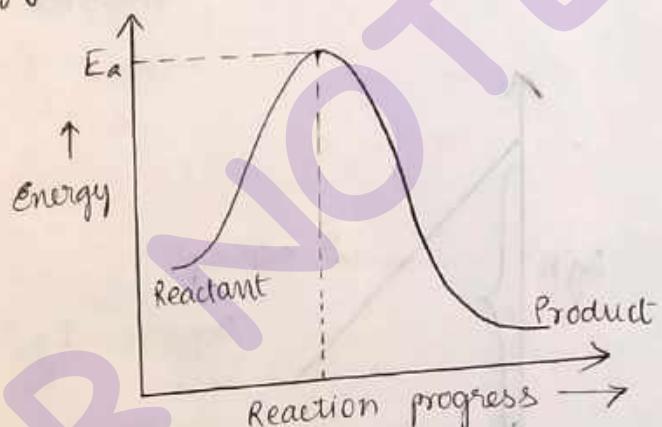
$$\frac{r_2}{r_1} = 3.643$$

$$\Rightarrow r_2 = r_1 \cdot 3.643$$

That means in increase of Temperature,



Concept of Activation Energy



Arrhenius Eqⁿ

from collision theory, we know

$$\text{Rate} = Z \cdot b \cdot P$$

$$\text{Rate} = A \cdot f \Rightarrow \text{Rate} = A e^{-E_a/RT}$$

where, $A = Z \cdot P$ and $f = e^{-E_a/RT}$ (Boltzmann factor)

According to law of mass action,



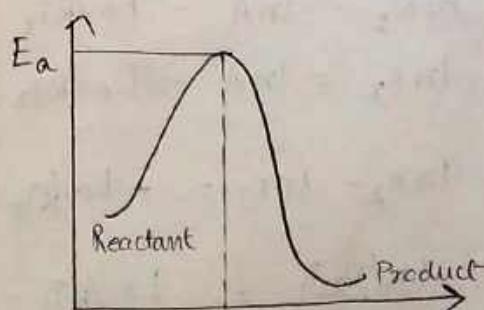
$$\text{Rate} = K[A][B] = r_1$$

$$\text{Rate} = r_2 = K' [A][B]$$

where

$r_2 > r_1$ if Rate \uparrow , Rate constant \uparrow .

$$K' > K.$$



According to Arrhenius, the relation betⁿ rate constant and Boltzmann constant

$$K = A e^{-E_a/RT} \quad \text{--- (1)}$$

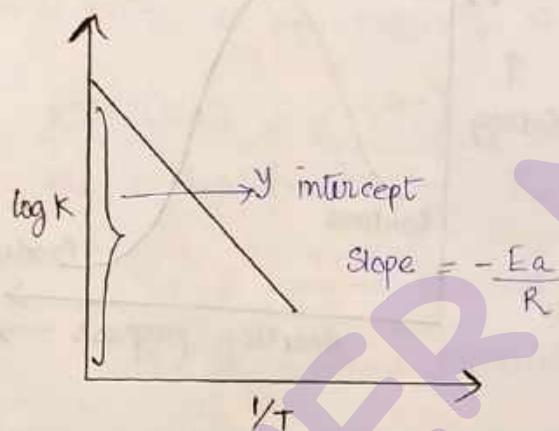
Evaluation of activation energy by graphical method :-

By taking logarithm of both sides of eqⁿ(1),

$$\Rightarrow \ln K = \ln(A e^{-E_a/RT})$$

$$\Rightarrow \ln K = \ln A - E_a/RT$$

$$\Rightarrow \log K = \log A - \frac{E_a}{2.303 RT} \quad (y = mx + c)$$



Evaluation of activation energy (E_a) by analytical method :-

Let, k_1 and k_2 be the rate constants at 2 different temp.

T_1 and T_2 respectively.

From the relation, it can be written as,

$$\ln k_1 = \ln A - E_a/RT_1$$

$$\ln k_2 = \ln A - E_a/RT_2$$

$$\Rightarrow \ln k_2 - \ln k_1 = -E_a/RT_2 - (-E_a/RT_1)$$

$$\Rightarrow \ln\left(\frac{k_2}{k_1}\right) = E_a/RT_1 - E_a/RT_2$$

$$\Rightarrow \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

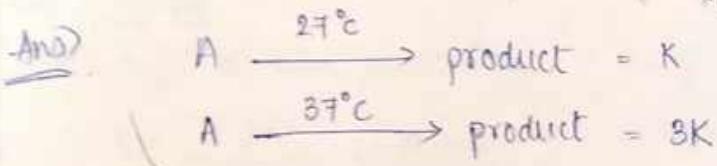
$$\Rightarrow \ln\left(\frac{K_2}{K_1}\right) = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \log\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

knowing the rate constants at 2 different temp, one can easily calculate E_a · (Activation Energy).

Numerical

Q1. A reactⁿ proceeds 3 times faster at 37°C as it does at 27°C . Find the activation energy.



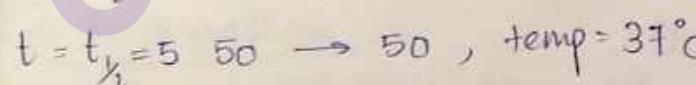
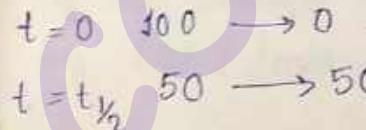
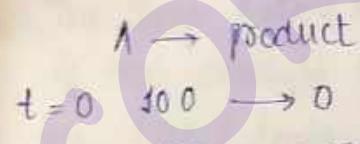
$$T_1 = 27 + 273 = 300\text{K}$$

$$T_2 = 37 + 273 = 310\text{K}$$

$$\Rightarrow \log\left(\frac{3K}{K}\right) = \frac{E_a}{2.303 \times 1.98} \left(\frac{310 - 300}{310 \times 300} \right)$$

$$\Rightarrow [E_a = 20.305 \text{ Kcal}]$$

Q2. A 1st order reactⁿ is 50% complete in 25 min. at 27°C . And ↑ of the same reactⁿ, completes at 5 min at 37°C . Calculate the activation energy.



(Let the rate constant = K_1)

$$t_{\frac{1}{2}} = \frac{0.693}{K_1} \Rightarrow \frac{0.693}{25} = K_1$$

$$\Rightarrow K_1 = 0.0277 \text{ min}^{-1}$$

We know,

Let the rate constant at $37^\circ\text{C} \rightarrow K_2$.

$$t_{\frac{1}{2}} = \frac{0.693}{K_2} \Rightarrow \frac{0.693}{5} = K_2$$

$$\Rightarrow K_2 = 0.1386 \text{ min}^{-1}$$

$$\log \left(\frac{K_2}{K_1} \right) = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \log \left(\frac{0.1386}{0.027} \right) = \frac{E_a}{2.303 \times 1.98} \left(\frac{310 - 300}{310 \times 300} \right)$$

$$\Rightarrow \boxed{E_a = 29.746 \text{ Kcal}}$$

Q8. At 300°C the half life for a 1st order reactⁿ is 350 min. The activation energy for the reactⁿ is 100 KJ mol^{-1} . Calculate the time reqd for completion of 90% of reactⁿ at 400°C

Ans) Given

$$E_a = 100 \text{ KJ mol}^{-1}$$

$$R = 8.314$$

$$K_1 = \frac{0.693}{t_{1/2} (\text{at } 300^\circ\text{C})} = \frac{0.693}{350} \text{ at } (300^\circ\text{C} = 573\text{K})$$

$$K_1 = 1.98 \times 10^{-3} \text{ min}^{-1}$$

$$\log \left(\frac{K_2}{K_1} \right) = \frac{E_a}{2.303 \times R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left(\frac{K_2}{1.98 \times 10^{-3}} \right) = \frac{100 \times 10^3}{8.314 \times 2.303} \left(\frac{673 - 573}{673 \times 573} \right)$$

$$\Rightarrow K_2 = 4.473 \times 10^{-2} \text{ min}^{-1}$$

Calc- Now, $A \longrightarrow \text{product}$

$$t = t=0 \quad 100 \longrightarrow 0$$

$$t = ? \quad (100-90) \longrightarrow 90$$

$$K = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$\Rightarrow 4.473 \times 10^{-2} = \frac{2.303}{t_{90\%}} \left(\frac{100}{100-90} \right)$$

$$\Rightarrow \boxed{t_{90\%} = 51.49 \text{ min}}$$

Q3 If $E_a = 80.9 \text{ kJ/mol}$, calculate the fraction of molecule at 400°C which have enough energy to form the product.

Ans $f = \frac{n'}{n} = e^{-E_a/RT}$

$$= e^{-80.9 \times 10^3 / 8.314 \times 673}$$

$$= 5.27 \times 10^{-7}$$

Q5 For a 1st order reactⁿ, the value of frequency factor and Activation energy are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ/mol respectively. At what temp. the half life will be 10 min.

Ans Given

$$t_{1/2} = 10 \text{ min} = 600 \text{ sec}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{600} =$$

$$K = A e^{-E_a/RT}, \text{ where } A \rightarrow \text{frequency factor}$$

$$= 4 \times 10^{13} \text{ sec}^{-1}$$

$$\Rightarrow \frac{0.693}{600} = 4 \times 10^{13} e^{-98.6 \times 10^3 / 8.314 \times T}$$

$$\Rightarrow \boxed{T = 311.35 \text{ K}}$$

Q6 A reactⁿ is carried out at 500K. The reactⁿ is carried out in the presence of a catalyst at the same rate. The temp. req'd is 400K. Calculate E_a of the reaction, if the catalyst is capable of lowering the energy barrier by 20KJ/mol.

Ans Acc to question

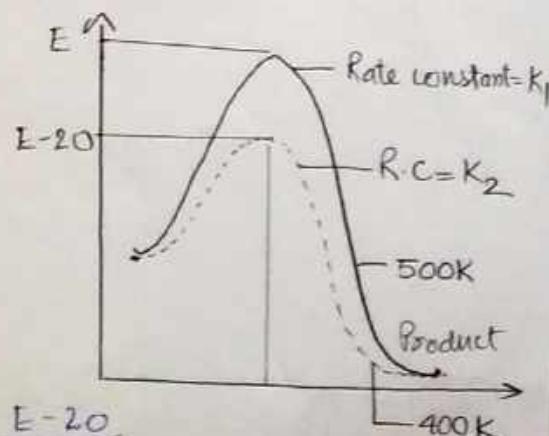
Both the reactⁿ have same rate.

$$\therefore K_1 = K_2$$

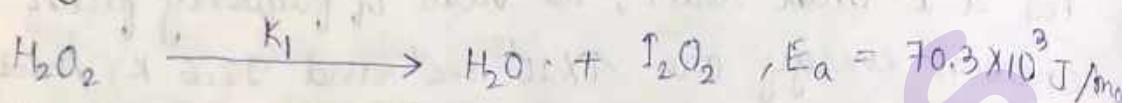
$$\Rightarrow A e^{-E_a/RT_1} = A e^{-(E-20)/RT_2}$$

$$\Rightarrow \frac{E}{RT_1} = \frac{E-20}{RT_2} \Rightarrow \frac{E}{500} = \frac{E-20}{400}$$

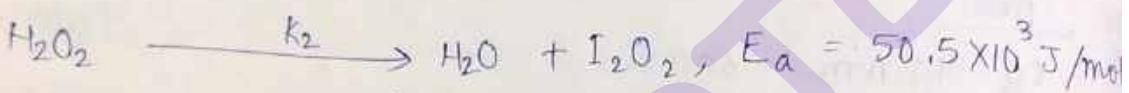
$$\Rightarrow \boxed{E = 100 \text{ kJ/mol}}$$



Q7. At 300K, the E_a for the decomposition of H_2O_2 has been measured to be 70.3 KJ/mol. In presence of iodine ion (I^-) with specified conc. as catalyst, the E_a of the same reactⁿ decreases to 50.5 KJ/mol. How much faster is the decomposition of H_2O_2 when iodide ion is present in the reactⁿ mix. in the as catalyst.



$$K_1 = A e^{-70.3 \times 10^3 / R \times 300}$$



$$K_2 = A e^{-50.5 \times 10^3 / R \times 300}$$

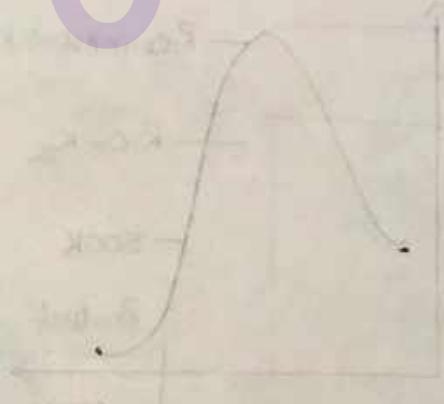
Now,

$$\frac{K_2}{K_1} = \frac{A e^{-50.5 \times 10^3 / R \times 300}}{A e^{-70.3 \times 10^3 / R \times 300}}$$

$$\Rightarrow \frac{K_2}{K_1} = 2807$$

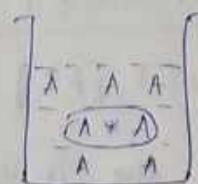
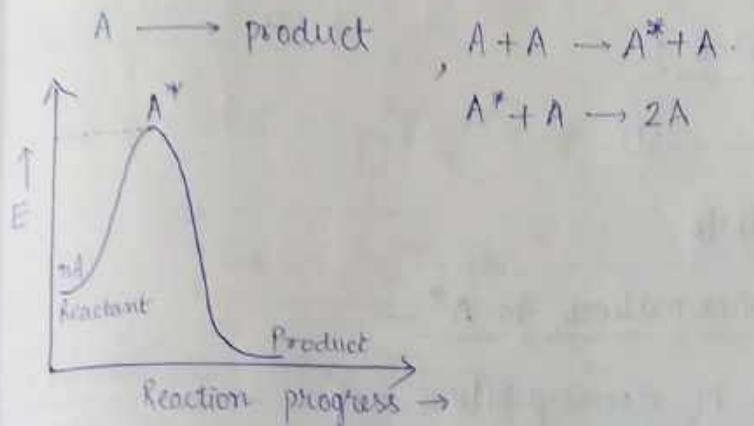
$$K_2 = 2807 K_1$$

In presence of I^- , the reactⁿ proceeds 2807 times faster than the normal reactⁿ.



23/03/2018

Theory of unimolecular reaction (Lindeman's Time Lag Theory)

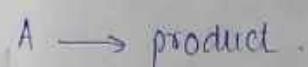


The postulates of Lindeman's Time lag Theory are:-

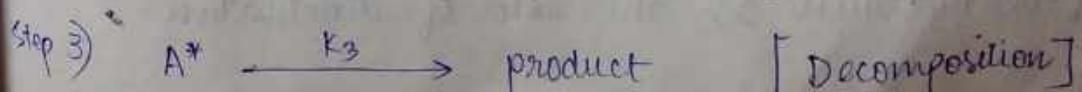
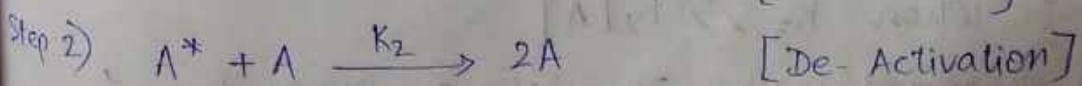
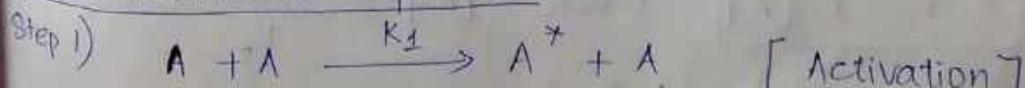
- ① Molecules get activation energy through collisions.
- ② Activated molecules (A^*) decompose only after some time has passed after collision i.e there is a time lag b/w activation and decomposition.
- ③ When the time lag is relatively large, there is every possibility that some of the activated molecules get deactivated through subsequent collisions to ordinary molecules (A). [A^* collides with A].
- ④ The rate of decomposition is not proportional to all activated molecules rather it is proportional to fraction of activated molecules which survive the time lag.
- ⑤ The activated molecules (A^*) disappear through 2 parallel processes such as deactivation and decomposition.

Mathematical treatment

Let us consider a hypothetical reaction :-



The mechanistic steps are :-



Step-3 is the slowest step and rate determining step.

According to chemical kinetics :-

$$\text{Rate} = k_3[A^*] \quad \dots \quad (1)$$

Here A^* is the intermediate

Applying steady state approximation to A^* -

$$\text{Rate of formation} - \text{Rate of decomposition} = 0$$

$$\Rightarrow k_1[A]^2 - k_2[A^*][A] - k_3[A^*] = 0$$

$$\Rightarrow (k_2[A] + k_3)[A^*] = k_1[A]^2$$

$$\Rightarrow [A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad \dots \quad (2)$$

Substituting the value of $[A^*]$ from eqⁿ(3) to eqⁿ(2) :-

$$\boxed{\text{Rate} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3}} \quad \dots \quad (3)$$

Case 1 :- When $k_2[A] \gg k_3$.

Rate of deactivation \gg Rate of decomposition

$$k_2[A] + k_3 \approx k_2[A]$$

So, eqⁿ(3) becomes \rightarrow

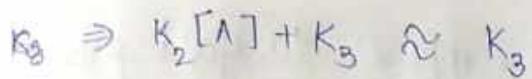
$$\text{Rate} = \frac{k_3 k_1 [A]^2}{k_2 [A]}$$

$$\text{Rate} = \frac{k_3 k_1 [A]}{k_2}$$

$$\boxed{\text{Rate} = K [A]}, \text{ where } K = \frac{k_3 k_1}{k_2} \quad \dots \quad (4)$$

Case 2 :- When $k_3 \gg k_2[A]$

Rate of decomposition \gg The rate of deactivation



so, eqⁿ ③ becomes →

$$\text{Rate} = \frac{K_3 K_1 [A]^2}{K_3}$$

$$\boxed{\text{Rate} = K_1 [A]^2} \quad \text{--- } ⑤$$

Transition State Theory :-
OR

Activated Complex Theory :-

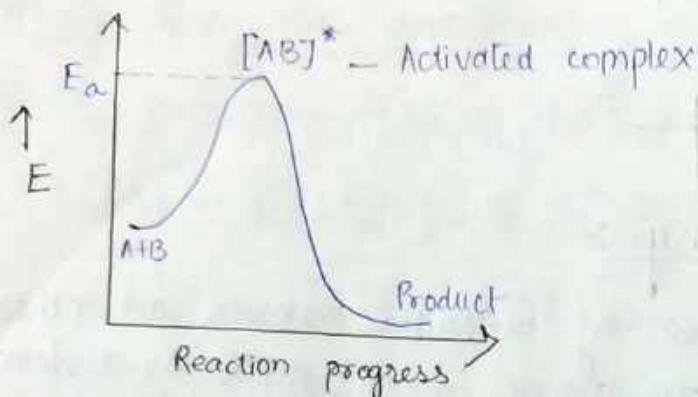
- ① With the approach of reacting molecules towards each other, there occurs a continuous change in intermolecular distance, net energy content and configuration i.e rearrangement of valency bonds.
- ② On reaching the equilibrium, the reactant molecules get transferred into an energy rich intermediate having specific configuration known as Transition state or activated complex.
- ③ The complex (activated) is very much unstable and has a transient existence.
- ④ The activated molecules remains in dynamic equilibrium with the reactants.
- ⑤ The activated complex must possess an unstable vibrational degrees of freedom to facilitate the bond rupture. The frequency of such a vibration is low and the average value is,

$$E = KT, \text{ where } K \rightarrow \text{Boltzmann constant.}$$

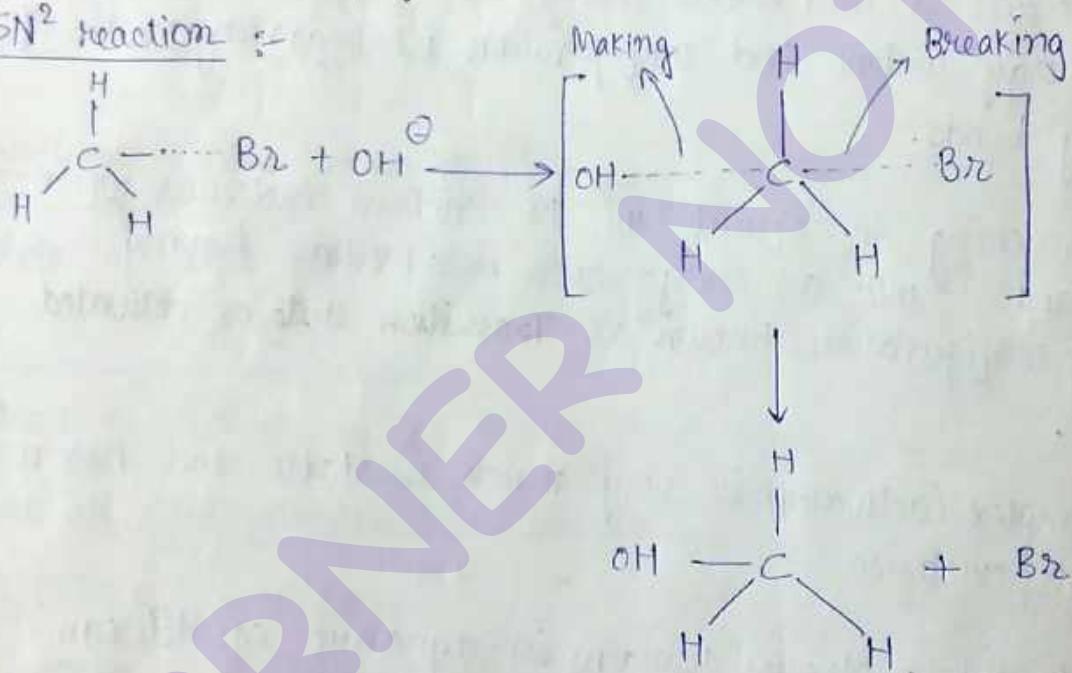
⑥ The activated complex finally decomposes to yield products and thus theory explains the kinetics of heterogeneous or bi-molecular reactions.

Suppose - Let us consider a hypothetical heterogeneous reaction -

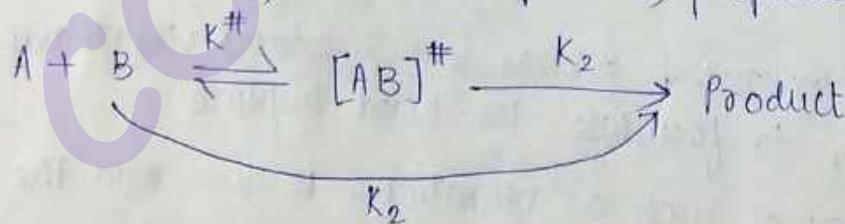
bimolecular



SN^2 reaction :-



for the reactn, $A + B \longrightarrow \text{product}$, proposed mechanism is



$$K^{\#} = \frac{[AB]^{\#}}{[A][B]}$$

$$\Rightarrow [AB]^{\#} = K^{\#} [A][B] \quad \text{--- } ①$$

According to the postulates of transition state theory

$$\Rightarrow \text{Rate} = [AB]^{\ddagger} \times \text{frequency of its decomposition } (1)$$

$$\Rightarrow \text{Rate} = K^{\ddagger} [A][B]. \checkmark$$

$$\Rightarrow \text{Rate} = K^{\ddagger} [A][B] \cdot E/h \quad [\because E = h\nu]$$

$$\Rightarrow \text{Rate} = K^{\ddagger} [A][B] \frac{KT}{h}$$

$$\Rightarrow \text{Rate} = K^{\ddagger} [A][B] \frac{RT}{Nh} - (2) \quad [\because k = \frac{R}{N}]$$

where, R → universal gas constant.

N → Avogadro's Number.

According to chemical kinetics,

$$\text{Rate} = K_2 [A][B] \quad (3)$$

From eqⁿ(2) and eqⁿ(3)

$$\Rightarrow K_2 [A][B] = K^{\ddagger} [A][B] \cdot \frac{RT}{Nh}$$

$$\Rightarrow K_2 = \boxed{K^{\ddagger} \frac{RT}{Nh}} \quad (4)$$

from Vant Hoff Reaction Isotherm,

$$\Delta G = -RT \ln K$$

$$\Rightarrow \Delta G^{\ddagger} = -RT \ln K^{\ddagger}$$

$$\Rightarrow -\ln K^{\ddagger} = \frac{\Delta G^{\ddagger}}{RT}$$

$$\Rightarrow \ln K^{\ddagger} = \frac{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})}{RT} \quad [\because \Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}]$$

$$\Rightarrow \boxed{K^{\ddagger} = e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S^{\ddagger}/R}} \quad (5)$$

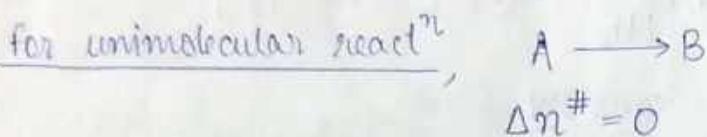
Substituting the value of K[#] in eqⁿ(4),

$$\rightarrow K_2 = e^{-\Delta H^\ddagger / RT} \cdot e^{\Delta S^\ddagger / R} \cdot \frac{RT}{Nh} \quad \text{--- (6)}$$

Case 1 - For unimolecular reaction,

As activation energy (E_a) is related to enthalpy of transition (ΔH^\ddagger) by the following relation -

$$E_a = \Delta H^\ddagger + RT - \Delta n^\ddagger RT$$



$$\therefore E_a = \Delta H^\ddagger + RT$$

$$\Rightarrow \Delta H^\ddagger = E_a - RT$$

Substituting value of ΔH^\ddagger in eq^n (6),

$$K_2 = e^{-\frac{(E_a - RT)}{RT}} \cdot e^{\frac{\Delta S^\ddagger / R}{R}} \cdot \frac{RT}{Nh} = e^{-\frac{(E_a - RT)}{RT}} \cdot e^{\frac{\Delta S^\ddagger / R}{R}} \cdot \frac{RT}{Nh}$$

$$\Rightarrow K_2 = e^{-\frac{E_a}{RT}} \cdot e^{\frac{RT}{RT}} \cdot e^{\frac{\Delta S^\ddagger / R}{R}} \cdot \frac{RT}{Nh}$$

$$\Rightarrow K_2 = e^{-\frac{E_a}{RT}} \cdot e^{\frac{\Delta S^\ddagger / R}{R}} \cdot \frac{RT}{Nh} \quad \text{--- (7)}$$

Case 2 - For bi-molecular reaction



$$\Delta n^\ddagger = 1-2 = -1$$

$$E_a = \Delta H^\ddagger + RT - (-1)RT$$

$$\Rightarrow E_a = \Delta H^\ddagger + 2RT$$

$$\Rightarrow \Delta H^\ddagger = E_a - 2RT$$

So eq^n (6) becomes \rightarrow

$$\Rightarrow K_2 = e^{-\frac{(E_a - 2RT)}{RT}} \cdot e^{\frac{\Delta S^\ddagger}{R}} \cdot \frac{RT}{Nh}$$

$$\Rightarrow K_2 = e^{-\frac{E_a}{RT}} \cdot e^{\frac{2RT}{RT}} \cdot e^{\frac{\Delta S^\ddagger}{R}} \cdot \frac{RT}{Nh}$$

$$\Rightarrow K_2 = e^2 \cdot e^{-\frac{E_a}{RT}} \cdot e^{\frac{\Delta S^\ddagger}{R}} \cdot \frac{RT}{Nh}$$

⑨

Catalysis

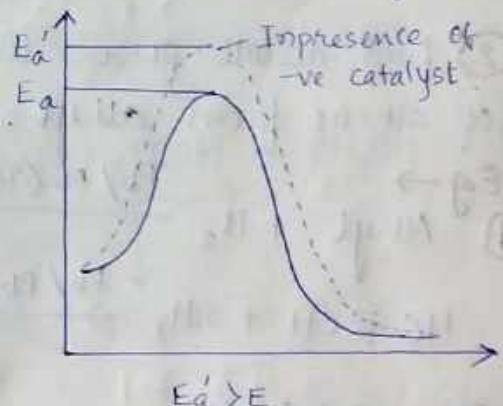
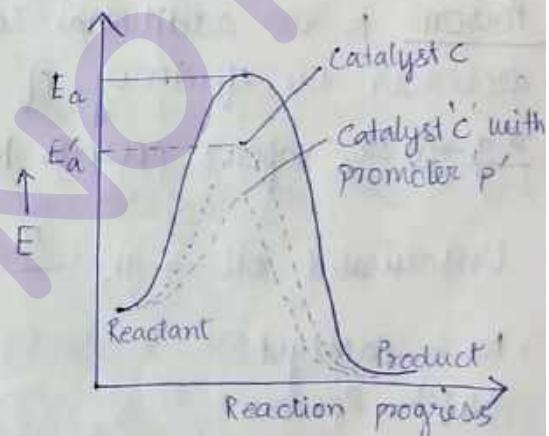
Terminologies

- ① +ve catalyst / catalyst.
- ② -ve catalyst.
- ③ Promoter.
- ④ Poison.
- ⑤ Self catalyst.



$Ea'' < Ea' < Ea$

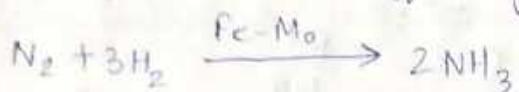
Catalyst with promoter Catalyst with poison



Promoter is an additional substance along with the catalyst to increase the efficiency and life span of a catalyst. However, it can not catalyze the process by itself.

used

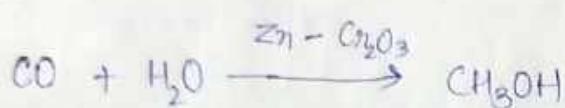
E.g. → Mo in Haver's process for the manufacturing of NH_3 which promotes the efficiency of Fe.



Fe - Catalyst

Mo - Promoter

② Cr_2O_3 used in the synthesis of ethyl alcohol with Zn catalyst.

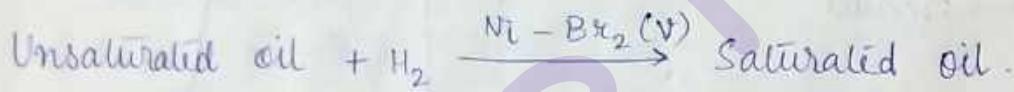


Zn - Catalyst

Cr_2O_3 - Promoter

Poison is an additional substance with the catalyst that decreases the efficiency of the catalyst.

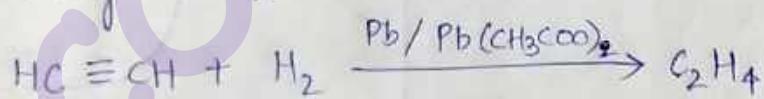
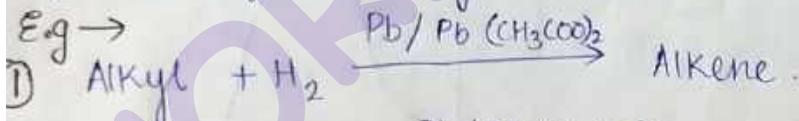
E.g. → ① Br₂ vapour poisons Ni catalyst in hydrogenation of oil.



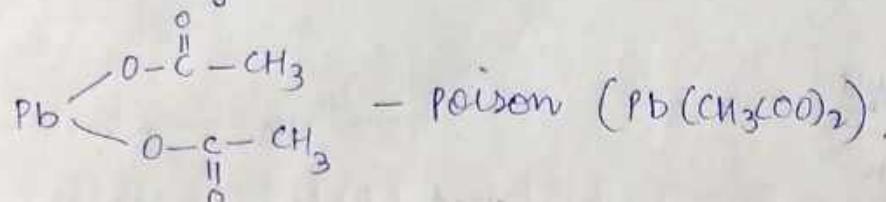
Ni - Catalyst

Br₂(v) - Poison

② Lead acetate poisons lead ~~acetate~~ during the preparation of alkene from alkyl.

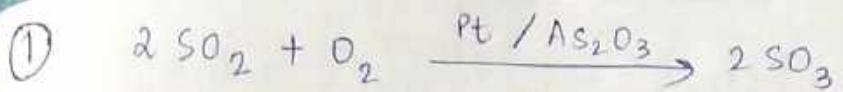


Pb - Catalyst



② ~~As~~ Arsenic oxide (As_2O_3) poisons Platinum during the manufacture of sulphuric acid in contact process.

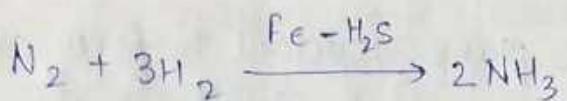
E.g. →



Pt : Catalyst

As_2O_3 : Poison

\textcircled{2} Iron catalyst poisoned by H_2S during the manufacturing of NH_3 in Haber's process.

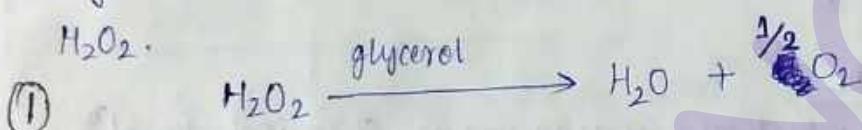


Fe : Catalyst

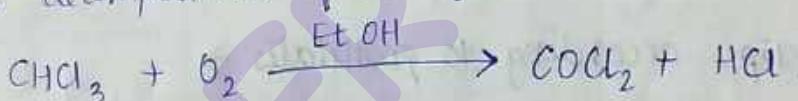
H_2S : Poison.

Negative catalyst / Retarder -

Glycerol acts as a -ve catalyst during the decomposition of H_2O_2 .

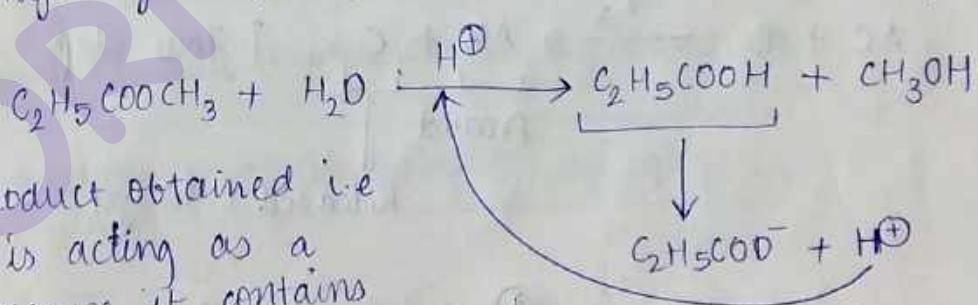


\textcircled{2} Ethyl alcohol can be used as a -ve catalyst for the controlled decomposition of chloroform.



Self catalysis :-

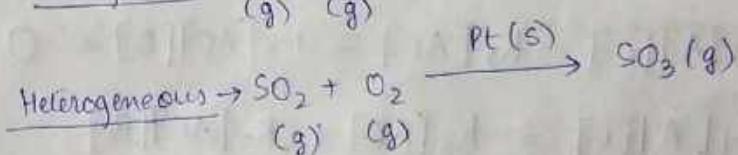
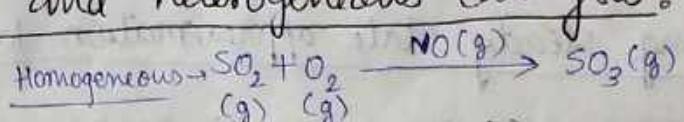
The acid hydrolysis of ethyl acetate is an example of self catalysis.



Here the product obtained i.e $\text{C}_2\text{H}_5\text{COOH}$ is acting as a catalyst because it contains H^+ ions.

Homogeneous catalysis and heterogeneous catalysis :-

Theories of catalysis



R.T.O

Theories

① Intermediate compound formation theory (homogeneous)
This theory successfully explains the homogeneous catalysis process.

According to this theory, the complete process occurs through the following steps :-

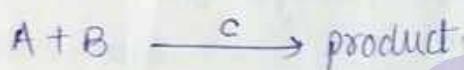
① The catalyst reacts with the prime reactant to form an intermediate compound.

② The intermediate compound subsequently reacts with other reactants to yield the products.

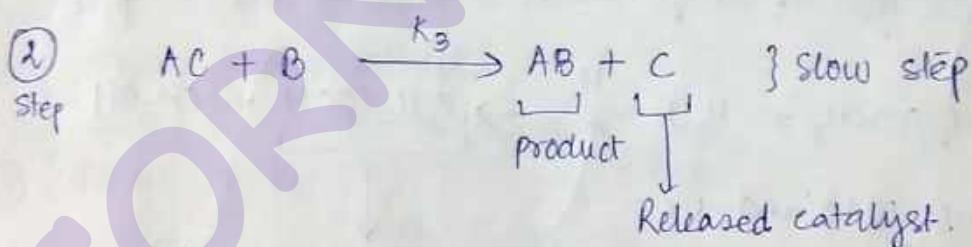
This step is slowest one and regarded as the rate determining step.

Mathematical Treatment

Let us consider a hypothetical homogeneous chemical react-



→ Mechanistic steps according to postulates →



$$\text{Rate} = K_3 [AC][B] \quad ①$$

'AC' → Intermediate

Applying steady state approximation to AC -

$$K_1[A][C] - K_2[AC] - K_3[AC][B] = 0$$

$$\begin{aligned} K_1[A][C] &= K_2[AC] + K_3[AC][B] \\ &= [AC](K_2 + K_3[B]) \end{aligned}$$

$$\Rightarrow [AC] = \frac{k_1[A][C]}{k_2 + k_3[B]} \quad \text{--- (2)}$$

Substituting the value of $[AC]$ from eqⁿ(2) to eqⁿ(1),

$$\text{Rate} = \frac{k_2 k_1[A][C][B]}{k_2 + k_3[B]} \quad \text{--- (3)}$$

Case 1 :- In extreme condⁿ, when $k_2 \ll k_3[B]$

$$k_2 + k_3[B] \approx k_3[B]$$

So eqⁿ(3) becomes,

$$\text{Rate} = \frac{k_3 k_1[A][C][B]}{k_3[B]}$$

$$\boxed{\text{Rate} = k_1[A][C]}$$

Case 2 :- In another extreme condⁿ, if $k_3[B] \ll k_2$.

$$k_2 + k_3[B] \approx k_2$$

So eqⁿ(3) becomes,

$$\text{Rate} = \frac{k_3 k_1[A][C][B]}{k_2}$$

$$\boxed{\text{Rate} = K[A][B][C]}, \text{ where } K = \frac{k_3 k_1}{k_2}$$

So, from both the rate expression it is found that.

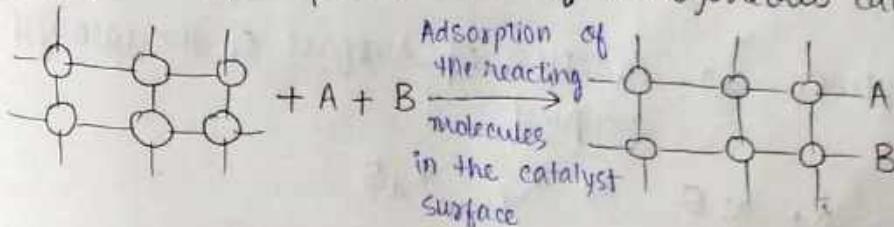
Rate of reaction \propto Concentration of catalyst.

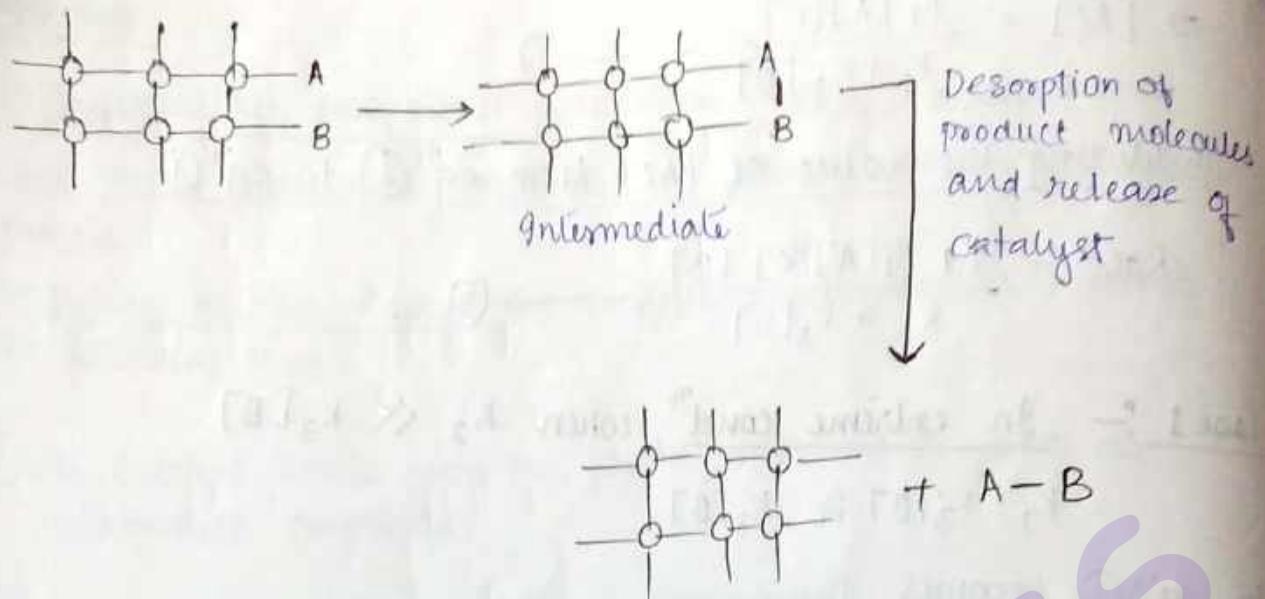
② Adsorption Theory :- (heterogeneous)

This theory successfully explains the heterogeneous catalysis process.



Diagram (Schematic representation of heterogeneous catalyst process)





The rate of the reaction $\rightarrow \frac{dx}{dt} \propto \theta$

$[\theta \rightarrow$ fraction of the surface of the catalyst occupied]

$$\therefore \frac{dx}{dt} = z\theta, [z \rightarrow \text{proportionality constant}]$$

where

$$\boxed{\frac{dx}{dt} = z \frac{K_1 P}{1 + K_1 P}}$$

$$\theta = \frac{K_1 P}{1 + K_1 P} \quad [\text{Langmuir Adsorption Isotherm}]$$

K_1 = coefficient of adsorption

Langmuir Adsorption Isotherm can be shown as follows:

Reactant + surface of the \rightleftharpoons Adsorbed surface of the catalyst

The rate of adsorption (R_a) \propto fraction of the surface of the catalyst unoccupied i.e. $(1-\theta)$

$$R_a \propto (1-\theta)$$

$$R_a = K_a (1-\theta) \quad [K_a \rightarrow \text{Proportionality Constant}]$$

Rate of desorption \propto fraction of surface of the catalyst occupied

$$R_d \propto \theta \Rightarrow R_d = K_d \theta$$

At equilibrium

$$R_a = R_d$$

$$\therefore K_a(1-\theta)P = K_d \theta$$

$$\Rightarrow K_a P - K_a \theta P = K_d \theta$$

Rate of adsorption \propto Pressure

$$R_a \propto P$$

$$R_a = K_a P$$

$$\Rightarrow K_a P = K_a \theta P + K_d \theta$$

$$\Rightarrow K_a P = \theta (K_a P + K_d)$$

$$\Rightarrow \theta = \frac{K_a P}{K_a P + K_d}$$

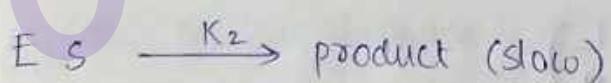
$$\Rightarrow \theta = \frac{K_a / K_d \cdot P}{K_a / K_d P + K_d / K_d}$$

$$\Rightarrow \boxed{\theta = \frac{K_1 P}{K_1 P + 1}}, \text{ where, } \boxed{K_1 = K_a / K_d}$$

Kinetics of Enzyme Action (Michaelis-Menton Mechanism)

Enzymes are biocatalyst and they catalyze bio-chemical reactions occurs in a biological system.

Let us consider a hypothetical enzyme catalysed reaction



E \rightarrow enzyme

S \rightarrow substrate/reactant

From the reactⁿ $ES \rightarrow$ intermediate

$$\text{Rate} = K_2 [ES] \quad \text{--- (1)}$$

Applying steady state approximation to ES :-

$$\Rightarrow k_1 [E][S] - k_{-1} [ES] - k_2 [ES] = 0.$$

$$\Rightarrow [ES] (k_{-1} + k_2) = k_1 [E][S]$$

$$\Rightarrow [ES] = \frac{k_1 [E][S]}{(k_{-1} + k_2)}$$

$$\Rightarrow [ES] = \frac{[E][S]}{\left(\frac{k_{-1} + k_2}{k_1} \right)}$$

$$\Rightarrow [ES] = \frac{[E][S]}{K_M}$$

where

$K_M = \frac{k_{-1} + k_2}{k_1}$ is known as Macholius's constant.

Let $E_0 \rightarrow$ total concentration of enzyme

$E \rightarrow$ conc. of free enzyme / unreacted enzyme.

Amount of unreacted enzyme

$$[E] = [E_0] - [ES]$$

$$[ES] = [E_0] - [E]$$

$$\Rightarrow \frac{[E][S]}{K_M} = [E_0] - [E]$$

$$\Rightarrow [E_0] = [E] + \frac{[E][S]}{K_M}$$

$$\Rightarrow [E_0] = [E] \left(1 + \frac{[S]}{K_M} \right)$$

$$\Rightarrow [E_0] = [E] \left(\frac{K_M + [S]}{K_M} \right)$$

$$\Rightarrow [E] = \frac{[E_0] K_M}{K_M + [S]} \quad \text{--- (3)}$$

From eqⁿ ①,

$$\text{Rate} = k_2 [ES]$$

$$\text{Rate} = \frac{K_2 [E][S]}{K_M}$$

$$\text{Rate} = \frac{K_2 [E_0] K_M \cdot [S]}{K_M + [S]} \cdot \frac{[S]}{K_M}$$

$$\boxed{\text{Rate} = \frac{K_2 [S][E_0]}{K_M + [S]}} \quad \text{--- (4)}$$

Case 1 :- Under extreme cond'n, the order wrt substrate can be evaluated, if

$$K_M \gg [S]$$

$$K_M + [S] \approx K_M$$

: Eqn (4) becomes, $\text{Rate} = \frac{K_2 [S][E_0]}{K_M}$

$$\boxed{\text{Rate} = K [S][E_0]}$$

So, it is first order wrt [S] and also 1st order wrt $[E_0]$.

Case 2 :- If $K_M \ll [S]$

$$K_M + [S] \approx [S]$$

So, eqn (4) becomes, $\text{Rate} = \frac{K_2 [S][E_0]}{[S]}$

$$\text{Rate} = K_2 [E_0]$$

So, it is order wrt [S] and 1st order wrt $[E_0]$.

Evaluation of Michaeli's constant (K_M) :-

Let us consider that all the enzyme has been converted to product

i.e. conc. of free enzyme = 0.

$$\Rightarrow [E] = [E_0] - [ES]$$

$$\Rightarrow 0 = [E_0] - [ES]$$

$$\Rightarrow \boxed{[E_0] = [ES]} \quad \text{--- (5)}$$

From eqn (1), $\text{Rate} = K_2 [ES]$

$$\boxed{R_{\max} = K_2 [E_0]} \quad \text{--- (6)} \quad [\text{from eqn (5)}]$$

Eqⁿ ④ can be written as -

$$R = \frac{r_{\max} [S]}{K_M + [S]} \quad \rightarrow \textcircled{7}$$

Reciprocating eqⁿ ⑦,

$$\Rightarrow \frac{1}{R} = \frac{K_M + [S]}{r_{\max} [S]}$$

$$\Rightarrow \frac{1}{R} = \frac{K_M}{r_{\max} [S]} + \frac{1}{r_{\max}}$$

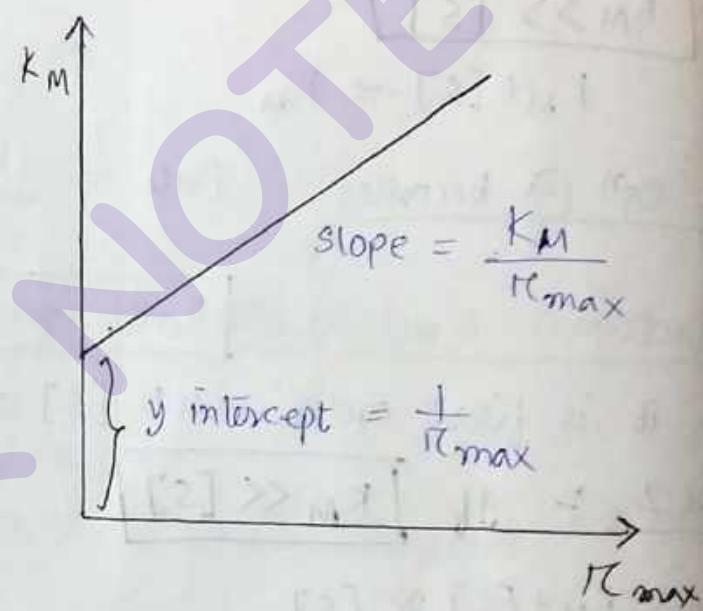
$\Rightarrow \frac{1}{R}$ vs $\frac{1}{[S]}$ (In graph)

$$\text{Slope} = \frac{K_M}{r_{\max}}$$

$$\Rightarrow \text{Slope} = K_M \left(\frac{1}{r_{\max}} \right)$$

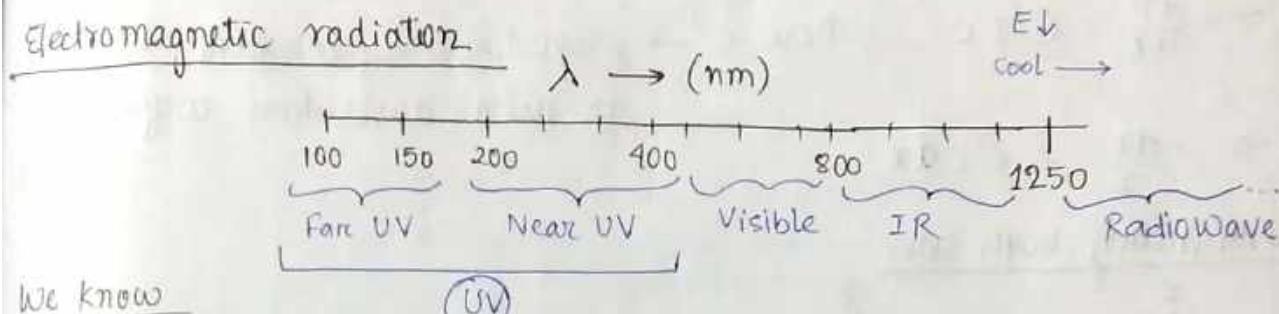
$$\Rightarrow \text{Slope} = K_M \cdot (\text{y intercept})$$

$$\Rightarrow K_M = \frac{\text{Slope}}{(\text{y-intercept})}$$



Spectroscopy

(Interaction of electro-magnetic radiation with matter)



We know

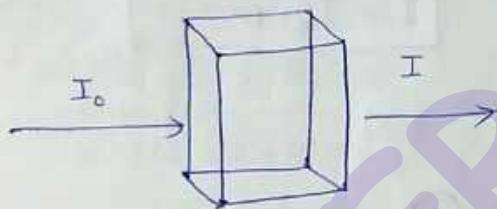
$$E = h\nu, \quad h \rightarrow \text{Plank's constant.}$$

⇒ $E \propto \nu$ Energy directly proportional to frequency.

Again $E = \frac{hc}{\lambda}, [h \text{ and } c \text{ are constant}]$

⇒ $E \propto \frac{1}{\lambda}$ Energy is inversely proportional to wavelength.

Beer Lambert's Law :-



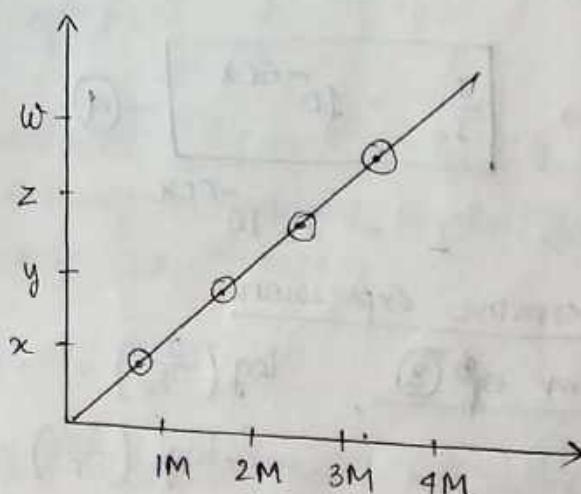
$$w > z > y > x$$

$$\begin{aligned} I_0 - I &= x = 1M \\ I_0 - I &= y = 2M \\ I_0 - I &= z = 3M \\ I_0 - I &= w = 4M \end{aligned}$$

Intensity loss is known as light absorbed.

Statement

When a beam of monochromatic light is passed through a pure homogeneous solⁿ of a light absorbing material, the decrease in the intensity of light with the thickness of solⁿ is directly proportional to the intensity of incident light (I) and the conc. of the solⁿ (c).



$$-\frac{dI}{dx} \propto I$$

$$\propto C$$

$\Rightarrow -\frac{dI}{dx} = \epsilon' I C$, where $\epsilon' \rightarrow$ proportionality constant known as molar absorption coefficient.

$$\Rightarrow -\frac{dI}{I} = \epsilon' C dx$$

Integrating both sides

$$-\int_{I_0}^I \frac{dI}{I} = \epsilon' C \int_0^x dx$$

$$\Rightarrow -[\ln I]_{I_0}^I = \epsilon' C (x-0)$$

$$\Rightarrow -\ln \left(\frac{I}{I_0} \right) = \epsilon' C x$$

$$\Rightarrow \boxed{\ln \left(\frac{I}{I_0} \right) = -\epsilon' C x} \quad \text{--- (1)}$$

$$\Rightarrow \boxed{\frac{I}{I_0} = e^{-\epsilon' C x}} \quad \text{--- (2)}$$

$$I = I_0 \cdot e^{-\epsilon' C x}$$

From eqⁿ(1),

$$\Rightarrow \log \left(\frac{I}{I_0} \right) = \frac{-\epsilon' C x}{2.303} \quad \text{--- (3)}$$

$$\Rightarrow \log \left(\frac{I}{I_0} \right) = -\epsilon C x, \text{ where, } \epsilon = \epsilon'/2.303$$

$\epsilon \rightarrow$ molar extinction coefficient or absorptivity.

$$\Rightarrow \boxed{\frac{I}{I_0} = 10^{-\epsilon C x}} \quad \text{--- (4)}$$

$$\Rightarrow I = I_0 10^{-\epsilon C x}$$

Alternative expression

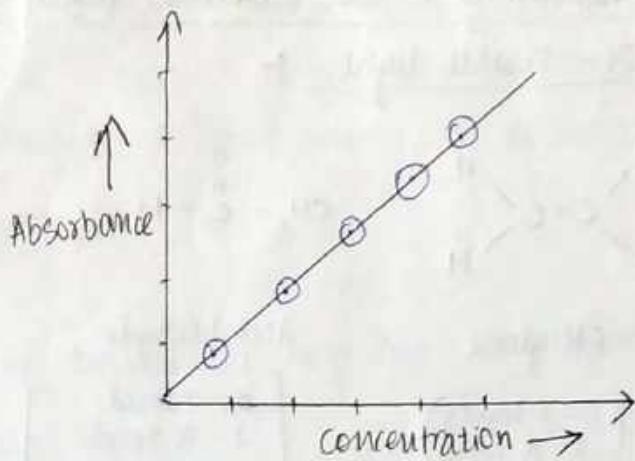
From eqⁿ(3), $\log \left(\frac{I}{I_0} \right) = -\epsilon C x$

$$\Rightarrow -\log \left(\frac{I_0}{I} \right) = -\epsilon C x$$

$$\Rightarrow \log \left(\frac{I_0}{I} \right) = \epsilon C x$$

$$\Rightarrow \boxed{A = \epsilon C x}, \text{ where } A = \log \left(\frac{I_0}{I} \right)$$

$A \rightarrow$ Absorbance.



$\frac{I}{I_0} \rightarrow \text{Transmittance } (T)$

Relation betⁿ absorbance and transmittance :-

$$\log\left(\frac{I_0}{I}\right) = \epsilon cx$$

$$\Rightarrow \log\left(\frac{1}{T}\right) = A \Rightarrow [-\log T = A]$$

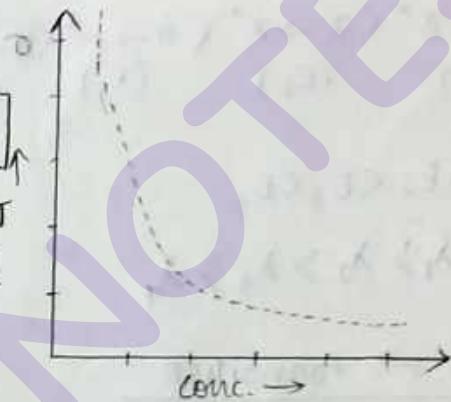
Physical significance of epsilon (ϵ)

We know, $A = \epsilon cx$

$$\Rightarrow \epsilon = A/cx$$

When $c = 1M$, $x = 1cm$

$$\Rightarrow [\epsilon = A]$$



The molar absorptivity / molar extinction coefficient (ϵ) = The absorbance (A) when the light absorbing material having conc. 1M and having thickness of 1 cm.

Q Molar absorptivity (ϵ) of a substance is $2 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$. Calculate the transmittance through a cuballe of thickness 5 cm containing solⁿ of conc. $2 \times 10^{-6} \text{ mol/l}$.

A/ Beer Lambert's Law,

$$A = \epsilon cx$$

$$A = 2 \times 10^4 \times 2 \times 10^{-6} \times 5 \times \text{cm}^{-1} \text{ mol}^{-1} \times \frac{\text{mol}}{l} \times \text{cm}$$

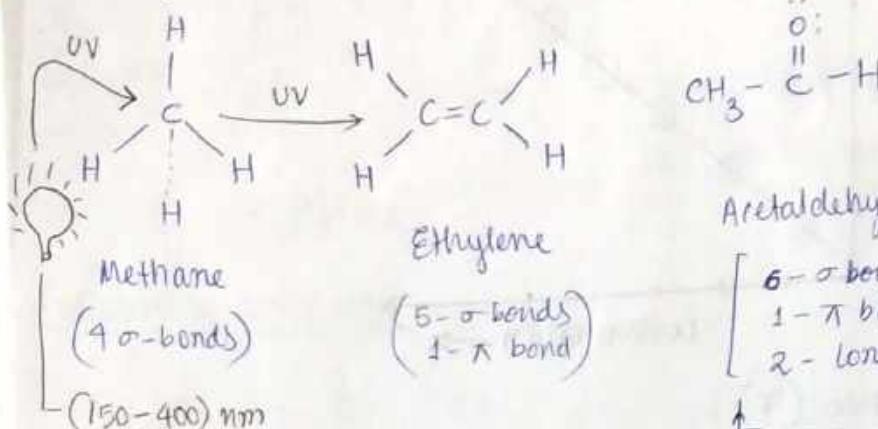
$$A = -\log T$$

$$\Rightarrow \log\left(\frac{1}{T}\right) = A = 0.2$$

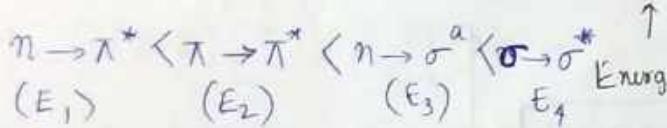
$$\Rightarrow \frac{1}{T} = 10^{0.2}$$

$$\Rightarrow T = 10^{-0.2} \Rightarrow [T = 0.63]$$

Different types of transitions e⁻ in molecules when they are subjected to UV-visible light :-



Energy order



$$E_1 < E_2 < E_3 < E_4$$

$$\lambda_1 > \lambda_2 > \lambda_3 > \lambda_4$$

$\sigma - \sigma^*$ transition

Compounds with only σ -bonds are req'd to have such transitions.

It appears in saturated hydrocarbons and λ req'd for this transition is less than 200 nm

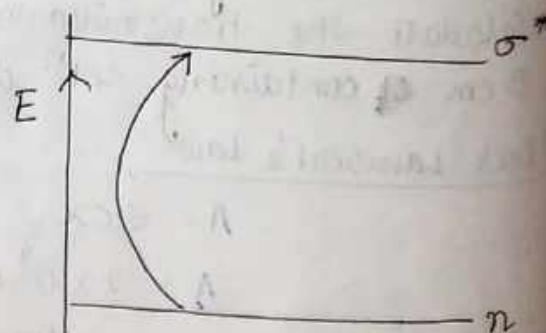
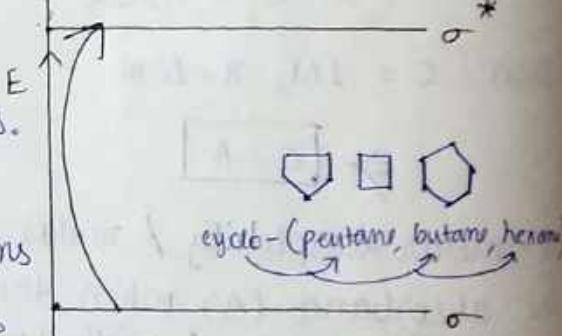
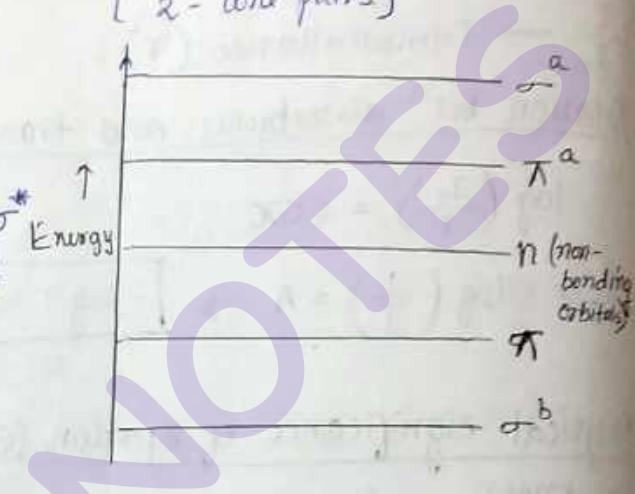
e.g. → Cyclo-alkane shows $\sigma \rightarrow \sigma^*$ transitions at $\lambda = 135 \text{ nm}$.

$n - \sigma^*$ transition

$\text{CH}_3 - \ddot{\text{Br}}$: - methyl bromide

$\text{CH}_3 - \ddot{\text{I}}$: - methyl iodide

They are having σ^b and σ^a orbitals as well as non-bonding (n) orbitals containing the lone pair.



This type of excitation takes place from a non-bonding orbital to σ^* orbital and this is found in saturated organic compound containing a heteroatom (e.g. N, O, I, Br).

This type of transition requires wavelength in the range of 170-260 nm.

Different types of electronic transitions (Done) $\pi - \pi^*$ transition

This is found in compounds containing double-bond, triple bond or aromatic rings.

Here the e^- is excited from $\pi - \pi^*$, this is usually symmetry wise as well as energy wise allowed transition.

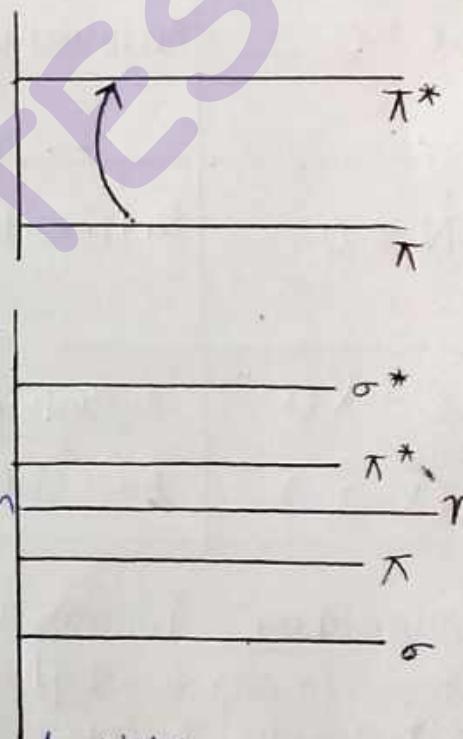
→ It requires the light having wavelength 190 nm or more than this.

 $n - \pi^*$ transition

This type of transitions found in unsaturated compounds containing a hetero-atom with unshared pair of e^- .

E.g. → carbonyl, nitril ($R-C\equiv\ddot{N}$)

This type of transitions occurs in the wavelength of 185-300 nm.

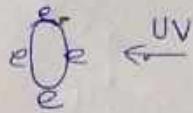
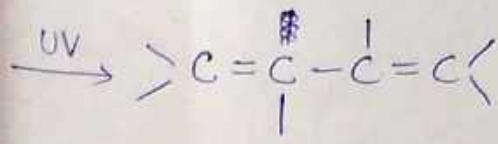
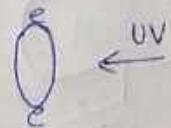
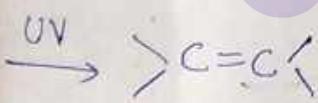
Selection Rule

$\sigma - \sigma^*$ symmetrically allowed ; energy wise forbidden

$n - \sigma^*$ symmetrically forbidden , energy wise allowed.

$\pi - \pi^*$ symmetrically allowed , energy wise allowed.

$n - \pi^*$ symmetrically forbidden , energy wise allowed.



Concept of chromophore and Auxochrome

Any isolated covalently bonded group that shows a characteristic absorption in UV visible region is known as chromophore

E.g. →

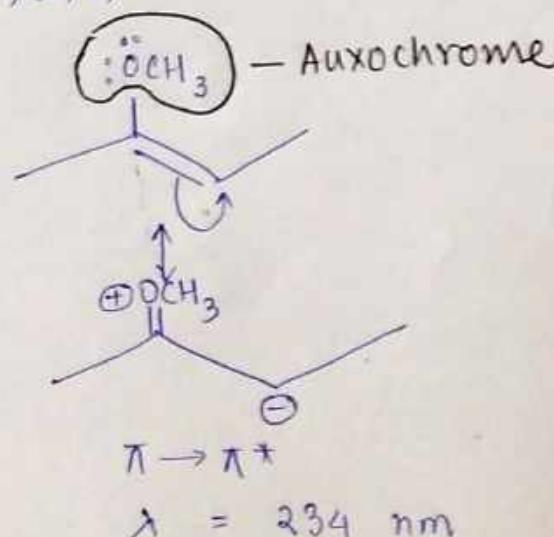
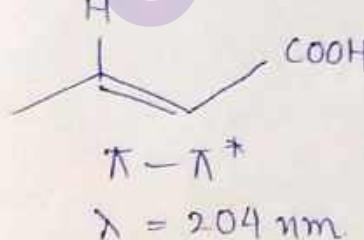
Chromophore	Example	Excitation	λ_{max} (in nm)	ϵ
$C=C$	Ethylene	$\pi \rightarrow \pi^*$	171	15000
$C \equiv C$	Acetylene	$\pi \rightarrow \pi^*$	180	10,000
$C=O$	Acetaldehyde	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10000
$N=O$	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5000
$C-X$ ($X=Br, I$)	Methylbromide Methyliodide	$n \rightarrow \sigma^*$ $m \rightarrow \sigma^*$	205 255	200 360

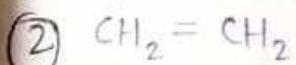
Auxochrome is an auxiliary grp. which interacts with the chromophore and causes a shift in the UV / visible absorption max. to a longer wavelength, however by itself, it doesn't absorb in UV-visible zone.

- The effect of chromophore is due to its ability to extend the conjugation of a chromophore by sharing non-bonding e^- .

E.g. → $-\text{NH}_2$, $-\text{NHR}$, $-X$ ($\text{Cl}, \text{Br}, \text{I}$), $-\text{OCH}_3$, $-\text{OH}$

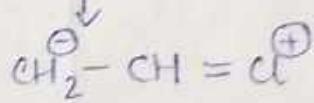
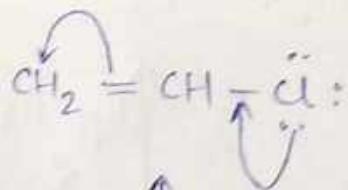
①





$\pi \rightarrow \pi^*$

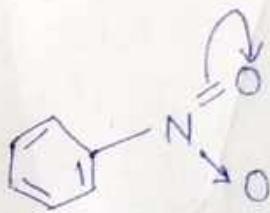
$\lambda_{\max} = 175 \text{ nm}$



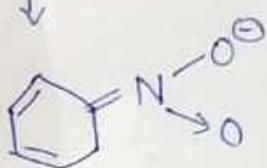
$(\pi \rightarrow \pi^*)$

$\lambda_{\max} = 185 \text{ nm}$)

③



(Benzene $\rightarrow \pi \rightarrow \pi^*$
 $\lambda = 200 \text{ nm}$)



(Benzene $\rightarrow \pi \rightarrow \pi^*$
 $\lambda = 175 \text{ nm}$)

Bathochromic shift / Red shift :-

It is the shift of λ_{\max} to the longer wavelength. Shift of an absorption max. to longer wavelength is called Bathochromic shift and it occurs due to substituent and solvent.

Hypsochromic shift / Blue shift :-

It is the shifting of λ_{\max} to shorter wavelength shift of absorption max. to shorter wavelength is called hypsochromic shift / blue shift.

It also occurs due to substituent / solvent effect.

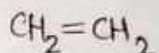
Hyperchromic shift :-

It is the effect leading to increased absorption max. i.e. higher value of epsilon (ϵ).

Hypochromic shift :-

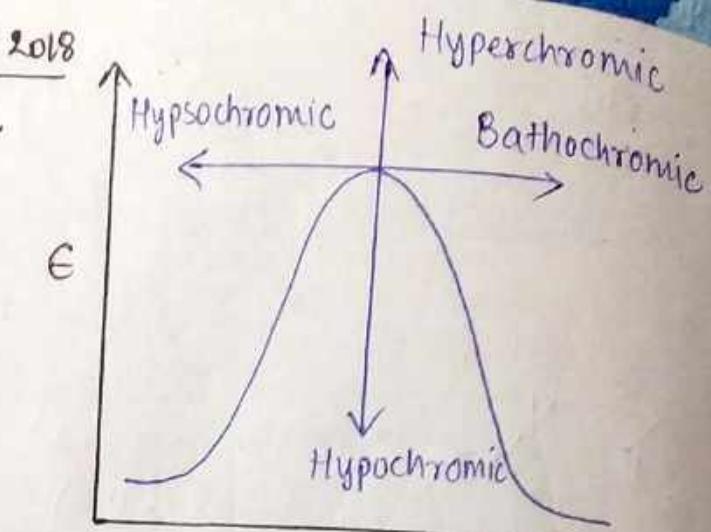
It is the effect leading to decreased absorption intensity, i.e. lower value of epsilon (ϵ).

λ associated with max. intensity $\rightarrow \lambda_{\max}$



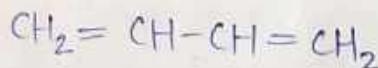
Graph →

21/4/2018



Woodward Fieser's Rule for calculation of λ_{max} for $\pi \rightarrow \pi^*$ transition.

According to Woodward, butadiene is the base.



1 → C-atoms

2 → conjugative double-bonds.

If in betⁿ 2 double bonds, if there is only one single bond, then the double bonds will be calculated as conjugative double-bond.



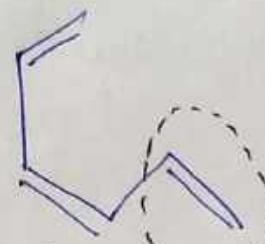
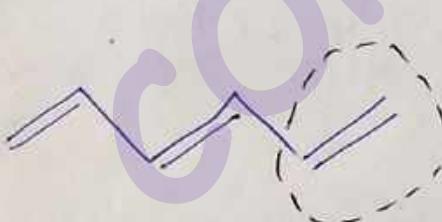
S-cis butadiene



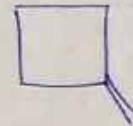
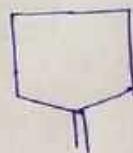
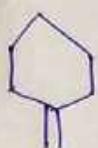
S-trans butadiene

[S → single bond]

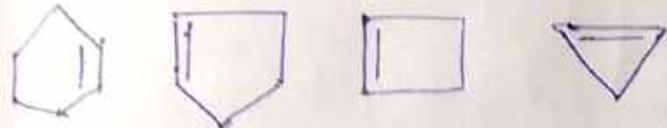
Extended conjugation



Double bond projecting outside of any ring → Exocyclic double bond

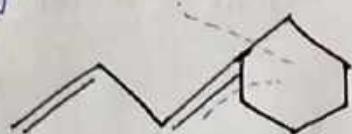
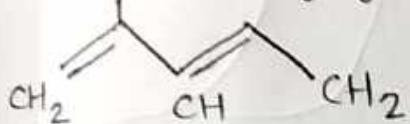


double bond contained inside the ring → Andocyclic Double bond



→ Double bond is exocyclic to $\beta\gamma$ and andocyclic for 4-ring

$R \rightarrow$ Alkyl group

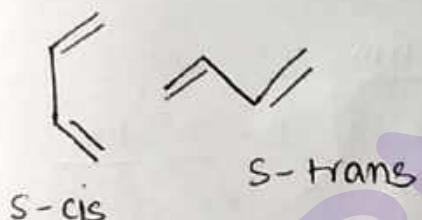


Here the system base is butadiene .

Ring residue → The base / system attached to the ring directly.

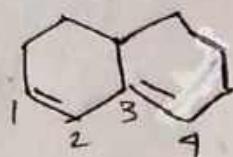
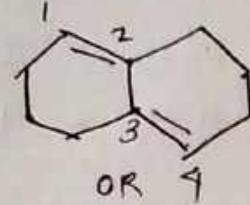
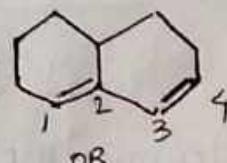
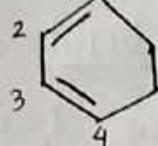
Butadiene

Acyclic butadiene



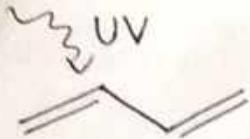
Cyclic butadiene

an Homonuclear



When the butadiene is a part of a single ring, it is known as homo-annular butadiene.

When the butadiene is part of 2 rings it is known as hetero-annular butadiene.

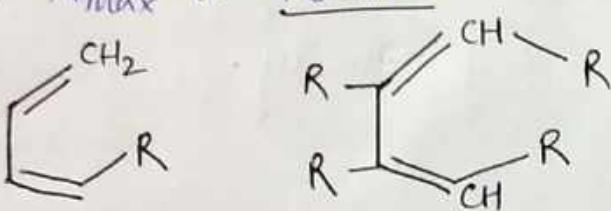
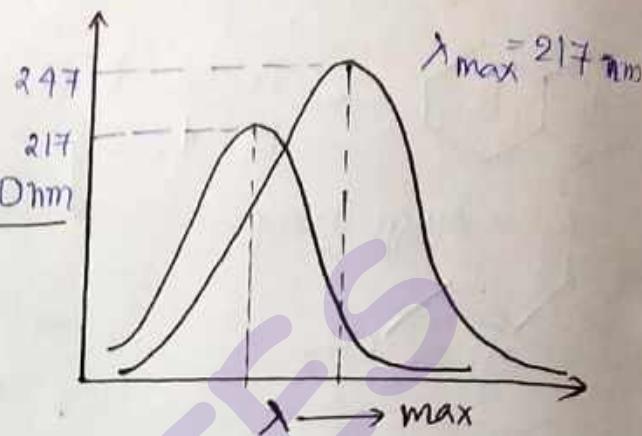


Acyclic butadiene

The base value for $\pi \rightarrow \pi^*$ transition for acyclic butadiene is 217 nm .

The incremental value for each extended conjugation in λ_{\max} is $+30 \text{ nm}$

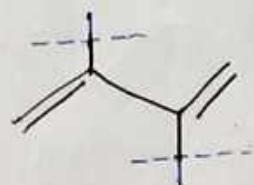
The incremental value for each alkyl group attached to system in λ_{\max} is $+5 \text{ nm}$



For each ring residue, incremental value is $+5 \text{ nm}$

For each exocyclic double bond, incremental value is $+5 \text{ nm}$.

Q1. Calculate the λ_{\max} value for

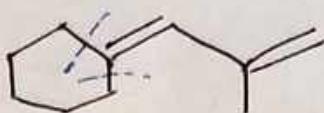


The base value for acyclic butadiene = 217 nm .

2 alkyl group = $2 \times 5 = 10 \text{ nm}$.

$$\lambda_{\max} = 217 + 10 \text{ nm} = 227 \text{ nm}.$$

Q2.



Base value (acyclic) = 217 nm .

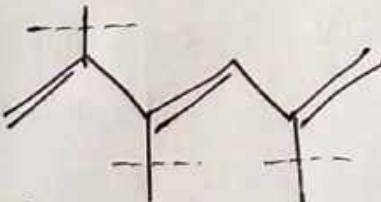
1 alkyl group = 5 nm

2 Ring residue = 10 nm $[5 \times 2]$

1 exocyclic = 5 nm

$$\lambda_{\max} = 237 \text{ nm}$$

Q3. Base value = 217 nm



Extended conjugation = 30 nm

3 alkyl group = 15 nm [5 × 3 = 15]

$$\lambda_{\max} = 262 \text{ nm}$$

Cyclic butadiene



Homoannular

Base value = 253 nm



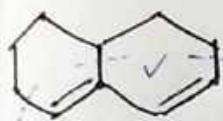
Heteroannular

Base value = 214 nm



Base value = 253 nm

2 ring residue = 10 nm [2 × 5 nm]
 $\lambda_{\max} = 263 \text{ nm.}$



Base value = 214 nm
3 ring residue = 15 nm.
1 exocyclic double bond

$$\lambda_{\max} = 234 \text{ nm}$$

Q1. Calculate λ_{\max} .

Base value for hetero = 214 nm



3 ring residue = 15 nm

1 exocyclic double = 5 nm

$$\lambda_{\max} = 234 \text{ nm}$$

Q2.

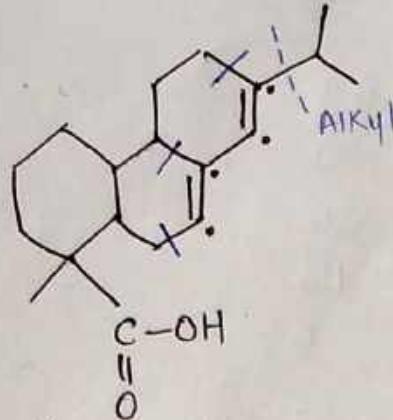
Base value = 214

3 ring residue = 15

1 alkyl group = 5

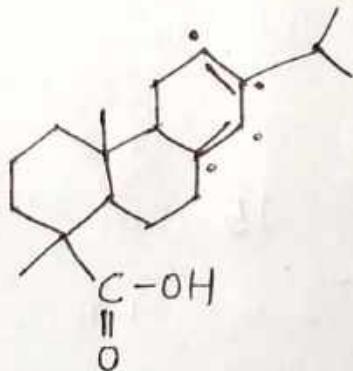
1 exocyclic double bond = 5

$$\lambda_{\max} = 239 \text{ nm}$$



Q3. Base value = 253 nm
 3 ring residue = 15 nm
 1-alkyl grp = 5 nm
 1-exocyclic double bond = 5 nm

$$\lambda_{\max} = 278 \text{ nm}$$

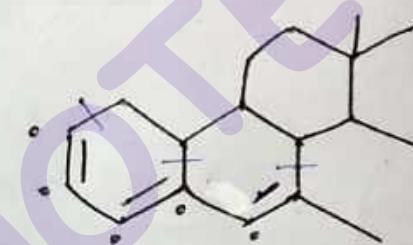


Q4.

NOTE If a system contains both homo-annular and hetero-annular then, we have to consider homoannular because of less energy consumption.

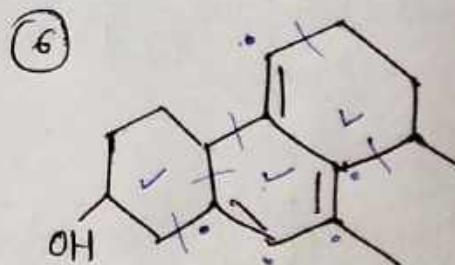
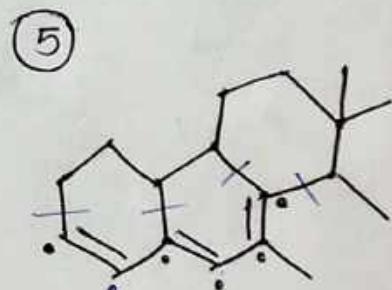
Base value = 253
 EXO = 5
 3R.R = 15
 1 Extended = 30
 1 alkyl = 5

$$\lambda_{\max} = 308 \text{ nm}$$



Q5. B.V = 253
 Ext = 30
 4 R.R = 20
 1 alkyl = 5
 2 EXO. = 10

$$\lambda_{\max} = 318 \text{ nm}$$

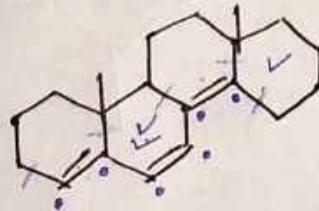


Q6. B.V = 253
 Ext = 30
 5 R.R = 25
 3 EXO = 15
 1 Alkyl = 5

$$\lambda_{\max} = 328 \text{ nm}$$

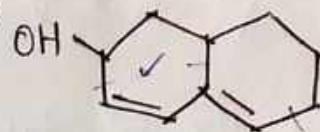
Q7. $B.V = 214 \text{ nm}$
 $5RR = 25 \text{ nm.}$
 $3EXO = 15 \text{ nm}$
 $1EXT. = 30 \text{ nm.}$
 $\lambda_{max} = \frac{323}{284} \text{ nm}$

(7)

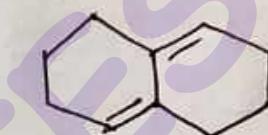


Q8. $B.V = 214 \text{ nm.}$
 $1EXO = 5 \text{ nm}$
 $3R.R = 15 \text{ nm}$
 $\underline{4 \text{ nm}}$

(8)



(9)



IR-SPECTROSCOPY

IR-region \rightarrow 800 nm - 1250 nm.

$$E = h\nu = \frac{hc}{\lambda} \rightarrow \text{constant}$$

$$E \propto \frac{1}{\lambda} \Rightarrow E \propto \bar{\nu}, \text{ where } \bar{\nu} \text{ wave no., unit} \rightarrow \text{cm}^{-1}$$

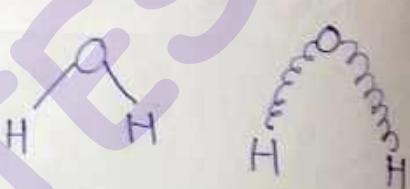
Generally the IR data / spectra expressed in terms of wave no. ($\bar{\nu}$)

IR light can produce 2 types of controlled vibrations :-

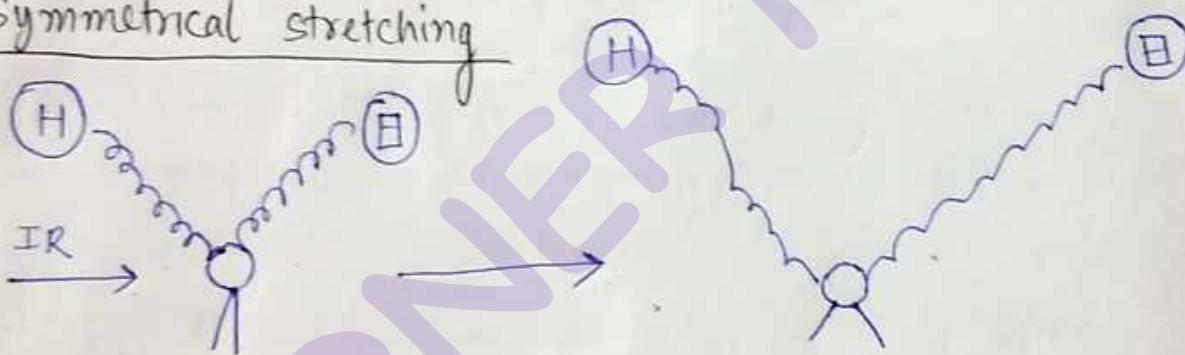
① Stretching

Symmetrical \rightarrow Asymmetrical

② Bending



Symmetrical stretching

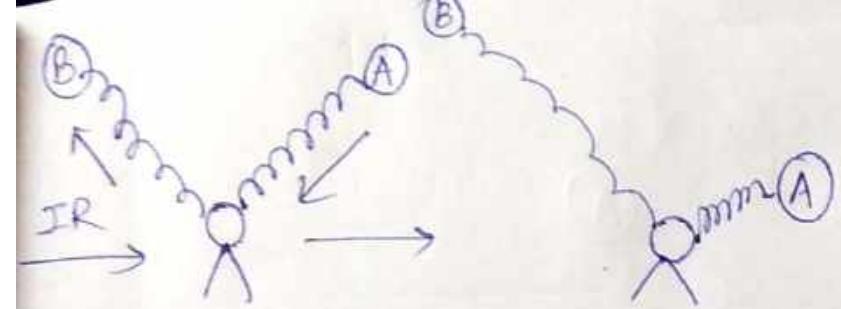


The bonds are stretched in same directⁿ, however the bond axis remains fixed.

Only bond length will change.

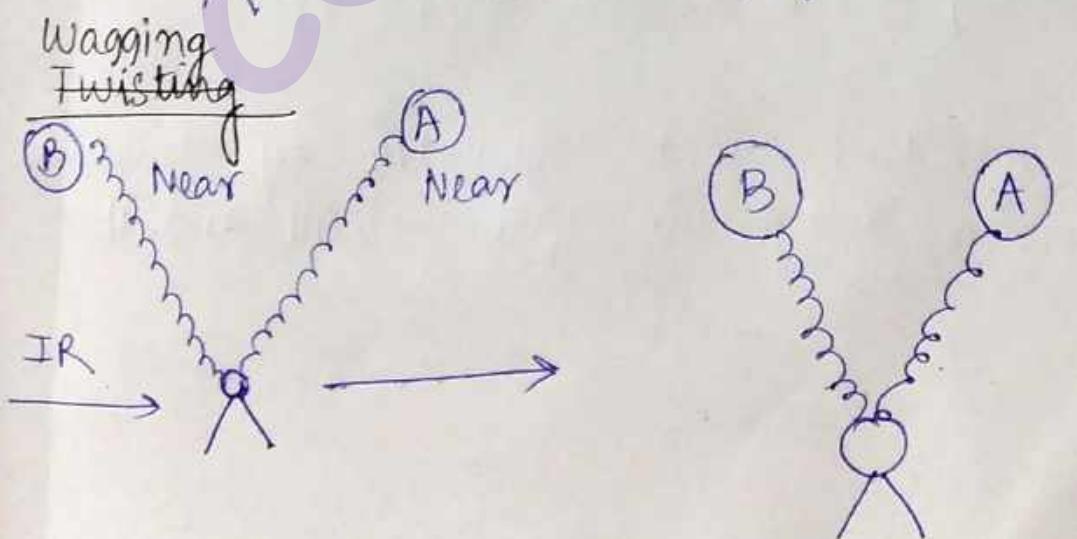
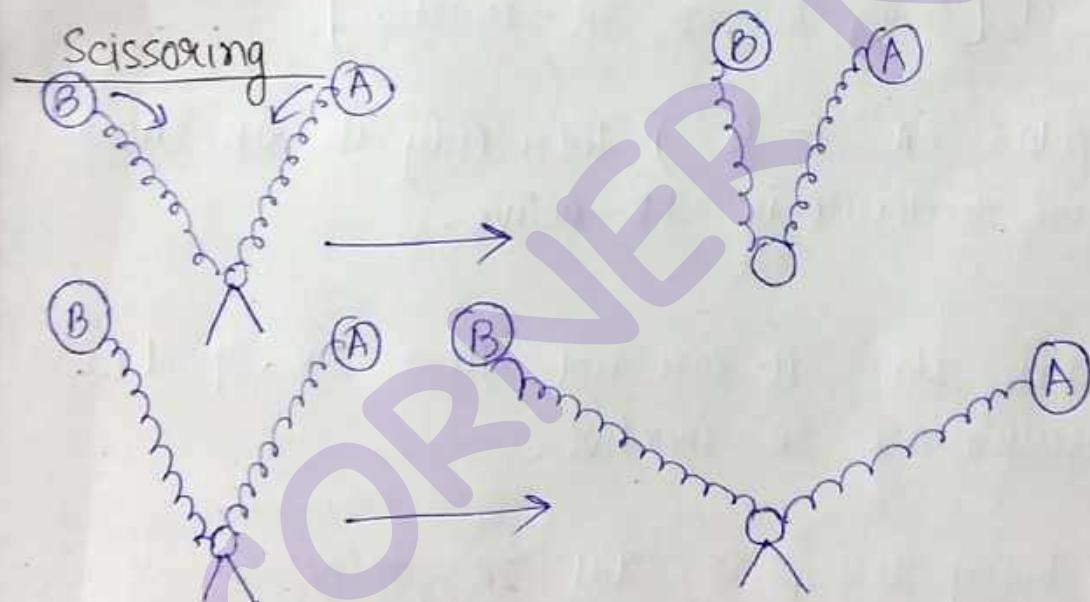
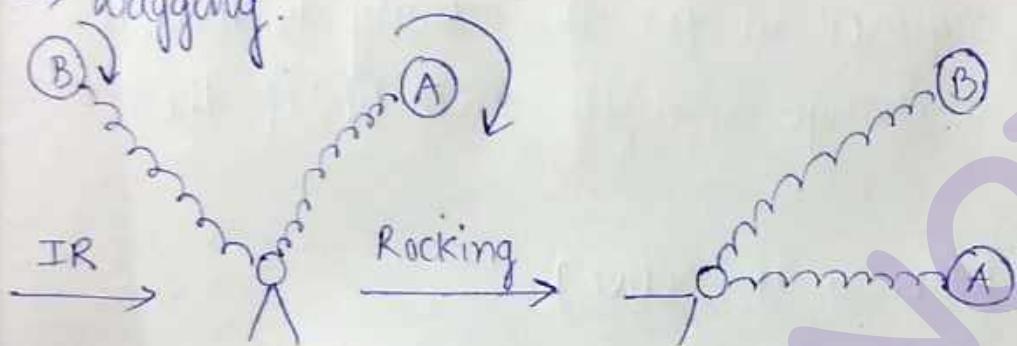
Asymmetric stretching

The bonds are stretched in opp. directⁿ keeping the bond axis same, only the bond length will change.

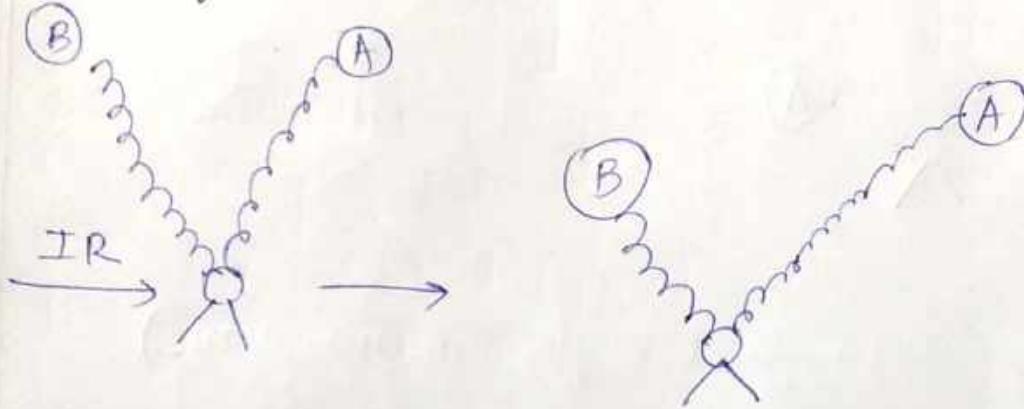


② Bending

- Rocking (Bond axis changes, bond length remains same)
- Scissoring
- Twisting
- Wagging.



Twisting



Selection Rule for IR Spectroscopy

The most fundamental requirement for IR-activity is that a vibration must cause a change in dipole moment of the molecule.

E.g. → ① HCl, CO [Polar, so IR-active]

② H₂, N₂, O₂, Cl₂ [Non-polar, so, IR-inactive]

If a molecule is polar ($A^{+s} - B^{-s}$), then only it can show some IR-spectra and molecule is IR-active.

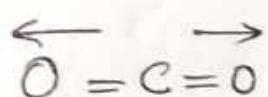
If a molecule is non-polar, it can not show IR-spectra, so, non-polar molecules are IR-inactive.

Exception - CO₂ is being non-polar, still IR-active.

Reason

This is due to the fact that due to asymmetric stretching of CO₂, there occurs a change in dipole moment and it becomes IR-active.

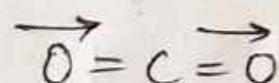
Both possible bondings in CO_2 also induce some dipole moment, hence CO_2 becomes IR-active.



Symmetric stretching

Net charge in dipole moment, $\mu = 0$.

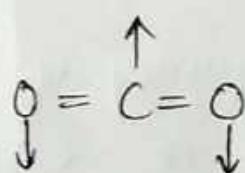
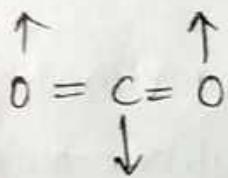
IR-inactive



1. Asymmetric stretching.

2. Net charge in dipole moment, $\mu \neq 0$.

3. IR-active peak at 2350 cm^{-1}

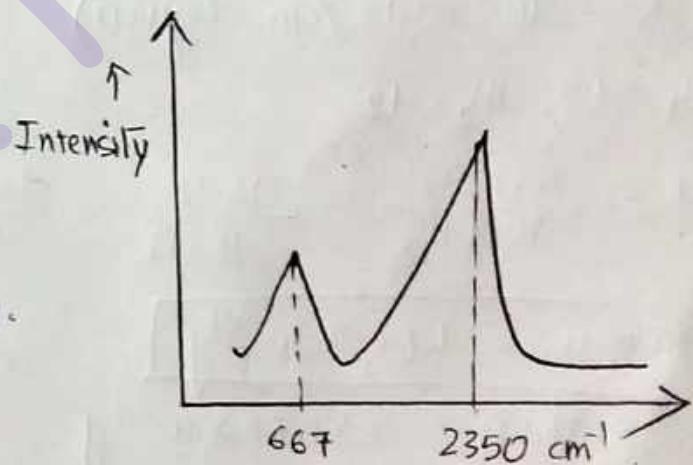


\Rightarrow The net charge in dipole moment, $\mu \neq 0$.

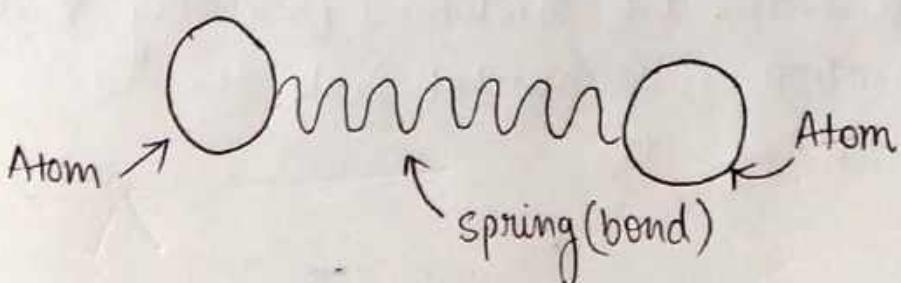
Hence, IR active : 667 cm^{-1} peak is found.

Vibrational frequency and (Hooke's law)

The stretching frequency of a bond can be approximated by Hooke's law.



\Rightarrow In this approximation and the connecting bonds are treated as simple harmonic oscillator composed of 2 masses of 2 atoms joined by spring as shown in the figure.



$$\text{The vibrational frequency, } \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$\bar{\nu}$ = vibrational frequency

c = velocity of light

K = force constant (given)

μ = reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ a.m.u}$$

1.

Calculate the wave no. or frequency of stretching vibration of C=C of ethylene molecule or C≡C acetylene molecule



$$K = 10^6 \text{ dyne/cm} \text{ (given)}$$

$$m_1 = 12, m_2 = 12$$

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} = \frac{12 \cdot 12}{12 + 12} = \frac{144}{24} = 6 \text{ a.m.u}$$

$$1 \text{ a.m.u} = 1.66 \times 10^{-24} \text{ g}$$

$$\text{So } 6 \text{ a.m.u} = 6 \times 1.66 \times 10^{-24} \text{ g}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{\frac{10^6}{6 \times 1.66 \times 10^{-24}}} \\ = 1680 \text{ cm}^{-1}$$

2 Calculate the wave no. i.e stretching frequency $\bar{\nu}$ due to stretching vibration fundamental peak due to stretching vibration of CO.

$$m_1 = 12, \quad m_2 = 16$$

$$> c=0$$

$$-c=c-$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$= \frac{12 \cdot 16}{12+16} = x \text{ a.m.u}$$

$$1 \text{ a.m.u} = 1.66 \times 10^{-29} \text{ g}$$

$$x \text{ a.m.u} = y \text{ g}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c} \sqrt{\frac{10^6}{y}} = z \text{ cm}^{-1}$$

No. of fundamental vibrations

- ① Rotational
- ② Translational
- ③ Vibrational



When a molecule is exposed to IR-light, the molecule may vibrate / rotate / transfer to its higher excited state.

$$\text{Rotational degrees of freedom} + \text{Vibrational degrees of freedom} + \text{Translational degrees of freedom} = 3n$$

n = no. of atoms present in that molecule.

Translational degrees of freedom = 3

Linear degrees of freedom = 2 [for CO_2].

$$\therefore 2 + \text{Vibrational degrees of freedom} + 3 = 9 \quad \underline{n = 3}$$

$$V.D.F = 9 \quad \checkmark$$

For non-linear molecule, methane (CH_4)

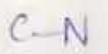
$$R \cdot D \cdot F = 3$$

~~$R \cdot D \cdot F = 3 + 3$~~

$$3 + VDF + 3 = 15$$

$$VDF = 15 - 6 = 9$$

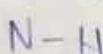
Some fundamental stretching vibrations of functional groups



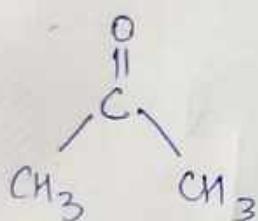
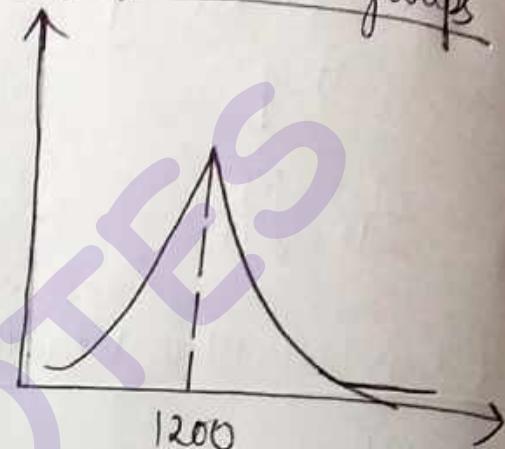
$$\bar{\nu} = 1200 \text{ cm}^{-1}$$

$$1600 \text{ cm}^{-1}$$

$$2200 \text{ cm}^{-1}$$

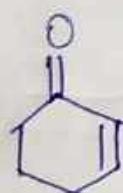


$$\left. \begin{array}{l} \\ \\ \end{array} \right\} 2700 \text{ to } 3800 \text{ cm}^{-1}$$



$$\left. \begin{array}{l} \\ \end{array} \right\} \bar{\nu} = 1720 \text{ cm}^{-1}$$

[Ketone, Aldehyde]

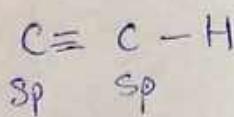


$$\left. \begin{array}{l} \\ \end{array} \right\} \bar{\nu} = 1680 \text{ cm}^{-1}$$

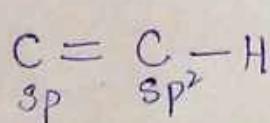
Total average peak,



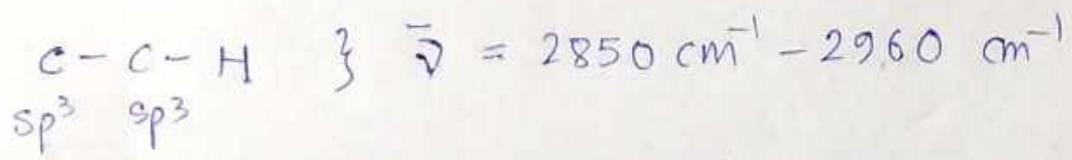
$$\left. \begin{array}{l} \\ \end{array} \right\} 1650 - 1750 \text{ cm}^{-1}$$



$$\left. \begin{array}{l} \\ \end{array} \right\} \bar{\nu} = 3300 \text{ cm}^{-1}$$



$$\left. \begin{array}{l} \\ \end{array} \right\} \bar{\nu} = 3020 - 3100 \text{ cm}^{-1}$$



Fingerprint region

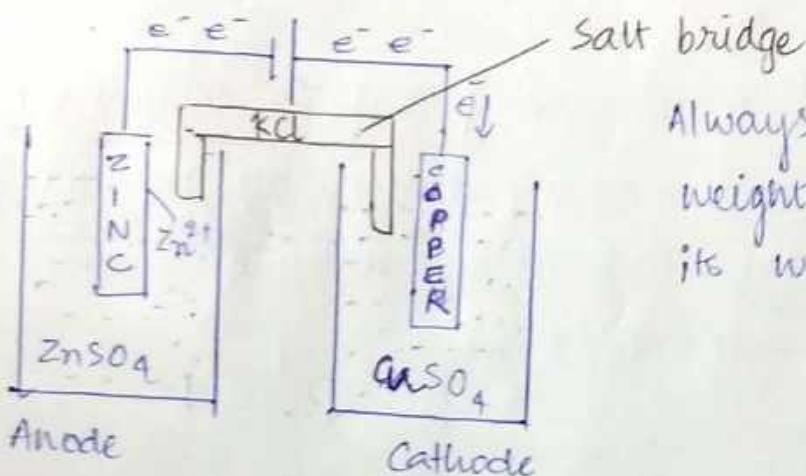
Region from about $500 - 1500 \text{ cm}^{-1}$ usually contains very complicated series of absorptions. These are mainly due to all manners of bending vibrations within within the molecule.

This This is called fingerprint region.

Electrochemistry

6/4/2018

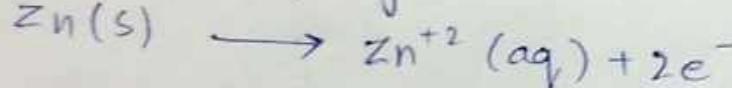
Galvanic cell / electrochemical cell



Always cathode gains the weight and anode loses its weight.

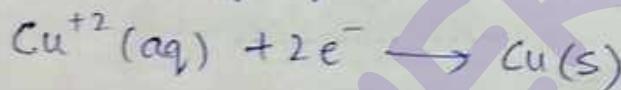
Anode / anodic half cell :

Oxidation is going on their oxidation means loss of e^-



Cathode / cathodic half cell

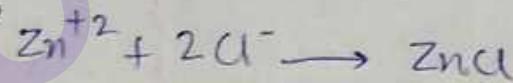
Reduction is going on, reduction means gain of e^-



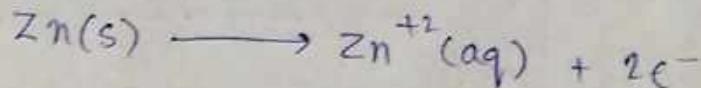
At cathode,



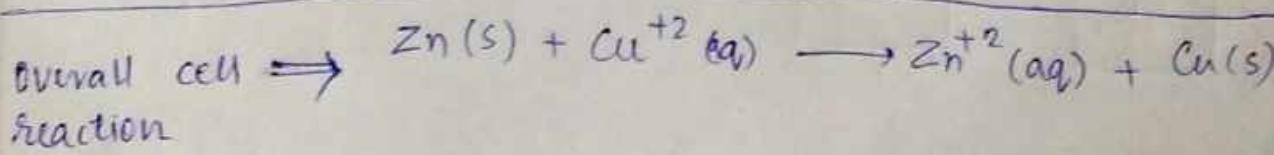
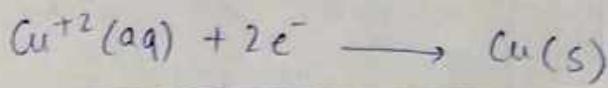
At anode



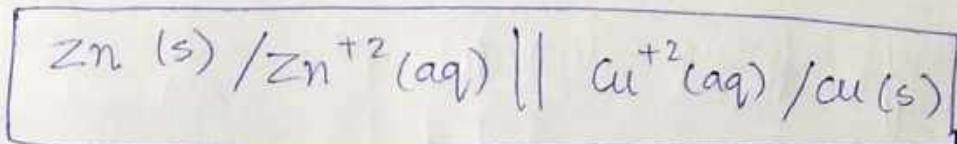
At anode



Cathode



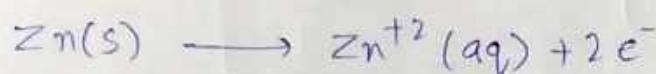
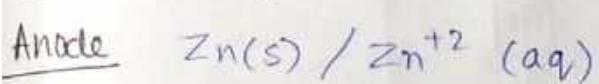
Cell representation



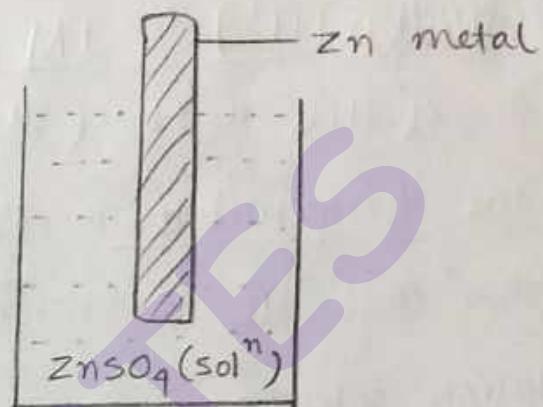
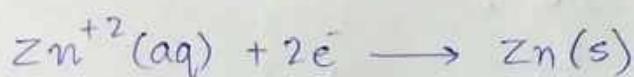
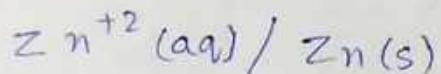
Anode || Cathode
(oxi) (Red)

Types of electrodes :-

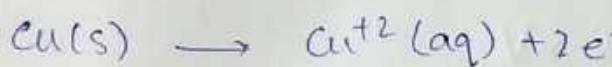
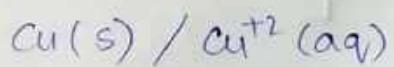
- ① Metal dipped in its own metal ion. :-



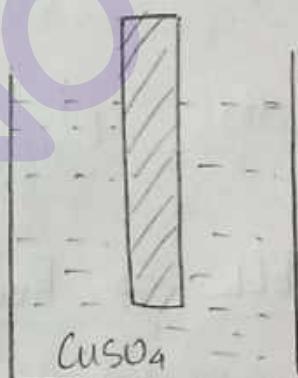
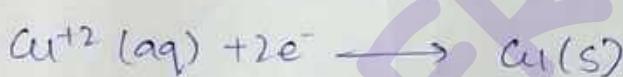
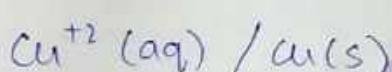
cathode



Anode



Cathode



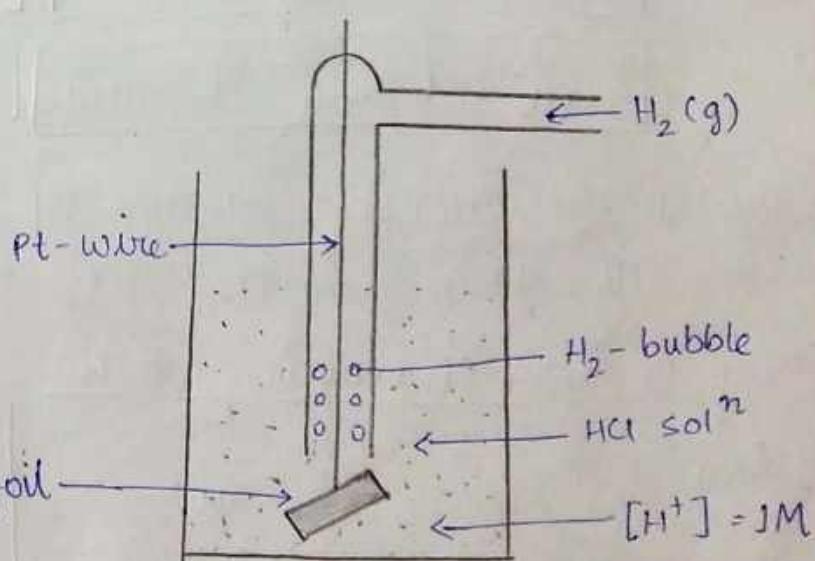
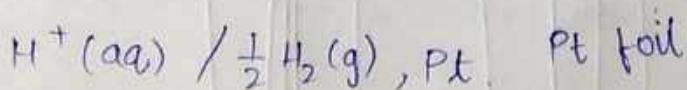
- ② Gas electrode

E.g. → Hydrogen Electrode (HE)

Anode



Cathode



Standard Hydrogen Electrode (SHE)

It is a primary reference electrode.

→ When HE will be called as SHE?

When the pressure of the $H_2(g)$ = 1 atm

Concentration, $[H^+]$ = 1 M

(1 mole of HCl in 1L of aq. soln)

And the temperature is 298 K or $25^\circ C$

In this case HE is known as SHE.

Oxidation potential

$$E_{\frac{1}{2}H_2/H^+}^\circ = 0.0V$$

$[E^\circ \rightarrow \text{standard cond^n}]$

Reduction potential

$$E_{H^+/\frac{1}{2}H_2}^\circ = 0.0V$$

EMF OF A CELL or E_{cell}

E_{cell} can be expressed as

$$E_{cell} = E_{\text{cathode}} - E_{\text{anode}} \quad [\text{In terms of reduction potential}]$$

$$E_{cell} = E_{\text{anode}} - E_{\text{cathode}} \quad [\text{In terms of oxidation potential}]$$

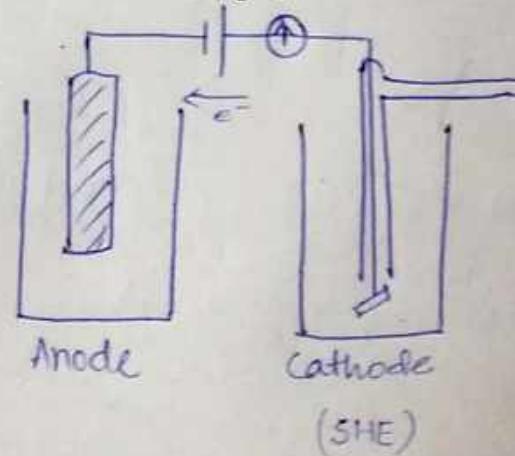
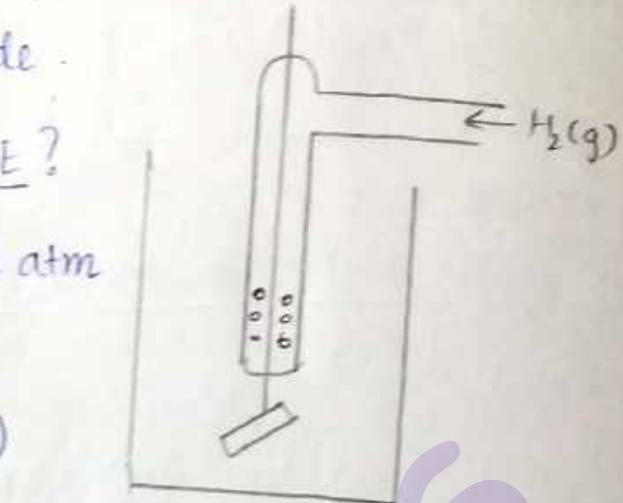
Calculate the oxidation potential of standard Zn electrode by coupling with SHE, given E_{cell} or emf of cell = 0.76 V

E_{cell} in terms of oxidation potential

$$E_{cell} = E_{Zn/Zn^{+2}}^\circ - E_{\frac{1}{2}H_2/H^+}^\circ$$

$$\Rightarrow 0.76V = E_{Zn/Zn^{+2}}^\circ - 0$$

$$\Rightarrow E_{Zn/Zn^{+2}}^\circ = 0.76V$$



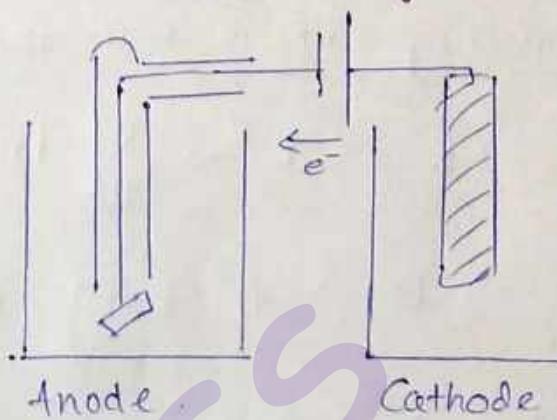
Zn is in a state to oxidize because of +ve
let us couple a standard Cu electrode with SHE.

$E_{\text{cell}} = 0.34 \text{ V}$, calculate the standard reduction potential of Cu.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$
$$= E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{H}^+/\frac{1}{2}\text{H}_2}$$

$$0.34 = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - 0$$

$$\boxed{E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}}$$



St. oxidation potential of Cu-electrode is, $E^{\circ}_{\text{Cu}/\text{Cu}^{2+}} = -0.34 \text{ V}$.

$$E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V} \quad [\text{Reduction Pot.}]$$

$$E^{\circ}_{\text{Ag}/\text{Ag}^+} = -0.80 \text{ V} \quad [\text{st. oxidation potential}]$$

zn, Cu, Ag

Nernst Eqⁿ²

Let us consider a hypothetical cell reaction,



Applying Vant Hoff Reaction Isotherm,

$$\Delta G = \Delta G^{\circ} + RT \ln Q \quad \text{where } Q \rightarrow \text{Reaction coefficient} \quad ①$$

$\Delta G \rightarrow$ change in Gibb's free energy

$$Q = \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

$\Delta G^{\circ} \rightarrow$ change in Gibb's free energy in std. cond'n.

$$\Delta G = -nFE$$

$$\Delta G^{\circ} = -nFE^{\circ} \quad \left. \begin{array}{l} E \rightarrow \text{emf} \\ E^{\circ} \rightarrow \text{emf in std. cond'n} \end{array} \right\}$$

$n \rightarrow$ no. of e^- taking part in redox reactn.

$F \rightarrow$ Faraday = 96500 coulomb.

Now eqⁿ ① becomes,

$$-nFE = -nFE^\circ + RT \ln \frac{[L]^l [M]^m}{[A]^a [B]^b} \quad \text{--- } ②$$

Dividing $-nF$ in both the sides

$$\Rightarrow E = E^\circ - \frac{RT}{nF} \ln \frac{[L]^l [M]^m}{[A]^a [B]^b} \quad \text{--- } ③$$

$$\Rightarrow E = E^\circ + \frac{RT}{nF} \ln \frac{[A]^a [B]^b}{[L]^l [M]^m} \quad \text{--- } ④$$

When $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$f = 96500 \text{ Coulomb} \quad ① \frac{RT}{F} = 0.059$$

$$T = 298 \text{ K}$$

② converting \ln to \log .

Eqⁿ ④ becomes

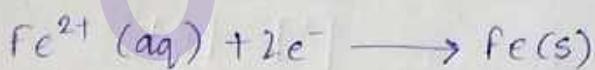
$$\Rightarrow E = E^\circ + \frac{0.059}{n} \log \frac{[A]^a [B]^b}{[L]^l [M]^m} \quad \text{--- } ⑤$$

$$\Rightarrow E = E^\circ + \frac{0.059}{n} \log \frac{\text{[Reactant]}}{\text{[Product]}}$$

Application of Nernst Eqⁿ

① To calculate the electrode potential and cell potential.

② $\text{FeSO}_4(0.1 \text{ M})/\text{Fe}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$, Calculate the reduction potential.



$$\begin{aligned} E_{\text{Fe}^{2+}/\text{Fe}} &= E^\circ_{\text{Fe}^{2+}/\text{Fe}} + \frac{0.059}{2} \log [\text{Fe}^{2+}] \\ &= -0.44 \text{ V} + \frac{0.059}{2} \log (0.1) \end{aligned}$$

$$E_{\text{Fe}^{2+}/\text{Fe}} = -0.4695 \text{ V}$$

[when the product is a neutral species, discard the concentration and make it unity]

Represent the cell in which the following reaction is taking place, calculate the cell potential,



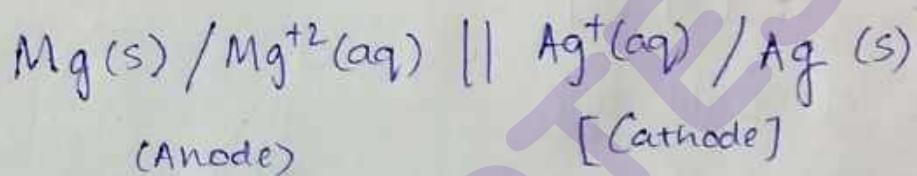
Given, $E^\circ_{Mg^{+2}/Mg} = -2.37\text{ V}$, $E^\circ_{Ag^+/Ag} = 0.80\text{ V}$

$$[\text{Ag}^+] = 0.02 \text{ M}, [\text{Mg}^{+2}] = 0.001 \text{ M}.$$

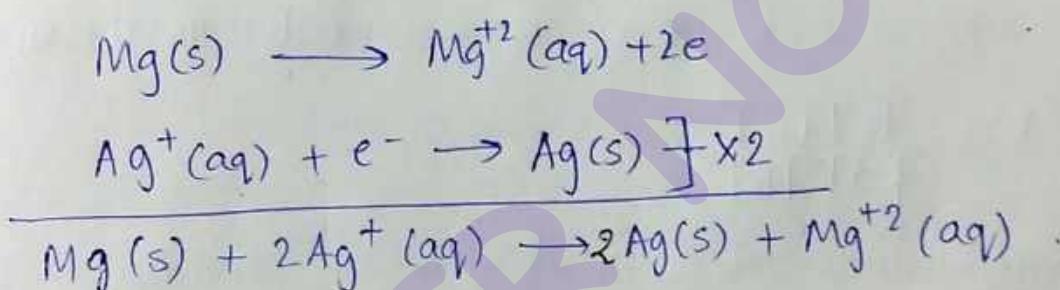
oxidised - Mg

Reduced - Ag.

cell representation



reaction



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{Ag}^+]^2}{[\text{Mg}^{2+}]}$$

$$= \left(E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \right) + \frac{0.059}{2} \log \frac{(0.02)^2}{0.001}$$

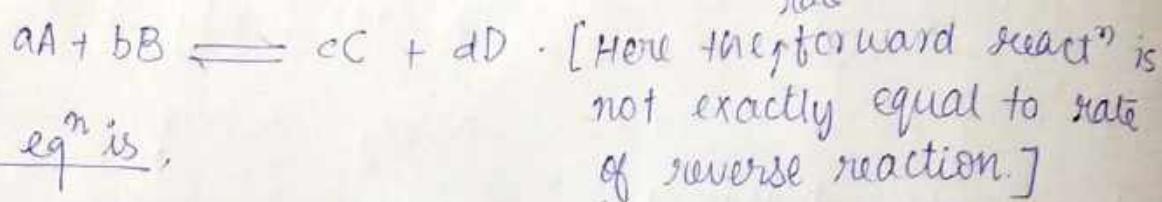
$$= \left(E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Mg}^{2+}/\text{Mg}}^\circ \right) + \frac{0.059}{2} \log \frac{(0.02)^2}{0.001}$$

$$= 0.80 - (-2.37) + \frac{0.059}{2} \log \frac{(0.02)^2}{0.001}$$

$$E_{\text{cell}} = 3.1583 \text{ V}$$

2. Calculation of equilibrium constant.

For a hypothetical cell reaction, we know that,



The Nernst eqⁿ is,

$$E = E^\circ + \frac{0.059}{n} \log Q$$

where,

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

However at equilibrium,

Rate of forward reactⁿ = React Rate of reverse reaction.

So Q will be replaced by K, where K → equilibrium constant.

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

When an electrochemical cell is in equilibrium condition,

At that time, $E_{\text{cell}} = 0$.

Nernst eqⁿ will be,

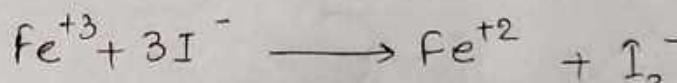
R.P ↑ → C
O.P ↑ → A.

$$\Rightarrow 0 = E^\circ - \frac{0.059}{n} \log K$$

$$\Rightarrow E^\circ = \frac{0.059}{n} \log K$$

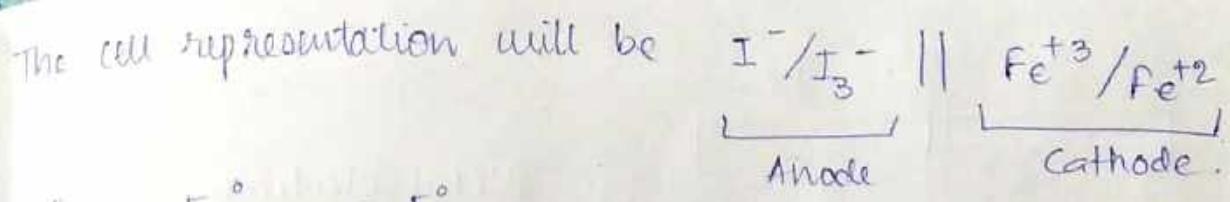
$$\Rightarrow \boxed{\log K = \frac{nE^\circ}{0.059}}$$

Q1. calculate the equilibrium constant for the reaction.



The standard reduction potential for $\text{Fe}^{+3}/\text{Fe}^{+2}$ i.e. $E^\circ_{\text{Fe}^{+3}/\text{Fe}^{+2}} = 0.77\text{V}$

$$E^\circ_{\text{I}_3^-/\text{I}^-} = 0.54\text{V}$$



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{Anode}}$$

$$E_{\text{cell}} = E_{Fe^{+3}/Fe^{+2}} - E_{I_3^-/I^-}$$

$$E_{\text{cell}} = 0.77 - 0.54 = 0.23V$$

$$\log K = \frac{nE^\circ}{0.059} = \frac{1 \times 0.23}{0.059}$$

$$\log K = 3.898$$

$$\Rightarrow K = 10^{3.898}$$

$C \downarrow -4$

$C \uparrow -C$

To find the emf of a concentration cell

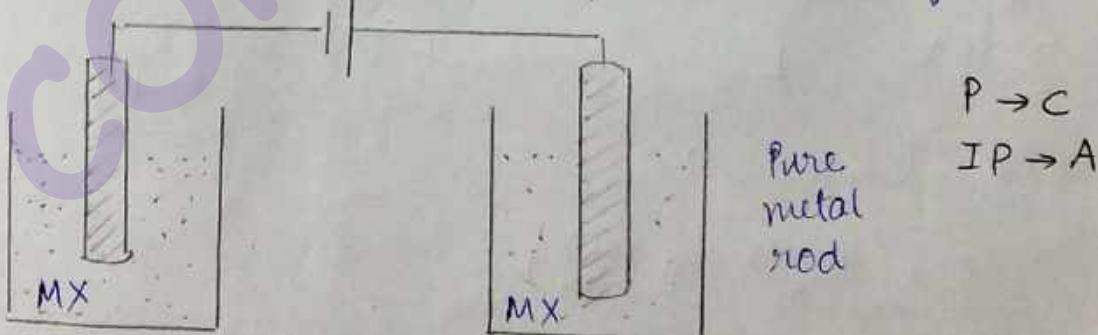
A concentration cell is that in which potential difference across the electrodes arises due to the difference in concentration of electrode material and due to the difference in concentration of electrolyte.

Therefore, conc. cells are of 2 types:-

- 1) Electrode concentration cell.
- 2) Electrolyte concentration cell.

Electrode concentration cell

In electrode conc. cell difference is there in conc. of electrode material



$$[M^{+n}] = 1M$$

[Anodic half cell]

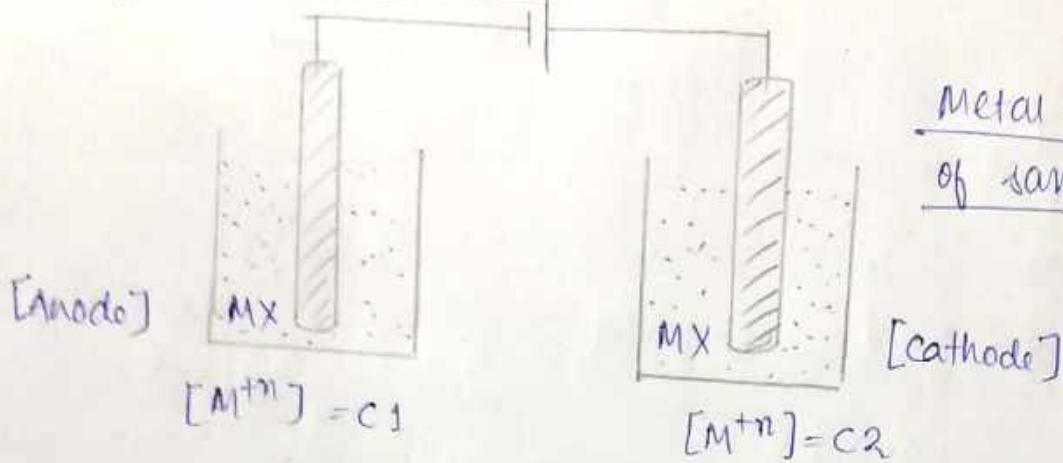
$$[M^{+n}] = 1M$$

[Cathodic half cell]

Impure metal rod will be acting as Anode.

Pure metal rod will be acting as Cathode.

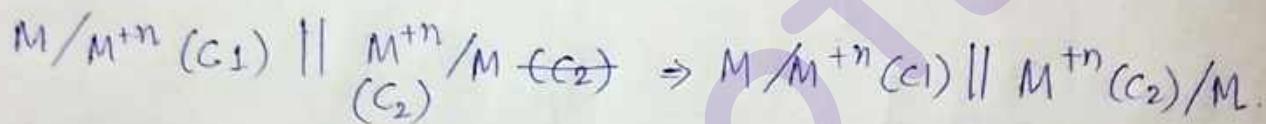
Electrolytic concentration cell



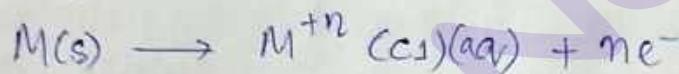
Metal electrodes are of same purity.

c₂ > c₁ More conc. containing electrode - Cathode
 Less conc. containing electrode - Anode

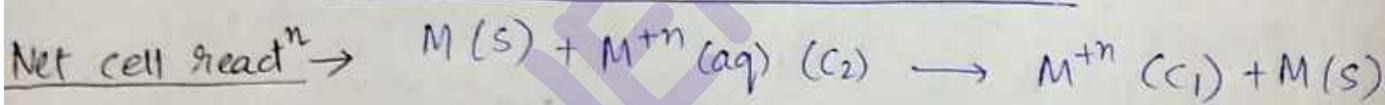
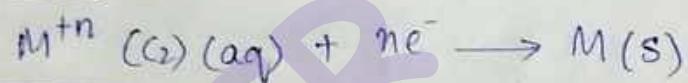
Cell representation



Reaction at Anode,



Reaction at cathode



$$E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.059}{n} \log \frac{[\text{conc. of reactant}]}{[\text{conc. of product}]}$$

$$E_{Zn^{+2}/Zn}^\circ = -0.76 \text{ V}, \quad E_{Zn^{+2}/Zn}^\circ = -0.76 \text{ V}$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{Anode}}^\circ = 0.$$

$$\therefore E_{\text{cell}} = 0 + \frac{0.059}{n} \log \left(\frac{c_2}{c_1} \right)$$

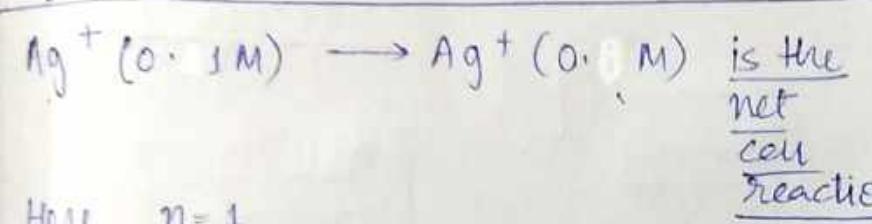
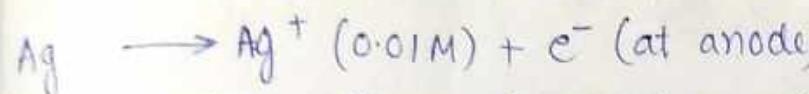
$E_{\text{cell}} = \frac{0.059}{n} \log \left(\frac{c_2}{c_1} \right)$

$$c_2 > c_1$$

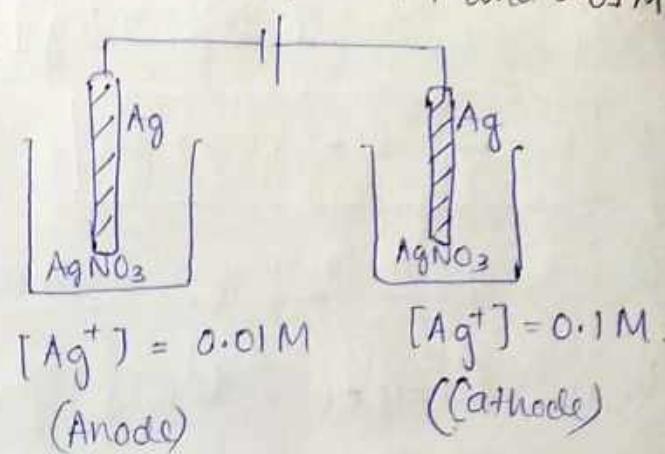
Problems

2 silver rods are placed in AgNO_3 solⁿ of concentration 0.1 M and 0.01 M in a cell. Calculate the emf of the cell.

low conc. always acts as anode.



Hence, $n=1$



$$E_{\text{cell}} = \frac{0.059}{1} \log \left(\frac{0.1}{0.01} \right)$$

$$E_{\text{cell}} = 0.059 \log (10)$$

$$E_{\text{cell}} = 0.059\text{V}$$

4. To find the pH of unknown aqueous solⁿ

The pH of an aq. solⁿ can be measured by using different electrodes such as H_2 electrode.

Quin hydrome electrode

Type-1 - Using hydrogen electrode

Let us put a hydrogen electrode in a solⁿ of unknown pH with Pt-wire.

The representation will be, $\text{H}^+ (?) / \frac{1}{2}\text{H}_2 (\text{1 atm}), \text{Pt}$

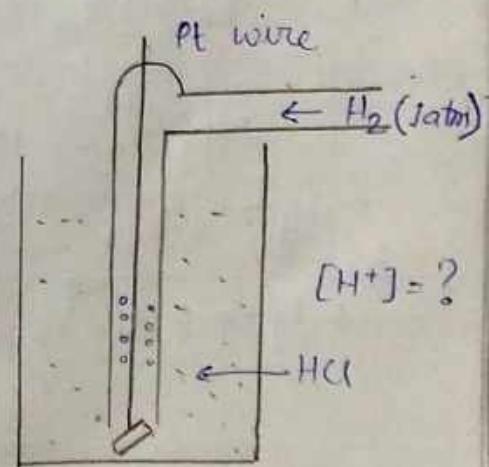
Pt → conduction of electricity.



$$E_{\text{H}^+ / \frac{1}{2}\text{H}_2} = E_{\text{H}^+ / \frac{1}{2}\text{H}_2}^\circ + \frac{0.059}{1} \log [\text{H}^+]$$

$$\Rightarrow E_{\text{H}^+ / \frac{1}{2}\text{H}_2} = 0.059 \log [\text{H}^+] + 0$$

$$\Rightarrow E_{\text{H}^+ / \frac{1}{2}\text{H}_2} = 0.059 \log [\text{H}^+]$$



$$E_{H^+/\frac{1}{2}H_2} = -(-0.059 \log [H^+])$$

$$\Rightarrow E_{H^+/\frac{1}{2}H_2} = -0.059 \text{ pH} \quad [\because -\log[H^+] = \text{pH}]$$

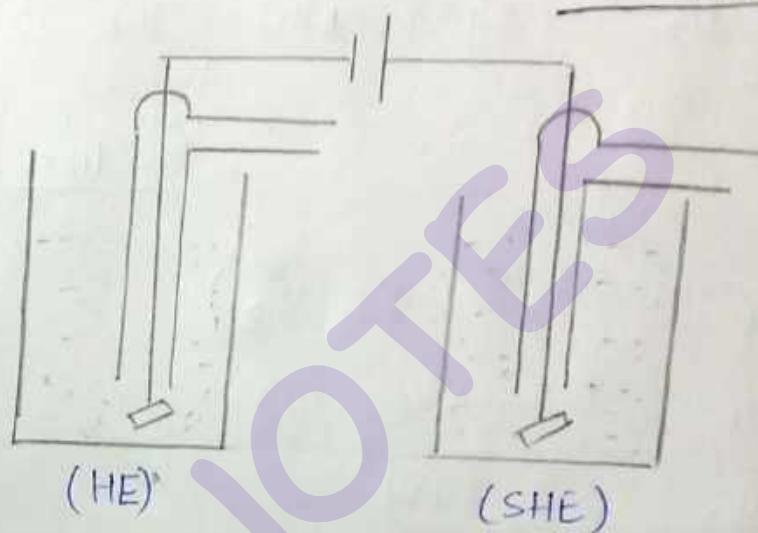
Case-1 When hydrogen electrode coupled with standard hydrogen electrode (SHE)

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

$$E_{\text{cell}} = E_{\text{SHE}}^\circ - E_{H^+/\frac{1}{2}H_2}^\circ$$

$$E_{\text{cell}} = 0.0 - (-0.059 \text{ pH})$$

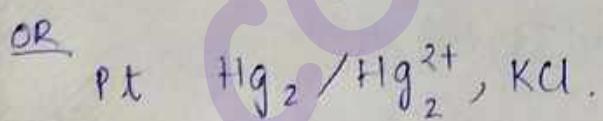
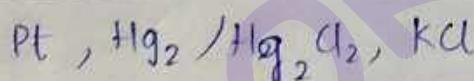
$$\boxed{\text{pH} = \frac{E_{\text{cell}}}{0.059}}$$



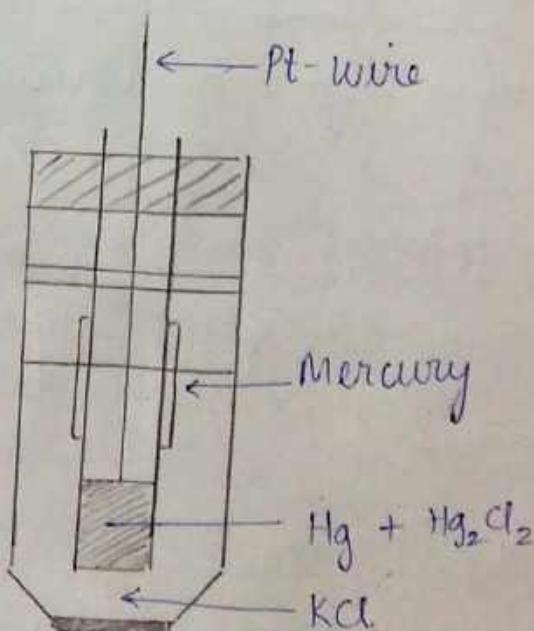
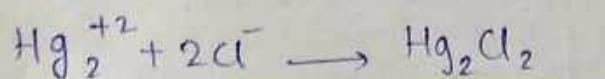
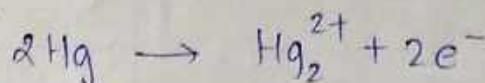
Case-2 By coupling with standard calomel electrode

Calomel electrode is Hg electrode. It consists of Hg as an electrode, an insoluble salt of Hg (Hg_2Cl_2) and a soluble salt having common anion (KCl).

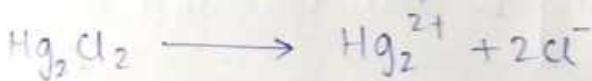
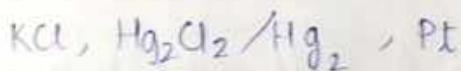
Anodic representation will be



Reaction



Cathodic representation



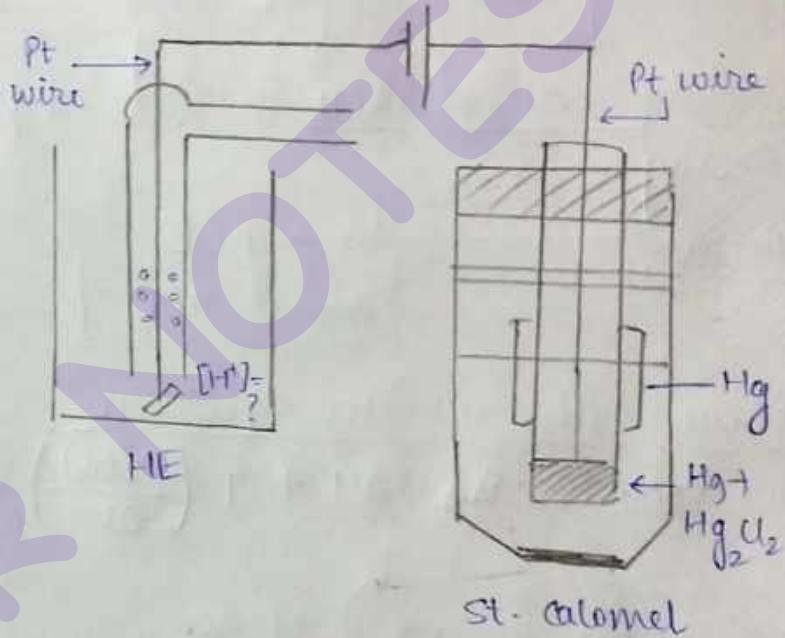
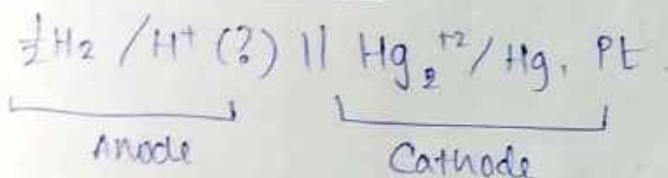
if thus calomel electrode is in its standard condition,

$$\Rightarrow [\text{Hg}_2^{2+}] = 1\text{M}$$

$$T = 298\text{ K}$$

$$\Rightarrow E^\circ_{\text{Hg}_2^{2+}/2\text{Hg}} = 0.2422\text{ V}$$

Cell representation



St. calomel

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{Anode}}$$

$$= E^\circ_{\text{calomel}} - E^\circ_{\text{H}^+ / \frac{1}{2}\text{H}_2}$$

$$E_{\text{cell}} = 0.2422 - (-0.059 \text{ pH})$$

$$E_{\text{cell}} = 0.2422 + 0.059 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.059}$$

\geq The emf of a cell or $E_{\text{cell}} = \frac{\text{Pt, H}_2(\text{atm}) / \text{H}^+ (?)}{\text{Anode}} \parallel \text{KCl(1M), Hg}_2\text{Cl}_2 / \text{Hg, Pt}$,
 $= 0.52\text{ V}$, $T = 298\text{ K}$.

\rightarrow calculate the pH.

$$\text{pH} = \frac{0.52 - 0.2422}{0.059}$$

$$\text{pH} =$$

(for the same cell above)

Thermodynamics of cell

Thermodynamic parameters accompanying a cell operation are

- (1) Enthalpy (ΔH)
- (2) Entropy (ΔS)
- (3) Free energy (ΔG) change

The details of finding the above parameters are described in Thermodynamics chapter.

During cell operation, decrease in free energy appears as electrical energy.

Hence,

$$-\Delta G = nFE$$

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

from Gibbs-Helmholtz equation

$$\text{we know, } \Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P \quad \text{--- (2)}$$

Substituting the value of ΔG ,

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

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

$$\Rightarrow \Delta H = T nF \left(\frac{\partial E}{\partial T} \right)_P - nFE \quad \text{--- (a)}$$

$$\Rightarrow \boxed{\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right)_P - E \right]} \quad \text{--- (3)}$$

From (a), $\Delta H = TnF \cdot \left(\frac{\partial E}{\partial T} \right)_P + \Delta G \quad \text{--- (4)}$

Again from thermodynamics, $\Delta H = \Delta G + T\Delta S \quad \text{--- (5)}$

By combining eqⁿ ④ and eqⁿ ⑤,

$$\Rightarrow TnF \left(\frac{\partial E}{\partial T} \right)_P + \Delta G = \Delta S + TAS.$$

$$\Rightarrow TnF \left(\frac{\partial E}{\partial T} \right)_P = TAS.$$

$$\Rightarrow \boxed{\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P}$$

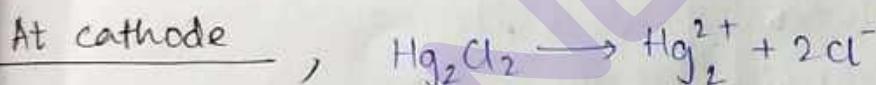
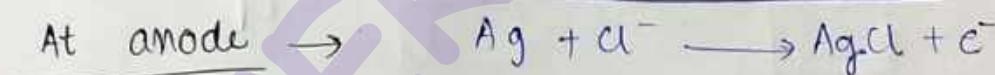
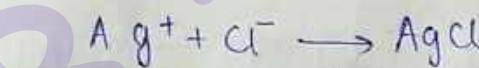
Q1. The galvanic cell $\text{Ag(s)}/\text{AgCl(s)}/\text{KCl(1M)}/\text{Hg}_2\text{Cl}_2/\text{Hg(l)}$ is an example of a cell without a liquid junctⁿ potential. Since, the 2 electrodes are dip into same electrolyte i.e KCl. The emf of the cell, $E_{\text{cell}} = 0.058 \text{ V}$ at 298 K .

$$E_{\text{cell}} = 0.0614 \text{ V} \text{ at } 298 \text{ K}.$$

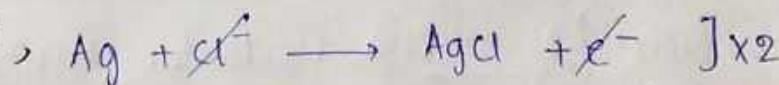
a) Write down the cell reaction

b) calculate ΔS , ΔG , ΔH at 308 K .

Ans) The cell reaction will be, $\text{Ag} \rightarrow \text{Ag}^+ + e^-$



Total cell reaction



$$\left(\frac{\partial E}{\partial T} \right)_P = \frac{dE}{dT} \text{ at constant pressure} = \frac{0.0614 - 0.058}{308 - 298} = 3.4 \times 10^{-4} \text{ VK}^{-1}$$

$$\Delta G = -nFE, n=2.$$

at 298K = $-2 \times 96500 \times 0.058$

$$\boxed{\Delta G = -11.194 \text{ kJ K}^{-1}}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p$$

$$\Delta S = 2 \times 96500 \times 3.4 \times 10^{-9}$$

$$\boxed{\Delta S = 65.65 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta H = nF \left[T \cdot \left(\frac{\partial E}{\partial T} \right)_p - E \right]$$

$$= 2 \times 96500 (298 \times 3.4 \times 10^{-9} - 0.058)$$

$$\boxed{\Delta H = 8.314 \text{ kJ}}$$

Imp ✓

Kohlrausch

→ Effect of dil. on conductivity

→ Equivalent conductance

→ Molar conductance

Fuel Cell :- The cell in which

Fuel energy is converted to electrical energy is known as fuel cell.

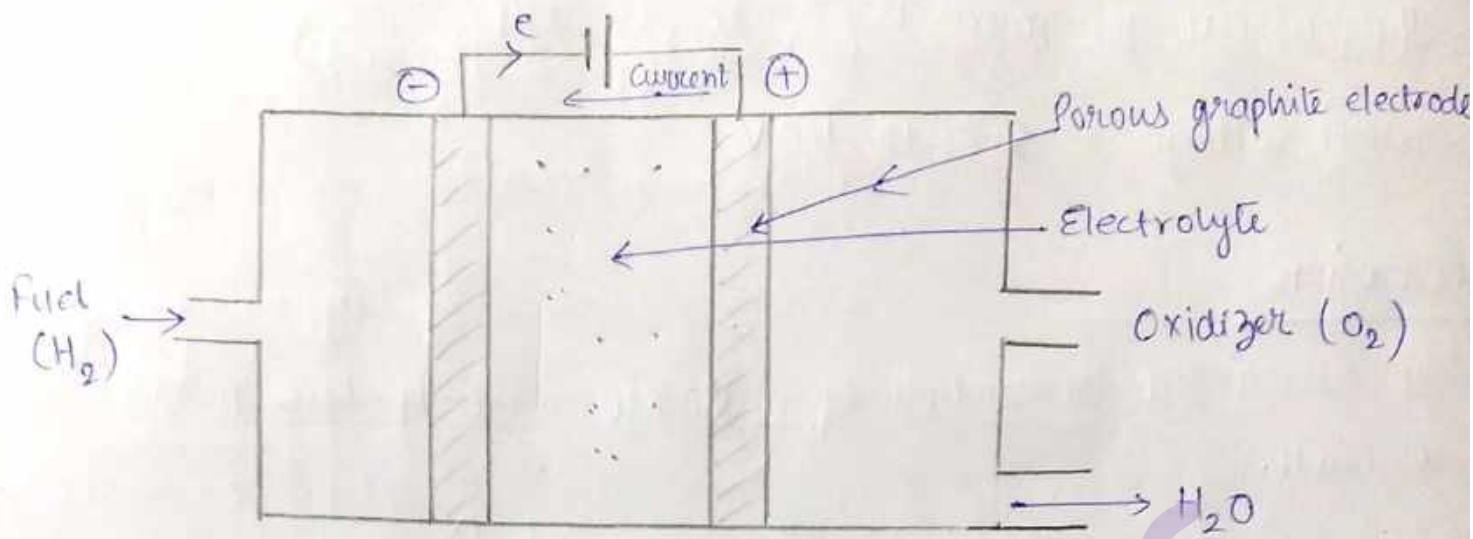
E.g. → Hydrogen, methane, butane, gasoline etc are converted directly into electrical energy.

→ Green technology.

H₂O₂ Fuel Cell

with

This cell is constructed of 2 porous electrodes impregnated with catalyst which sandwich an electrolyte



Fuel / Electrode / Electrolyte / Oxidant

Here the electrolyte is 25% KOH.

→ The electrodes are porous graphite coated with finely divided platinum or palladium.

Working principle

- ① Hydrogen → oxidised and the e⁻ lost in this process, migrate to cathode through the external metallic wire as shown in the figure.
- ② The O₂ diffuses ^{into} at the fuel cell at the cathode, which receives the e⁻ and get reduced to OH⁻ ions.
- ③ In the overall react "H" and "O" combine together to form water (H₂O) which drains out from the cell.
- ④ As long as the 'fuel' and oxidizer are supplied, the cell will continue to generate electricity.
- ⑤ The electrolyte plays a key role. It must ~~not~~ permit the appropriate ion to pass betⁿ anode to cathode.

The current generated is a DC current.

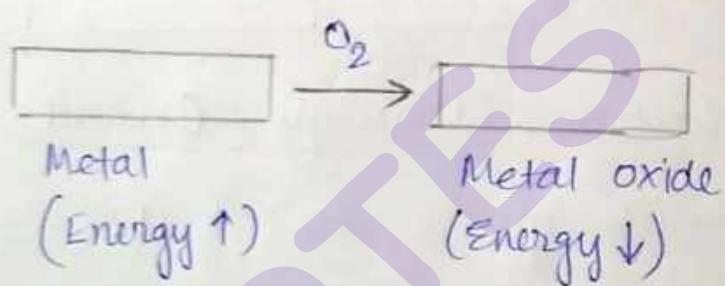
Output voltage = 0.8 to 1.0V.

Corrosion

The unwanted destruction of metallic wire is known as corrosion.

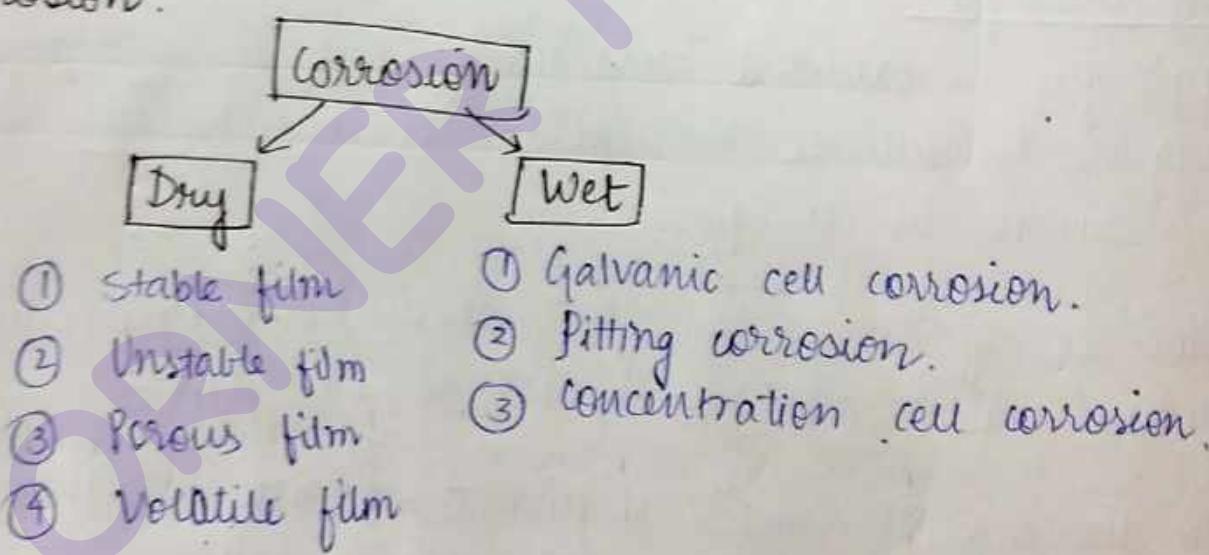
Hence, metal always

- wants to convert to it's oxide form. (Low energy form).

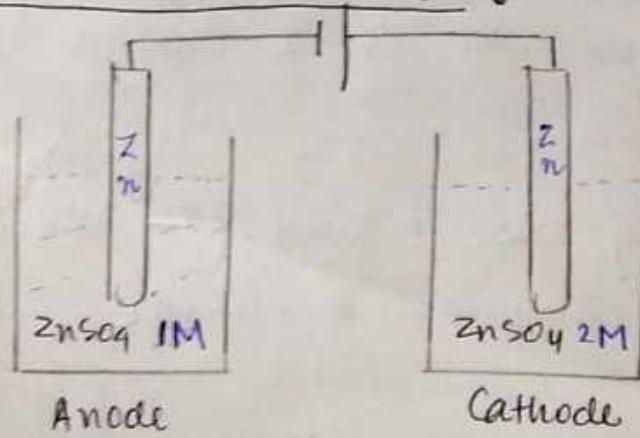


Types :-

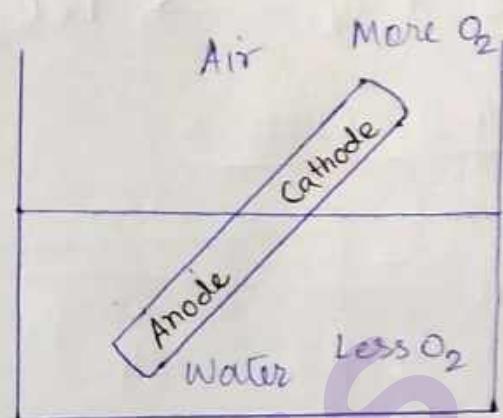
- 1) Dry corrosion
- 2) Wet corrosion.



Concentration cell corrosion :-



- In an electro-chemical cell, anode is always getting corroded.
- Such corrosion occurs when a metal surface is exposed to a conducting liq. of varying conc.
- The portion of metal that remains in contact with water or conducting liq. is less oxygenated area and the portion which is exposed to air → more oxygenated area.

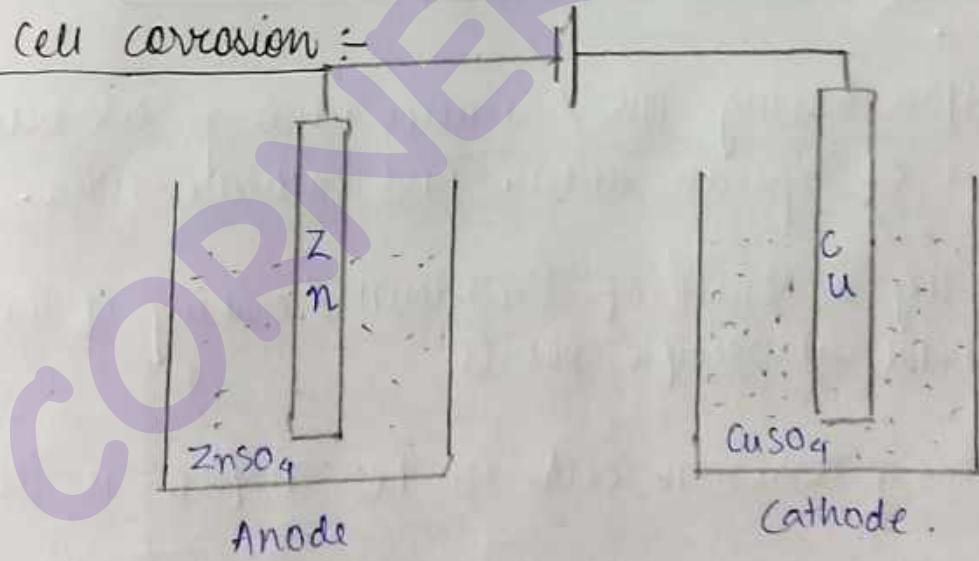


Hence, a natural galvanic cell will establish here.

Anode - The part of the metallic wire which is dipped inside water. as it is less oxygenated, corrosion will take place.

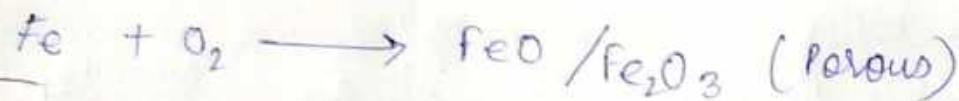
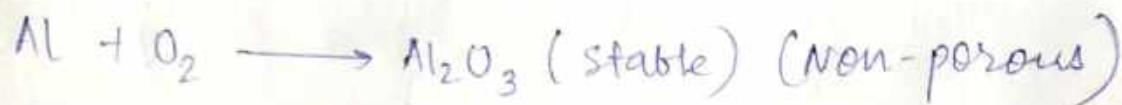
Cathode - No corrosion takes place.

Galvanic cell corrosion :-

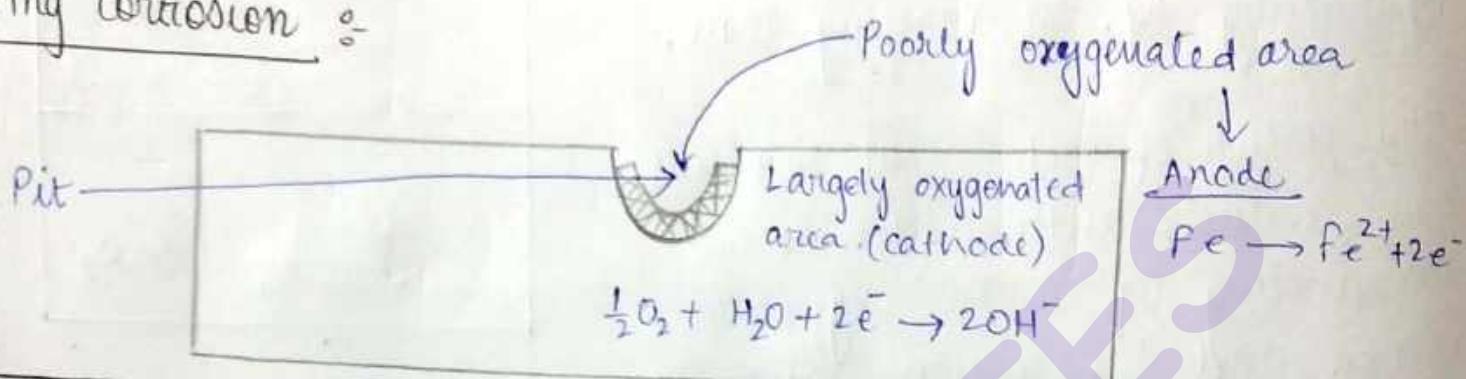


Anode is always getting corroded

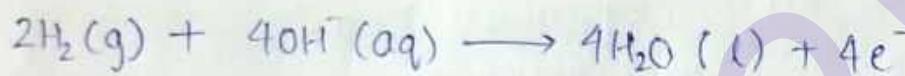
Hence, Zn will be corroded here.



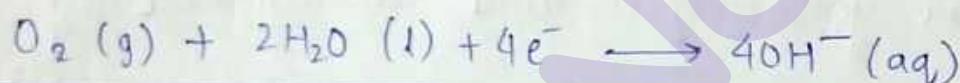
Pitting corrosion:



Anode



Cathode



Cell



Zn 0.76
↓
prone to oxidation

FUEL CELL REACTION

The metal surface having pits / cavities undergo corrosion due to development of separate anodic and cathodic area.

Pitting is usually a result of breakdown / cracking of the protective coating on a metal at specific points.

A typical pitting corrosion cell in Fe surface is illustrated above.

Here the corrosion is due to development of oxygen corrosion cell.

Remedies of corrosion :-

- If a metal is having more oxidation potential, it is very much prone toward oxidation.

Cathodic protection

The metal to be protected must be made cathode so as to avoid corrosion.

This can be achieved in 2 ways:-

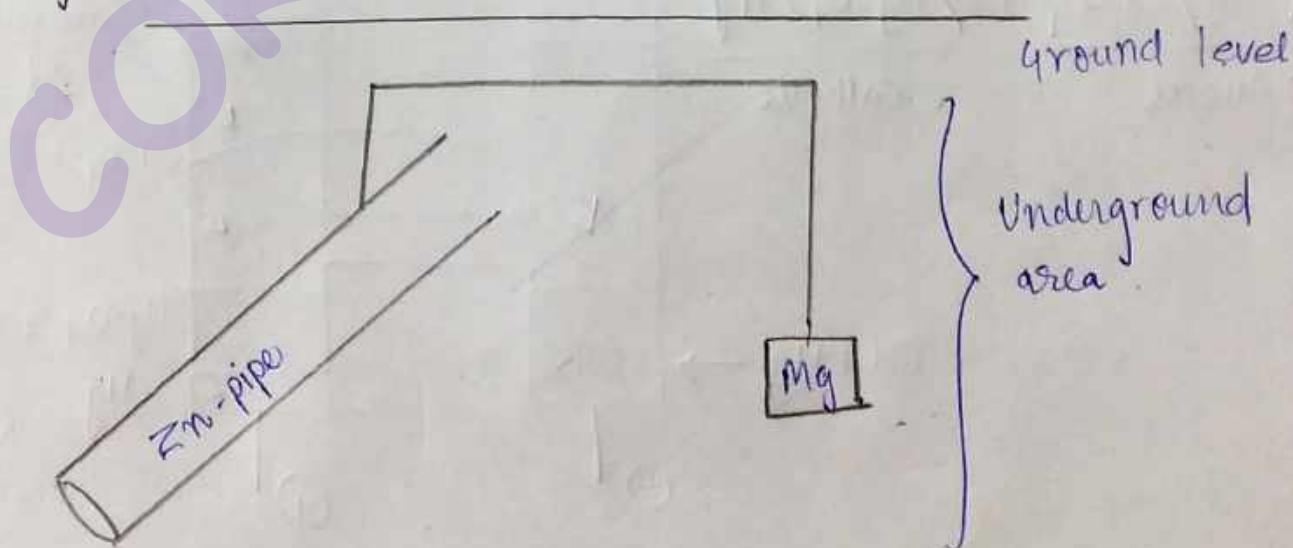
- 1) Sacrificial anodic protection
- 2) Impressed current cathodic protection.

Sacrificial anodic protection :-

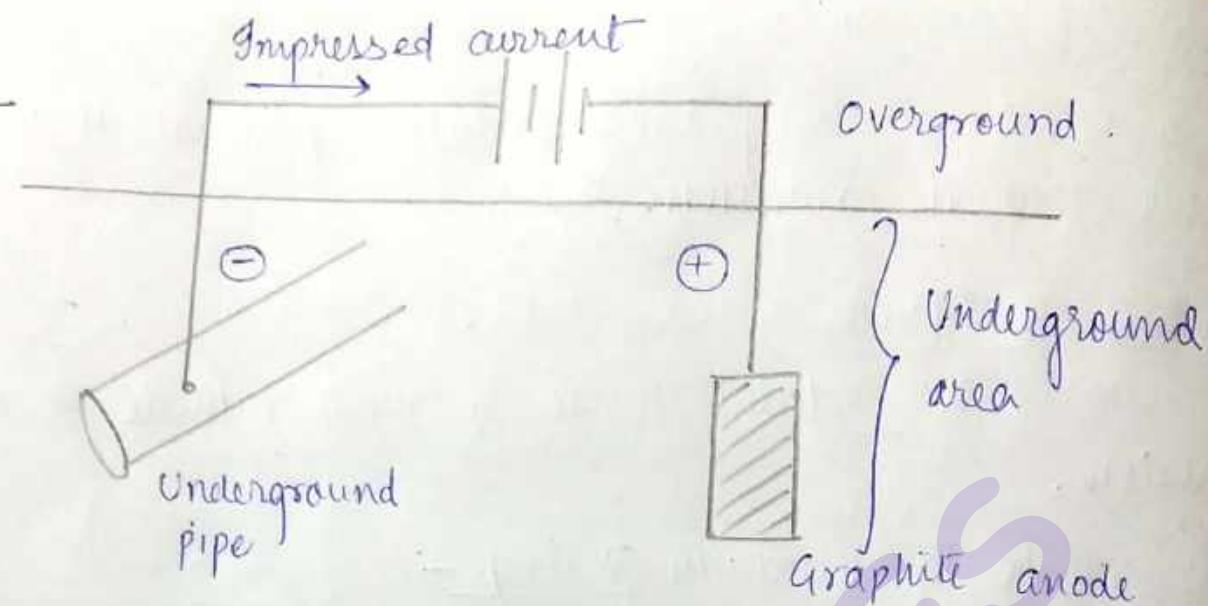
In this method, the metal to be protected is allowed to be connected to a more electropositive metal so that the latter operates as anode.

→ In this process of corrosion → Cathode is protected at the cost of anode which sacrifices itself in this process.

e.g. → Underground Zn pipe can be protected by coupling with Mg through a metallic wire.



Impressed current cathodic protection

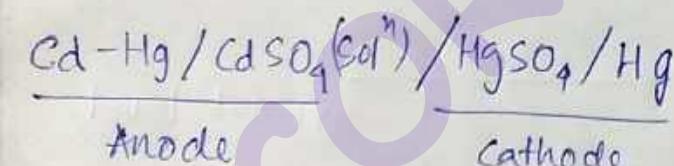


In this method an impressed current is allowed to pass through the circuit from an ext. DC source in an opp. directⁿ. As a result, anode is converted to cathode and protected from corrosion.

Standard cell

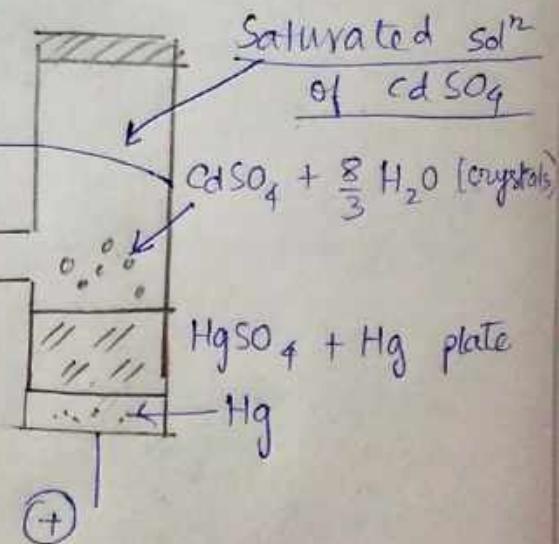
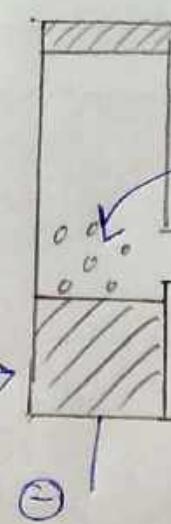
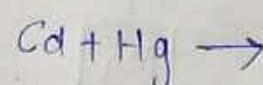
The cell which gives a constant output over a wide range of temperature.

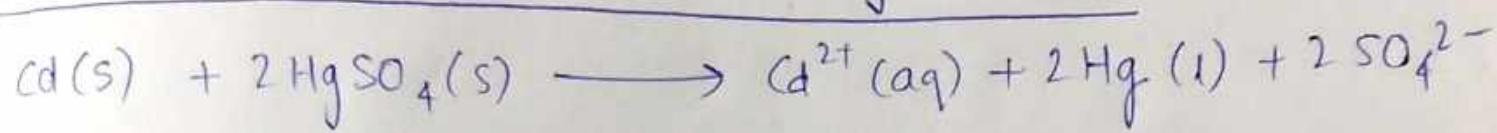
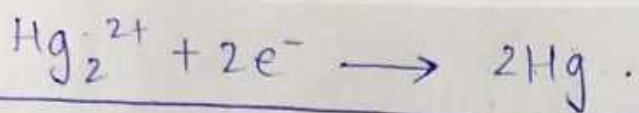
Eg → Weston standard Cadmium cell



Anode

cathode





Net output is 1.018V.