Module -5
chemistry

Phase Rule

phase rule is a generalilization given by williard Gibbs which seeks the equilibri Existing (1876) in heterogeneous systems.

Phase

Phase is defined as any homogeneous & uniform in composition, physical distinct portions of Matter which is mechanically separated from other such parts of the system by definite boundary surfaces & is in dynamic equilibrium with other pa

How to calculate no. of phases :-

① Mixture of Gas → Single phase. $P=1$

$$A_g + B_g \Rightarrow P=1$$

But if Vander waal force A >>> B

$$A_g + B_g \Rightarrow P=2$$

② Colloidal Solution ⇒ heterogeneous

p = no. of solute + solvent

③ True solution → homogeneous $P=1$

④ Polar + polar ⇒ $P=1$

eg $H_2O + C_2H_5OH$

non-polar + non polar ⇒ $P=1$

$CCl_4 + C_2H_5-O-C_2H_5$

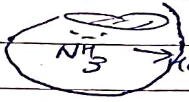
} Homogenous.

Polar + Non Polar ⇒ heterogeneous $\boxed{P=2}$
$H_2O + CCl_4$.

⑤ Gas in contact with liquid.
Gas + Liquid
↓ ↓
$SO_2 + H_2O$ ⟶ hetero $P=2$
But if dipole moment of gas ↑ stability↑
$NH_3 + H_2O$
$HCl + H_2O$ } Homogeneous $P=1$

⑥ Saturated solution above saturation → hetero $P \neq 1$
saturated solution below saturation → homo $P=1$

⑦ Mixture of solid → P = no. of solids ⇒ hetero
⑧ Alloy → Homo ⇒ $P=1$ Zn + Cu → Brass



⑨ $CaCO_{3(s)} \rightleftharpoons CaO(s) + CO_2(g)$ $P=3$

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ $P=2$

⑩ hydrate solution → each hydrate is a phase
$CuSO_4 \cdot 5H_2O + CuSO_4 \cdot 3H_2O + CuSO_4 \cdot H_2O \Rightarrow \boxed{P=3}$

Water consists of

Ice (s) $\rightleftharpoons$ Water (L) $\rightleftharpoons$ Water Vapour (g)

P = 3

Two immescible Liq (benzene & water) → P = 2
Two muscible Liq (alcohol & water) P = 1

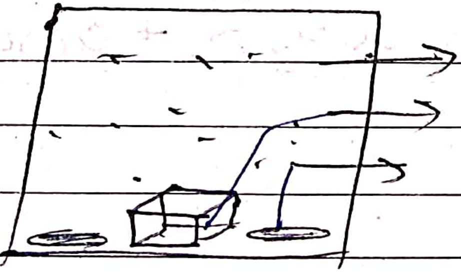
Component

Component is the smallest number of independent variable constituents in terms of which the composition of each phase can be expressed in the form of chemical equation

No. of components = No. of constituents − No. of eq^n relating to conc^n of constitu

$$\boxed{C = N - E}$$

eg. $H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$



$C = N - E$
$= 3 - 2$
$\boxed{C = 1}$

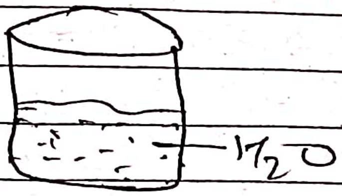
eg. $(S_{rhombic})_s + (S_{monoclinic})_s + S_{liquid} + S_{vapour}$

$p = 4$ $C = 4 - 3$

$\boxed{C = 1}$

eg. Sucrose solution

$\boxed{C = 2}$



eg. Saturated soln of NaCl consists of solid NaCl, NaCl soln & water vapour. The chemical comp. of all the three phases is NaCl & H_2O. Hence it is two component system.

$C = 2$

For chemically Reactive Reaction

No. of component (C) = constituents (N) − E

E → relation b/w them

N → every substance that can be separated from system

eg. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$P = 3$ $C = N - E = 3 - 1 \Rightarrow C = 2$

eg. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ $\boxed{p_{NH_3} = p_{HCl}}$

$P = 2$

$C = 3 - 2 = 1$

$C = 1$

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ $p_{NH_3} \neq p_{HCl}$

$C = 3 - 1 \Rightarrow C = 2$

water at its boiling point

$H_2O(l) \rightleftharpoons H_2O(g)$

$C = 2 - 1 = 1$

$\boxed{C = 1}$

① NaCl, KCl , Na^+ K^+ Cl^- $H_2O(l)$, $H_2O(g)$

Electrical Neutrality

⇓

Relation

⇒ electrical Neutrality | $NaCl \rightleftharpoons Na^+(aq) + Cl^-(aq)$

$KCl(s) \rightleftharpoons K^+ + Cl^-$

$H_2O(l) \rightleftharpoons H_2O(g)$

$C = N - E$

$C = \underset{\substack{\uparrow \\ \text{chemical species}}}{7} - 4 \Rightarrow \boxed{C = 3}$

Degree of Freedom :-

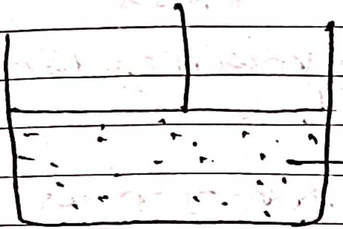
Degree of Freedom (DoF) is defined as the minimum number of independently variable factors, such as pressure, temperature & composition (conc^n or volume), which can completely define the equilibrium of a system.

The least no. of variable factors (conc^n, pressure & Temp) which must be specified so that the remaining variables are fixed automatically & system is completely defined.

Phase → (P)

component → $\boxed{C = N - E}$

H_2O

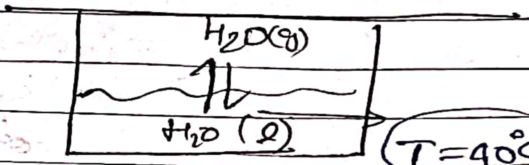


→ n = 2 moles

T, P, V → variables

↓

Minimum - 2 variable



T=40°C

P & T

Mono variant

$H_2O(s)$ $H_2O(l)$

$H_2O(g)$

Invariant

F = 0

Gibbs Phase Rule

Phase rule can be stated as in heterogeneou systems if equilibrium b/w phases are not influenced by gravity, magneti and electrical forces, but are influence only by pressure, temperature & concentration. then no. of degree of freedom of the system is related to no. of compone & no. of phases (P) by the following phase

$$\boxed{F = \underbrace{C}_{\text{component}} - \underbrace{P}_{\text{Phases}} + 2}$$

→ A system with F=0 is known as non-varient or having no dof

→ A sysem with F=1 is known as univarint or having one dof.

→ A system with F=2 is known as bivariant or having 2 dof.

1component system (C=1)

⇒ single phase $P = 1$ (ice / liquid / gas)

$F = 1 - 1 + 2$

$\boxed{F = 2}$ Bivarient

⇒ 2 phase

$H_2O(s) \rightleftharpoons H_2O(l)$

$H_2O(l) \rightleftharpoons H_2O(g)$

$F = C - P + 2$

$F = 1 - 2 + 2$

$\boxed{F = 1}$ monovarient

3 phase

ice ⇌ liquid ⇌ gas

$F = C - P + 2$

$F = 1 - 3 + 2$

$F = 1 - 1$

$F = 0$ Non-varent

when P ↑ F ↓

when Pmax then F = 0.

For Pmax.

$$0 = C - P_{max} + 2$$

$$\boxed{P_{max} = C + 2}$$

① 1 component

$C = 1$

$P_{max} = C + 2 = 1 + 2$

$$\boxed{P_{max} = 3}$$

② 2 component

$P_{max} = C + 2 = 2 + 2$

$$\boxed{P_{max} = 4}$$

F_{max} ↑ P_{min} ↓ $P \neq 0$

$$\boxed{F_{max} = C - P_{min} + 2}$$

$$F_{max} = C - 1 + 2$$

$$\boxed{F_{max} = C + 1}$$

for eg. $H_2O \longrightarrow F_{max} = 1 + 1 = 2$

$$\boxed{F_{max} = 2}$$

$$P_{max} = C + 2 \rightarrow \boxed{F = 0}$$

$$F_{max} = C + 1 \rightarrow P = 1$$

Merits of phase Rule

1. It is applicable to both physical & chemical equilibria.
2. It is a convenient method Of classifying the equilibrium states in terms of phases, components & degree of freedom.
3. It indicates different system with same degree of freedom behave similarly.
4. It helps us to predict the behaviours of a system under different sets of variables
5. It helps in deciding whether no. of substances remains in equilibrium or not

Limitations of Phase Rule :-

1. These rule is only applicable for those systems which are in equilibrium. It is not of much use for those systems which attain the equilibrium state very slow.
2. Only 3 variables like P, T & C are considered but not electrical, magnetic & gravitational forces
3. It is applied only to a single equilibrium system
4. It requires utmost care in deciding no. of phases existing in equilibrium.
5. Solid & liquid phases must not be in finely divided state otherwise deviations occur.

Derivation of Phase Rule :-

Consider a heterogeneous system in equilibrium, having Ⓒ components in which Ⓟ phases are present.
A/C to defⁿ of dof, Ⓕ - min. no. of independent variables which must be fixed arbitrarily to define the system completely.

No. of Independent Variables
= Total No. of Variables - no of relations b/w them at eqm.

Calculate total no of independent variables:

(1) Temperature : At eqᵐ, temp. of every phase is same so there is only one temp. variable of the entire system

(2) Pressure - At eqm, each phase has same pressure so there is only one pressure variable of the entire system.

(3) Concentration - concⁿ of each components is generally expressed in terms of mole fraction.

If we have C components we must know the concⁿ of C−1 components . So for P phases the total composition variables are $P(C-1)$.

Total no. of Variables.

$$= 1(\text{For temp}) + 1(\text{For press}) + P(C-1) \; (\text{For composition})$$

$$= P(C-1) + 2$$

when Phases are present, $(P-1)$ eqns are available for each component for C component total no. of eqns are $(C(P-1))$

F = Total no. of variables − no. of eqⁿs b/w them at

$$F = P(\cancel{C}-1) + 2 - C(\cancel{P}-1)$$

$$\boxed{F = C - P + 2}$$

Phase diagram

Phase diagram is a graph obtained by plotting one degree of freedom against another. If temp is plotted against pressure the diagram is called P-T diagram. Similarly, plot of temp against Composition is known as T-C diagram.

Systems are classified on the basis of no. of components into 3 types.

① one component systems
② Two component systems
③ Three component systems

Phase Diagram of one component system :-

In any system, the minimum no. of phases is 1

$$F = C - P + 2 = 1 - 1 + 2$$

$$\boxed{F = 2}$$

For one component system max no. of freedom is 2. The max no. of phases in any system is 3.

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$F = 0$ Minimum no. of dof = 0 for one component system.

Water system :-

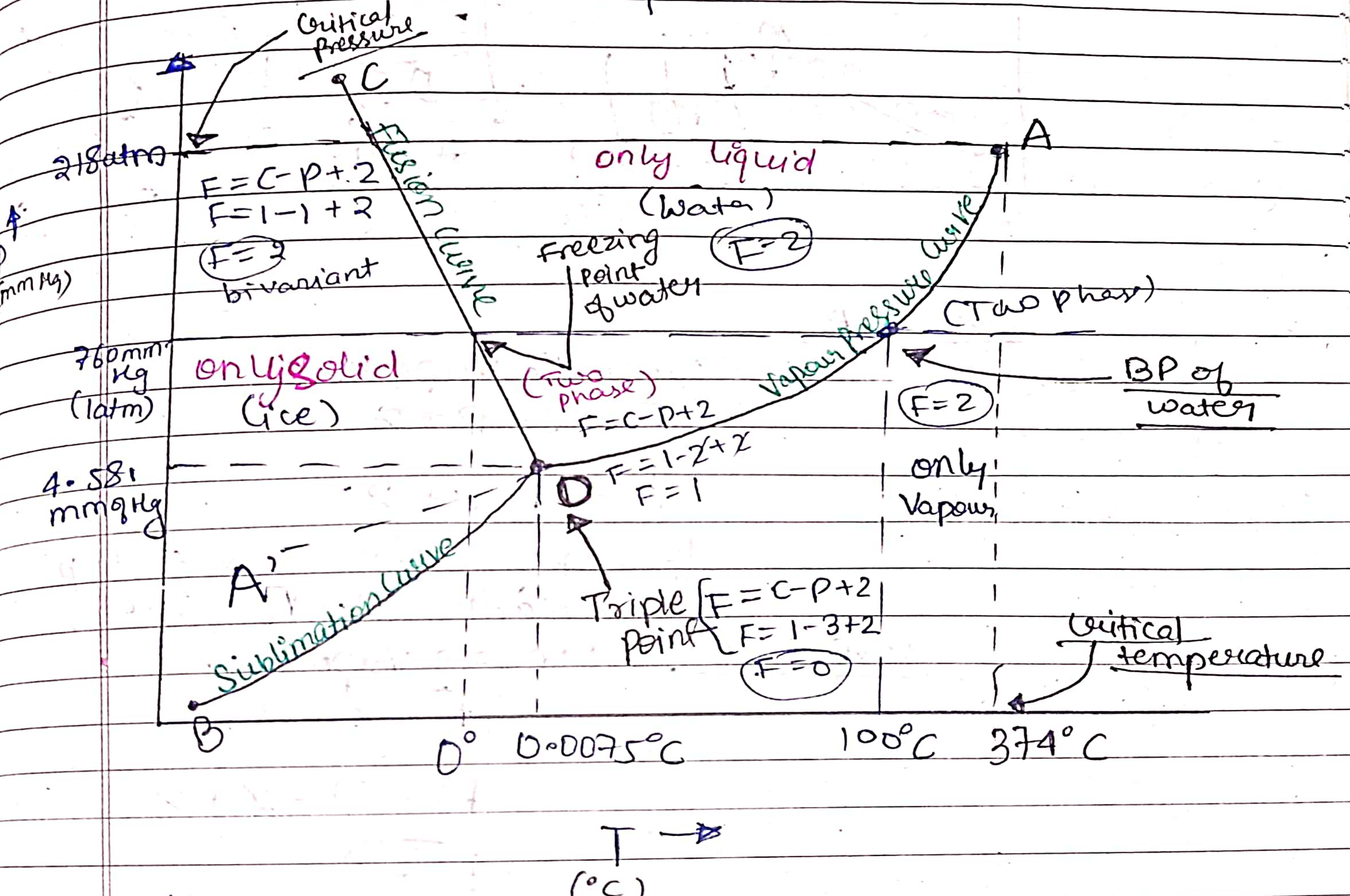
water exists in 3 possible phases namely solid, liquid & vapour.

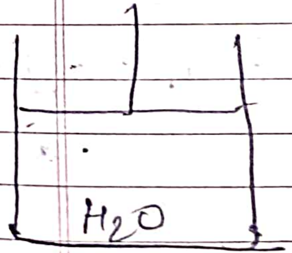
Three eqm with two phases for each eqm with two phases for each eqm.

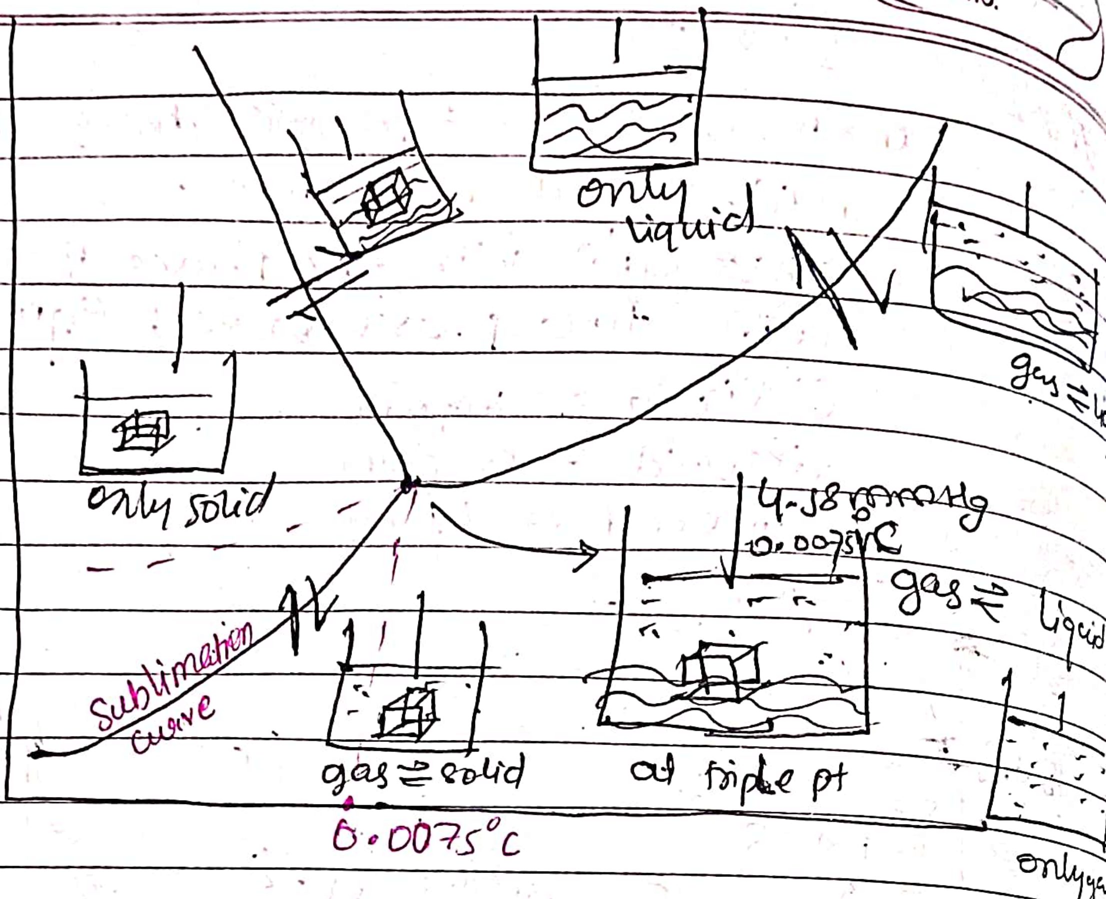
(i) Liquid ⇌ Vapour

(ii) Solid ⇌ Vapour

(iii) Solid ⇌ liquid.







Curve OA

Liquid ⇌ Vapour

$$F = C - P + 2$$

$$F = 1 - \cancel{2} + \cancel{2}$$

$$\boxed{F = 1}$$

univarient

eqm will extend up to T_c (374°C)

Curve OB

Ice ⇌ Vapour.

$$F = C - P + 2$$

$$F = 1 - \cancel{2} + \cancel{2}$$

$$F = 1$$

eqm will extend up to absolute zero

Triple point

Curve OA & OB meet at pt O where 3 phases (solid, liq and vap. coexist.) such a pt is called triple point.

Temp at the triple pt = 0.0078°C

Pressure at the triple pt = 4.58 mm Hg.

$$F = C - P + 2$$

$$= 1 - \cancel{2}3 + 2$$

$$\boxed{F = 0}$$ invarient

Curve OC

Ice ⇌ water.

$$F = C - P + 2$$

$$= 1 - \cancel{2} + \cancel{2}$$

$$F = 1$$ univariant

MP of ice ↑ by P↑

Curve OA'

super cool water ⇌ vapour.

$$F = C - P + 2$$

$$F = 1 - \cancel{2} + \cancel{2}$$

$$F = 1$$ univarient

Area OAB, OAC, BOC contain vapour, liquid & ice phases respectively within these single phase areas the system is bivariant $F = C - P + 2 \Rightarrow F = \cancel{1} - \cancel{1} + 2$

$$F = 2$$

1 component system

$F = C - P + 2$

$F = 1 - P + 2$

$\boxed{F = 3 - P}$

$P\uparrow \; F\downarrow \quad P_{min} = 1$

$F_{max} \; P = 1 \quad F_{max} = 3 - 1$ $\quad F_{max} = 2$

$F_{min} \; P_{max} = 3 \quad F_{min} = 3 - 3 = 0$

Invariant

↓

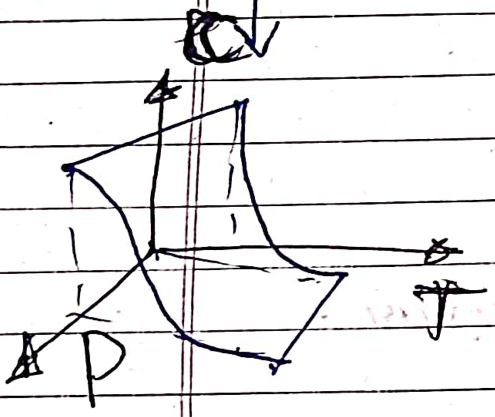
Triplet

Two component system

$F = C - P + 2$

$F = 2 - P + 2$

$\boxed{F = 4 - P}$



$F_{max} = ?$

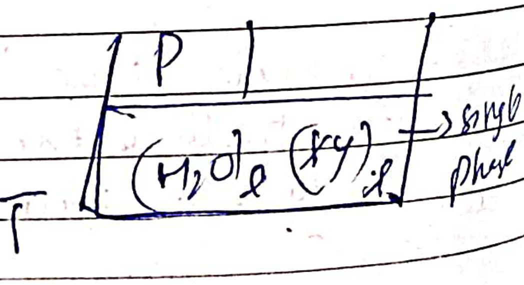
$P_{min} = 1$

$F = 4 - P$

$= 4 - 1$

$\boxed{F = 3}$

P T conc



Modify

$F' = (4 - P) - 1$

$\boxed{F' = 3 - P}$ Reduced Gibb's equation

T & Conc^n

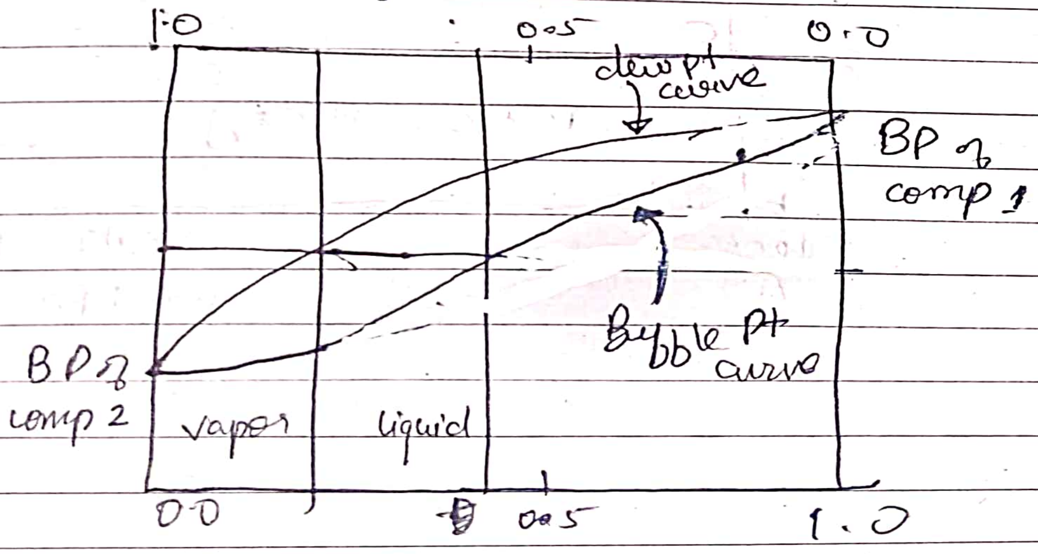
(A) ↓ (B)

miscible   Non-miscible.

↓

Eutectic mixture

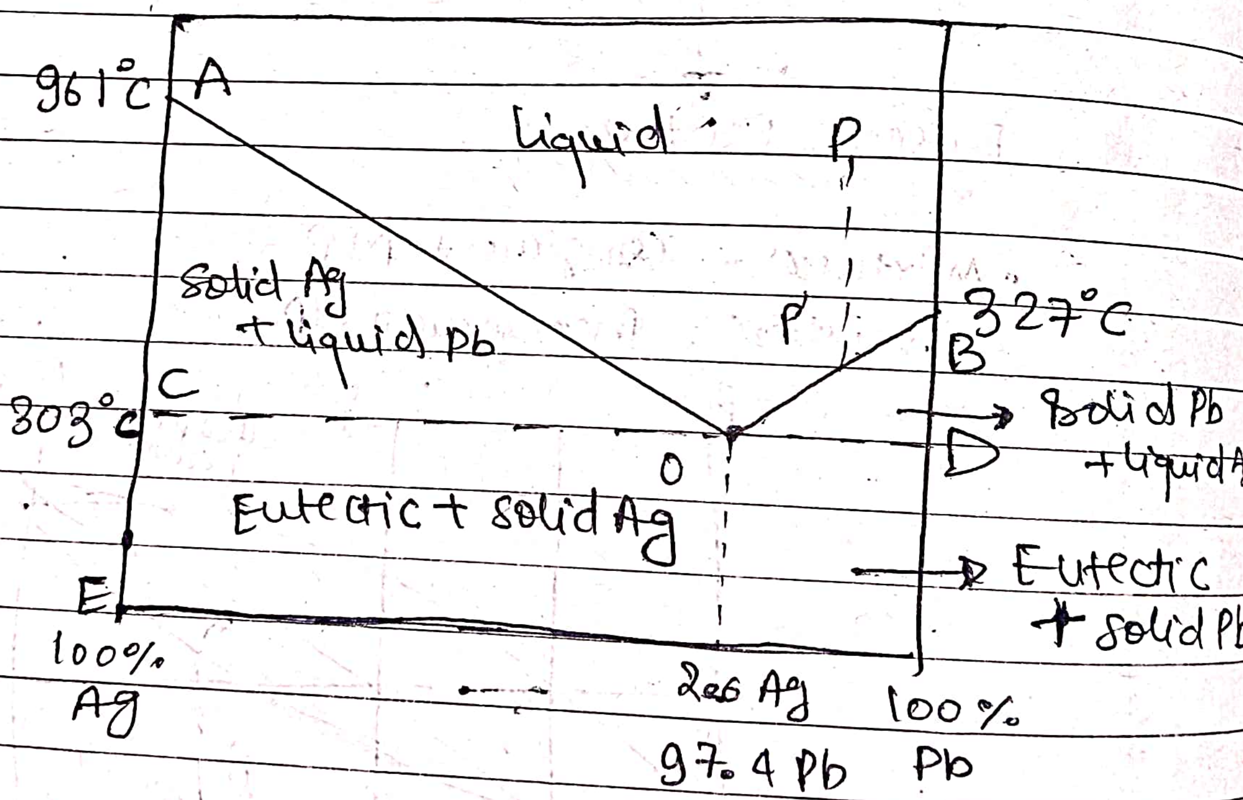
- Mixture - Congruent MP
- mixture - Incongruent MP.

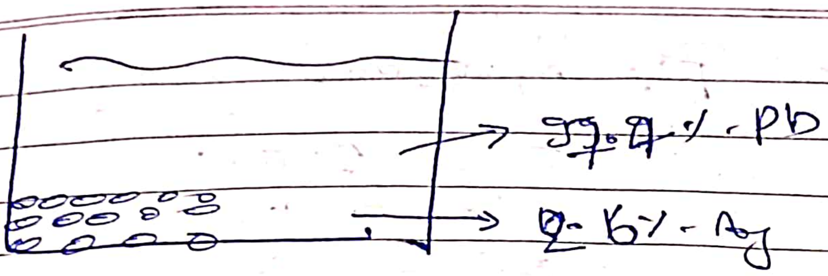


Simple Eutectic formation :-

If two substances are completely miscibl in the liquid state, but completely immisci in the solid state, form a simple eutectic. Of the various mixture one mixture has lowest MP such a mixture is known as a eutectic mixture.

Pb-Ag system





Pb → solidification

when Pb starts solidify the % composition of Ag in solution (liquid)

Curve AO : A : MP of Pure Ag (961°C)
AO : (Melting Pt depression of Ag by addition of lead.

$F = C - P + 1$

$F = 2 - 2 + 1$

$F' = 1$ Univarient

Curve BO B : MP of Pure Lead (327°C)
BO : melting pt depression of lead on gradual addition of Silver.

O (Eutectic Pt) : (Ag = 2.6%. Pb = 97.4%.)
temp 303°C (eutectic temp.

$F = C - P + 1$

$F' = \cancel{2} - \cancel{P} + \cancel{3}$

$F' = 0$

invarient

Area
AOB : Pb Ag soln

$F' = C-P+1$

$F' = 2-1+1$

$\boxed{F'=2}$ bivariant

Applications :

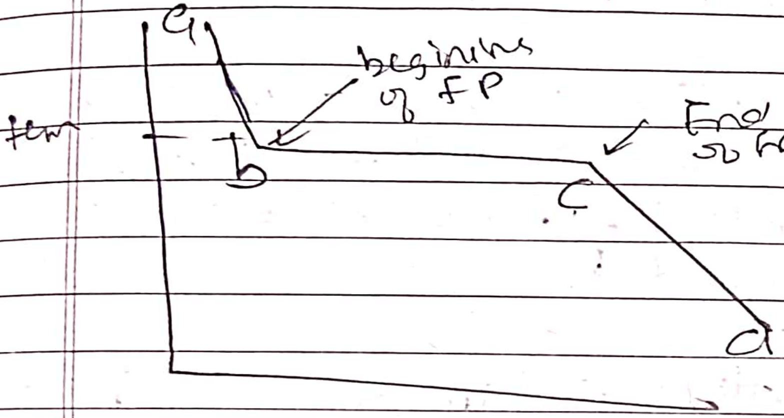
(1) Pattison's Process :-

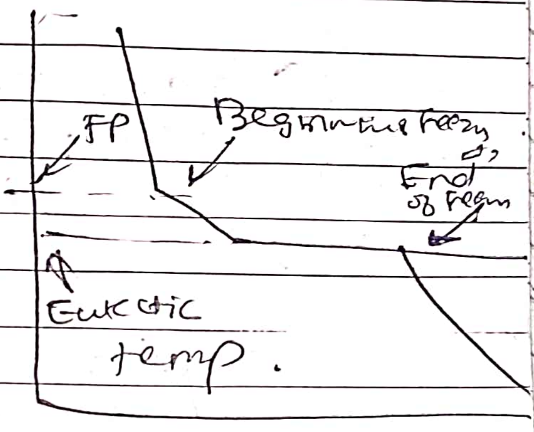
If a sample of Argent ferrous lead, containing less than 2.6 % Ag is allowed to cool gradually lead will separate out & the solution will become progressively riches in Ag till the % 2.6 of Ag is reached and on further cooling the whole mass will solidify as such. on other hand, if lead-silver allow containing Ag greater than 2.6% is allowed to cool, & then pure silver separates along the curve AO, till the eutectic composition at O is reached.

② Thermal analysis or cooling curve :—

The shape of cooling curve can be determined by thermal analysis. Thermal analysis is a method involving a study of cooling curves of various compositions of a system during solidification

The cooling curve is obtained by plotting fall of temp. with time.





a compd is said to possess incongruent MP if it decomposes completely at a temp below MP yielding a new solid phase with a composition diff from original.

Uses

① MP & Eutectic temp can be noted from cooling curve

② Percentage purity of the compd can be known

③ Behaviour of compd can be used to derive the phase diagram of any two component system

Heat treatmement of steel

→ Hardening : plunging into cold or oil to 200°C
(lower temp

Temp is carried about 200°C to
make hard steel resistant to abrasion
or higher temp (~540°C) to
make tough steel capable of
with standing shock loads.

→ Casehardening : Surface treatment by which
inside soft core of steel is hardened
on the surface. Low C steels are
case hardened $

Cyaniding : Article is immersed in a molten
bath of sodium.

Nitriding hard surface on alloy steels
heating alloy in presence of ammonia
to about 550°C . form .

Annealing Involves heating & holding steel
at suitable temp for some times
to facilitate the dissolution
of carbon in γ-iron followed
by slow cooling in a controlled
manner in a furnace

Chemical Equilibrium

Rxns which occur in one direction are called Irreversible reactions.

$C + O_2 \rightarrow CO_2$

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

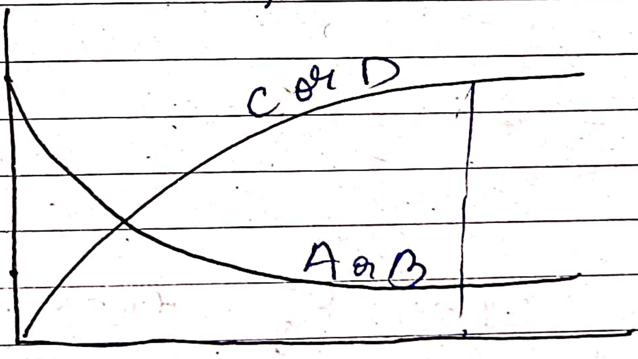
$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Reversible rxn : In certain condn of T & P

If Forward & reverse rxn occurs simultaneously then rxn is reversible.

A reversible rxn is said to be in eqm state when Forward & backward rxn occur simultaneously at same rate in closed system.

$A + B \rightleftharpoons C + D$



~~Charackristic~~
Properties of equilibrium state :-

(I) Chemical eqm is dynamic in nature

(II) Eqm can be attained from either side

(III) Eqm can be attained ~~from~~ in a closed system

(IV) A catalyst can't change eqm state.

Law of chemical equilibrium

$$aA + bB(g) \rightleftharpoons cC(g) + dD(g)$$

Forward Rxn rate = Backward rxn Rate

$$K_1 [A]^a [B]^b = K_{-1} [C]^c [D]^d$$

$$K_c = \frac{K_1}{K_{-1}}$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Law of chemical eqm defined as ratio of pdt of concn of product to product concn of reactant with each concn raised to power by

Eqm constant & Gibbs free energy :—

$$\Delta G^0 = -RT \ln K_{eq}.$$

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

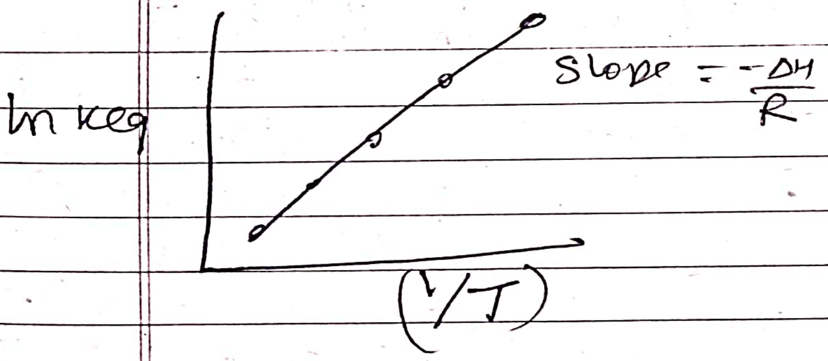
$$-RT \ln K_{eq} = \Delta H^\circ - T\Delta S$$

$$\boxed{\ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S}{R}}$$

$$\boxed{\ln \frac{K_2}{K_1} = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Exothermic Reaction

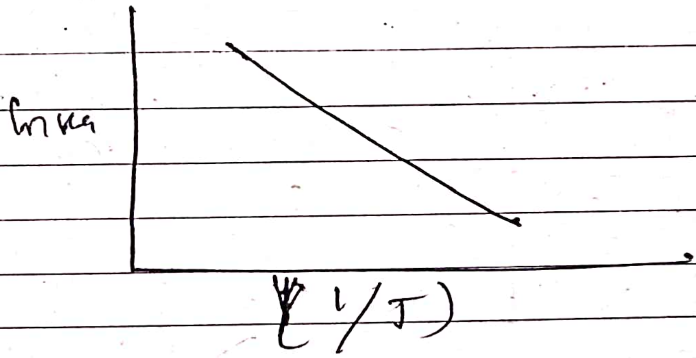
- heat is released
- $\Delta H < 0$ $\left(-\frac{\Delta H}{R} \Rightarrow +ve\right.$ slope)
- Van't Hoff Plot has positive slope



Endothermic Reaction

- heat is absorbed
- $\Delta H > 0$ $\left(-\frac{\Delta H}{R} \Rightarrow -ve\right)$ slope

→ Van't Hoff Plot has −ve slope



Q. what is equilibrium constant? what is Kp & K_c? What are their significances?

Ans → The concⁿ values in the law of equilibrium are the eqm concⁿ of reactants & products. K_c is called concⁿ eqm constants

In case of gases their partial pressures can also be used in the place of molar concⁿ ($\because P \propto C$) the eqm Kp is called pressure equilibrium constant.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI$$

$$K_c = \frac{[HI]}{[H_2][I_2]} \qquad Kp = \frac{P_{HI}^2}{P_{H_2} P_{I_2}}$$

$$aA(g) + B(g) \rightleftharpoons cC(g) + dD(g)$$

$$\boxed{K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}}$$

$$\boxed{Kp = \frac{P_C^c \, P_D^d}{P_A^a \, P_B^b}}$$

Eqm constant changes when temp changes.

magnitude of eqm constant is a measure of the extent upto which a reaction proceeds before equilibrium is reached.

K is large ⇒ Pdt is present in larger amt than rxt.

Types of chemical Equilibria.

Two types of chemical equilibria :- ① Homogeneous Equilibria
② Heterogeneous Equilibria.

Homogeneous Equilibria :-

The equilibrium rxn in which all the reactants & the products are in same phase are known as homogeneous equilibrium reactions.

No. of Pdt molecules = No. of reactant molecules

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

No. of Pdt molecule ≠ No. of reactant molecules

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

In gaseous phase $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$

In soln phase $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$

$CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

The eqm constant for homogeneous rxn in gaseous systems :

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

$$P = CRT \qquad R = 0.0831 \text{ bar L}$$

$$aA + bB \rightleftharpoons cC + dD.$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_p = \frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b}$$

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

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

Δn = No. of moles of gaseous pdt − No. of moles of gaseous reactants

Heterogeneous equilibria :-

The eqm rxns in which reactants & products are present in different phases are known as heterogeneous equilibrium rxn.

$$CaCO_3(s) \underset{}{\overset{\Delta}{\rightleftharpoons}} CaO(s) + CO_2(g)$$

$$K_c = \frac{[CaO_{(s)}][CO_2(g)]}{[CaCO_3(s)]}$$

$$K_c' [CO_2(g)]$$

$$\boxed{K_p = P_{CO_2}}$$

Electrochemistry

weak & strong electrolytes :-

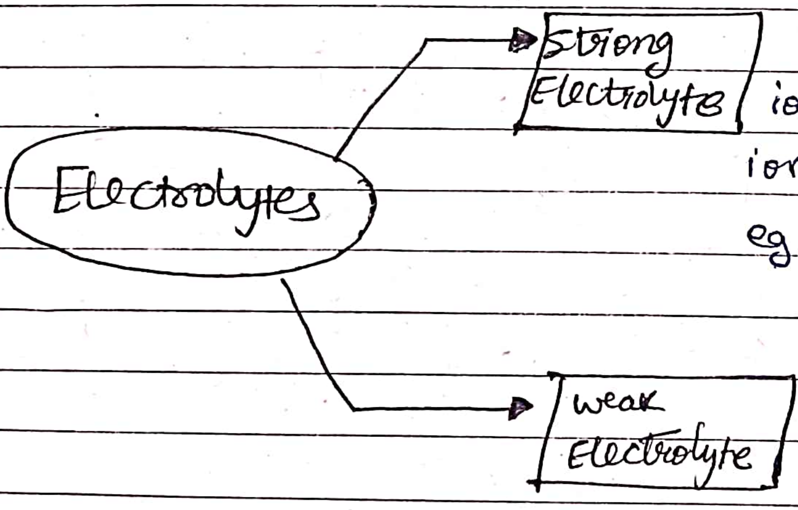
A redox rxn involves transfer of e⁻s from one chemical species to another.

Amt of moles) of salt that has made soln saturated per Litre of soln is called solubility of Salt.

AB salt

$$AB \rightleftharpoons A^+ + B^-$$

Those substances which allow the passage of electricity by way of aqueous solution or fused state & undergo chemical decomposition are called electrolytic conductors eg. Acid, base & salt soln.



Those electrolyte which ionise or dissociate into ions are known as strong electrolytes

eg. HCl, NaOH, K_2SO_4

Those electrolytes that dissociate partially ($\alpha < 1$) are known as weak electrolyte

eg. CH_3COOH, H_2CO_3, NH_4OH, H_2S, etc.

The energy from a redox rxn can be used to accomplish work by constructing an electrochemical cell. In an electrochemical cell, oxid^n & red^n process are separated into two half cells connected by an external wire. The cell with oxidation process is losing negative charge (e^- loss) while the half cell with the reduction is gaining -ve charge (e^- gain).. To connect the two half-cells to permit the transfer of ions b/w two sol^n & maintain electrical neutrality in both half cell a salt bridge must complete the ckt. b/w half cell.

Transfer of e^- through external wire create a current that can do work. The driving force pushing e^-s through wire is diff in attraction of e^- in two half cells. This voltage diff is called cell potential (E_{cell}) & is measured in Volts.

General representation of Electrochemical cells :-

Parameter	Cathode	Anode
Sign	+ve (due to consumption of e^-)	-ve (due to
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

Standard Electrode Potential (E^0_{cell})

$$\boxed{E^0_{cell} = E^0_{Reduction} + E^0_{oxidation}}$$

Standard conditions (1 M soln
1 atm pressure
298 K

What is EMF? Describe measurement of EMF of a cell?

Ans → The Voltage, which we usually refer to as cell potential is the potential difference between the electrodes and if the difference b/w the half-cell potentials of the right & left sid

$$E_{cell} = \Delta V = V_{right} - V_{left}$$

eg. $E_{cell} = V_{Cu} - V_{soln} + V_{soln} - V_{Zn}$ //

Reversible EMF of a cell is the EMF under the condition where rxn occurring in the cell is infinitesimally slow ie - practically no current is flowing.

Nernst eqn

$$\boxed{E_{cell} = E^0_{cell} - \frac{0.059}{n}\log Q}$$

Q : reaction Quotient
n : no. of e^- transferred.

~~E~~c. SHE electrode

$Pt \mid H_2(g) \mid H^+(aq) \parallel M^{2+}(aq) \mid M(s)$

$E_{cell} = V_m - soln$

$\frac{1}{2} H_2(g) \rightarrow H^+ + e^-$

$H_2(g) + M^{2+} \rightarrow 2H^+ + M(s)$

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

Batteries :-

A battery is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery.

An ideal battery would never run down, produce an unchanging voltage & be capable of withstandin environmental extremes of heat & humidity. Real batteries strike a balance b/w ideal & characte & practical limitations.

eg. mass of a car battery is about 18kg or 1% of mass of an average car or light-duty truck.

This type of battery could supply nearly unlimited energy if used in a smartphone but could be rejected for this application b'coz of its mass.

Thus no single battery is "best" & batteries are selected for a particular application keeping things like the mass of the battery, its cost, reliability & current capacity in mind.

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There are two basic types of batteries

(1) Primary Battery

(2) Secondary Battery

① Primary Batteries

→ Primary Batteries are single-use batteries b'coz they cannot be recharged.

→ A common primary battery is Dry cell.

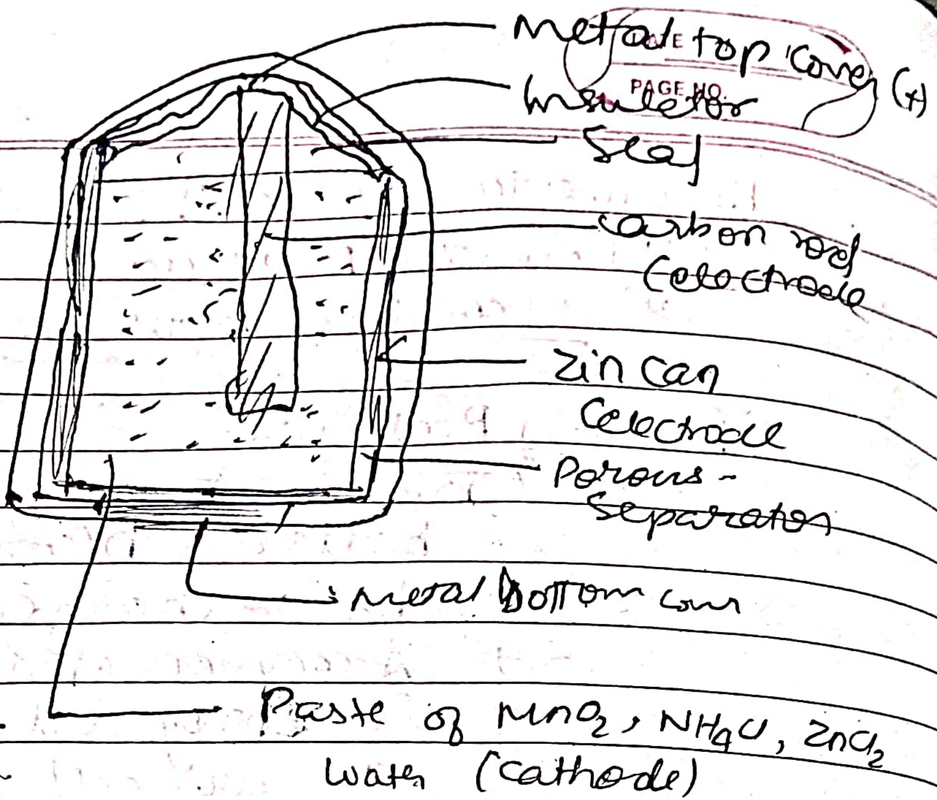
The dry cell is zinc-carbon battery.

The Zinc can serve as both a container & the -ve electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of Manganese (IV) oxide, Zinc chloride & Ammonium chloride, carbon powder & a small amount of water.

Anode (oxidⁿ) : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $E^\circ_{Zn^{2+}/Zn} = -0.76V$

Cathode (Redⁿ) : $2MnO_2(s) + 2NH_4Cl(aq) + 2e^- \longrightarrow \underset{(s)}{Mn_2O_3} + \underset{(aq)}{2NH_3} + H_2O(l)$ $+ Cl^- /6$

Overall Reaction : $\underset{(s)}{2MnO_2} + \underset{(aq)}{2NH_4Cl} + \underset{(s)}{Zn} \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2Cl^-$



Alkaline batteries They were developed in 1950s partly to address some of the performance issues with zinc-carbon dry cells. They are manufactured to be exact replacements for Zn-C dry cell. As name suggest these type of batteries use alkaline electrolytes, often potassium hydroxide.

Anode : $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

$E^\circ_{anode} = -1.28V$

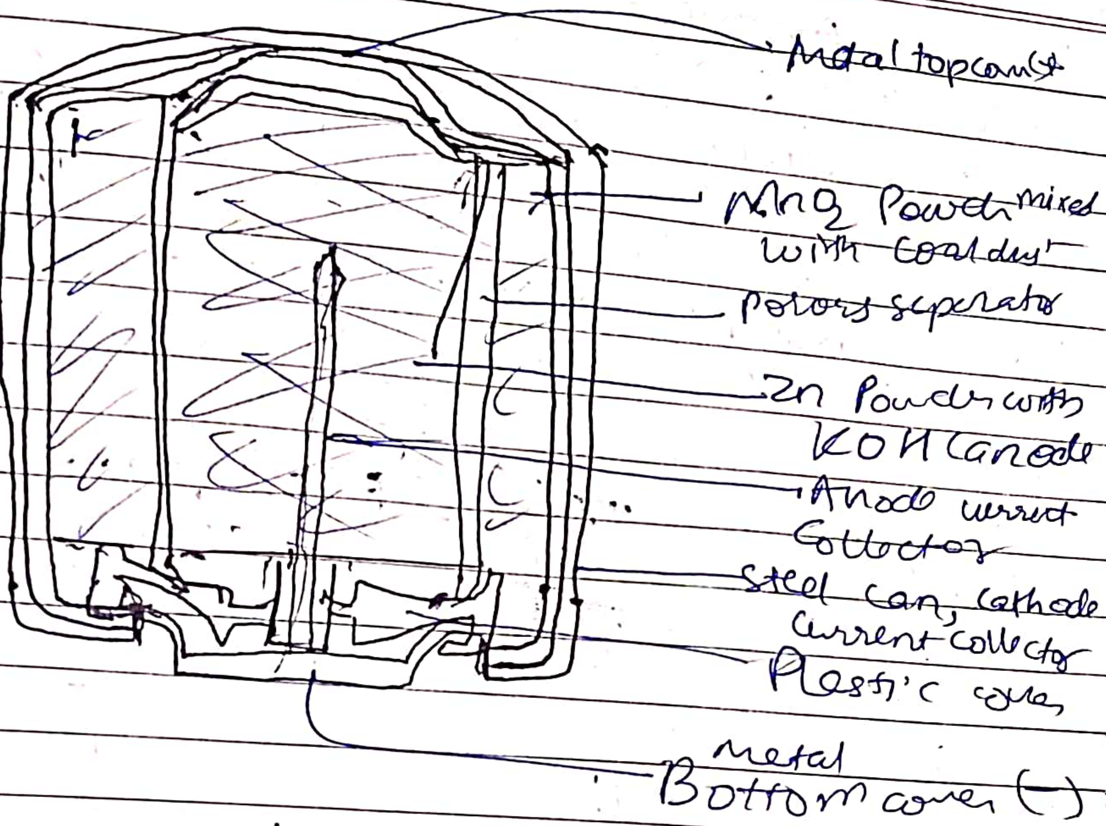
cathode : $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-$

$E^\circ_{cathode} = +0.15V$

overall : $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$. $E^\circ_{cell} = +1.43$

$$\boxed{E^\circ_{cell} = E_{cathode} - E_{anode}}$$

~~Secondary Batteries~~



Secondary Batteries

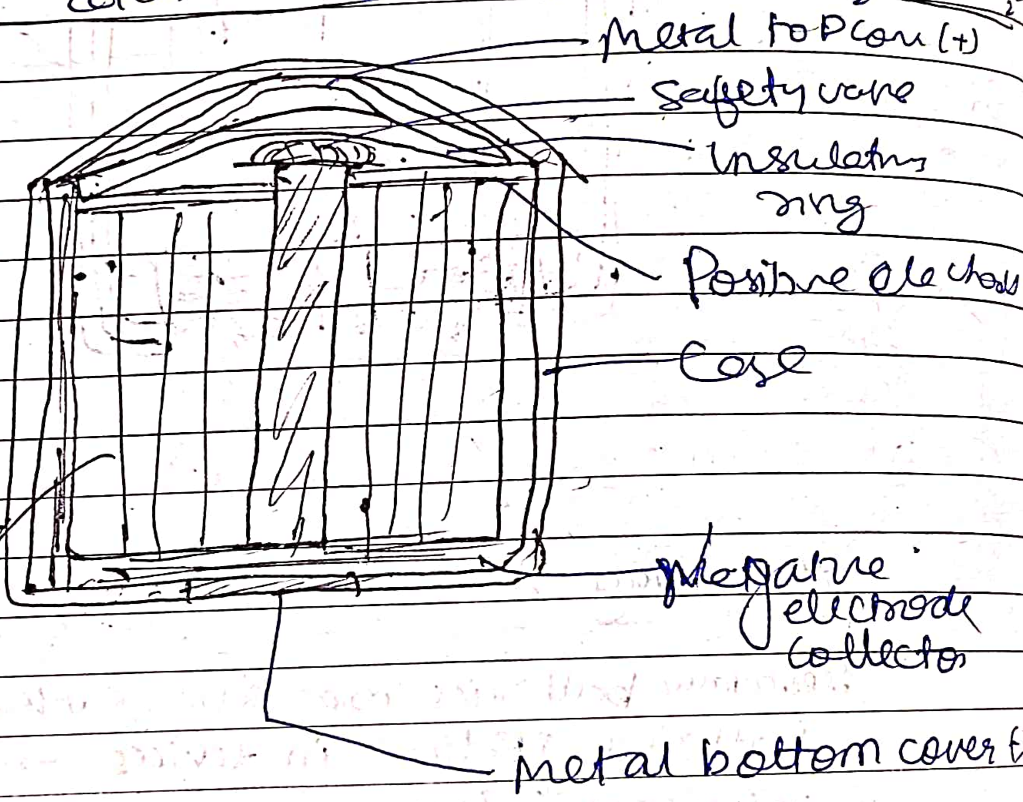
Secondary batteries are rechargeable. These are types of batteries found in devices such as smartphones electronic tablets & automobiles.

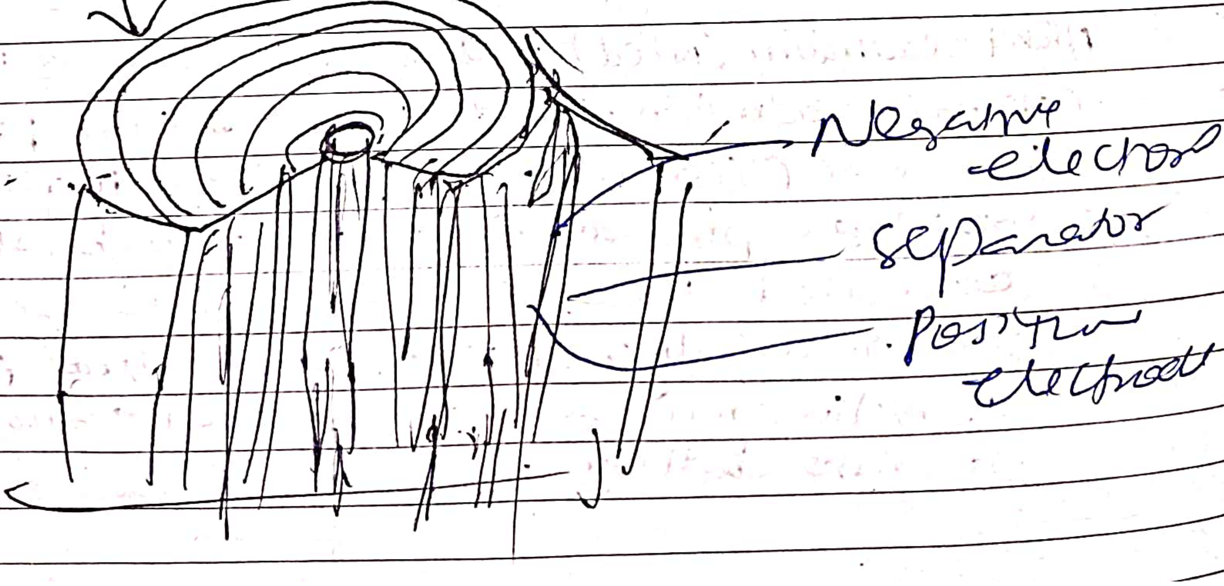
Nickel-cadmium (NiCd) batteries consist of a nickel-plated cathode, cadmium plated anode and a potassium hydroxide electrode. The positive & negative plates which are prevented from shorting by the separator are rolled together and put into the case. This is a jelly roll design and allows the NiCd cell to deliver much more current than a similar sized alkaline battery.

Anode : $Cd(s) + 2OH^-(aq) \longrightarrow \underset{(s)}{Cd(OH)_2} + 2e^-$

Cathode : $NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + \underset{(aq)}{2OH^-}$

Overall : $Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$



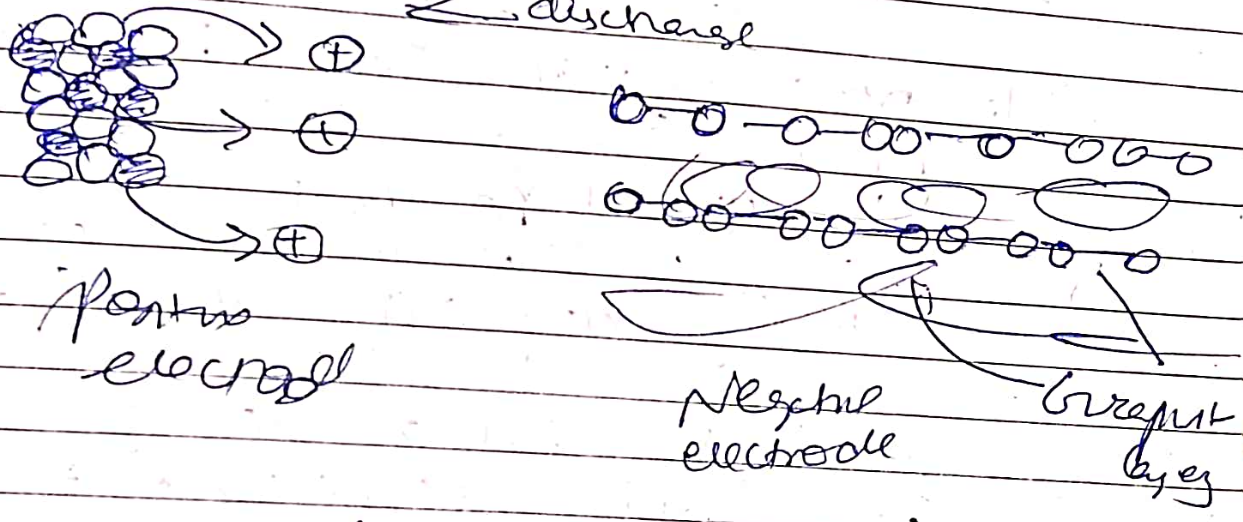


Lithium ion batteries It is the most popular rechargeable batteries and are used in many portable electronic device

anode : $LiCoO_2 \rightleftharpoons Li_{x-1}CoO_2 + xLi^+ + xe^-$
Cathode : $xLi^+ + xe^- + xC_6 \rightleftharpoons xLiC_6$

Overall rxn : $LiCoO_2 + xC_6 \rightleftharpoons Li_{x-1}CoO_2 + xLiC_6$

Charge →
← discharge



Lead acid battery : It is type of secondary battery used in your automobile it is inexpensive & capable of producing high current required by automobile the rxn

anode: $Pb(s) + H_2SO_4^-(aq) \rightarrow PbSO_4(s) + 2H^+(aq) + 2e^-$
Cathode : $PbO_2(s) + H_2SO_4^-(aq) + 2H^+(aq) + 2e^- \rightarrow PbSO_4 + 2H_2O(l)$

overall rxn : $Pb(s) + PbO_2 + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

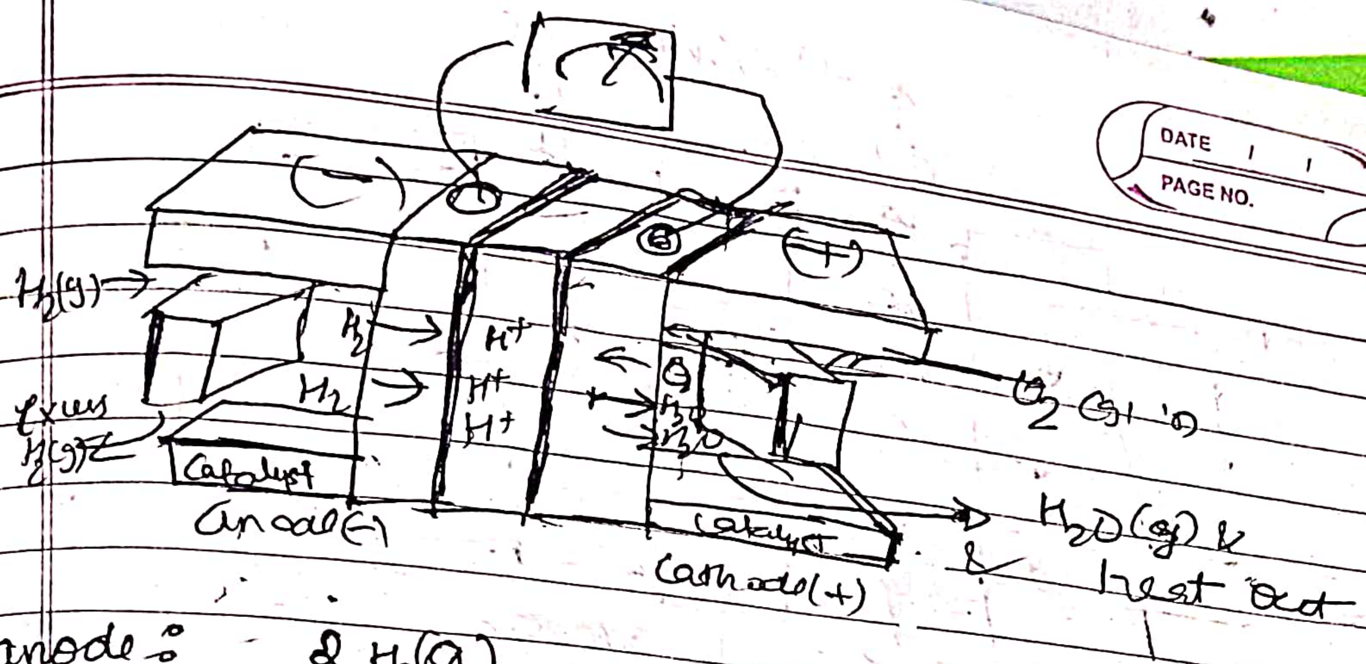
Describe principle of fuel cell.

Fuel Cells A fuel cell is a galvanic cell that requires a constant external supply of reactants b/coz pdt of reaction are continuously removed. Unlike battery, it does not store chemical or electrical energy a fuel cell allows electrical ~~current~~ energy to be extracted directly from a chemical reaction

In principle, this should be a more efficient process than eg. burning fuel to drive an internal combustion engine that turns a generator which is typically less than 40% efficient.

Efficiency of a fuel cell is generally 40%-60%. unfortunately significant cost & reliability problems have hindered the wide scale adoption of fuel cells

In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles. These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ & $O_2(g)$ as illustrated in fig.

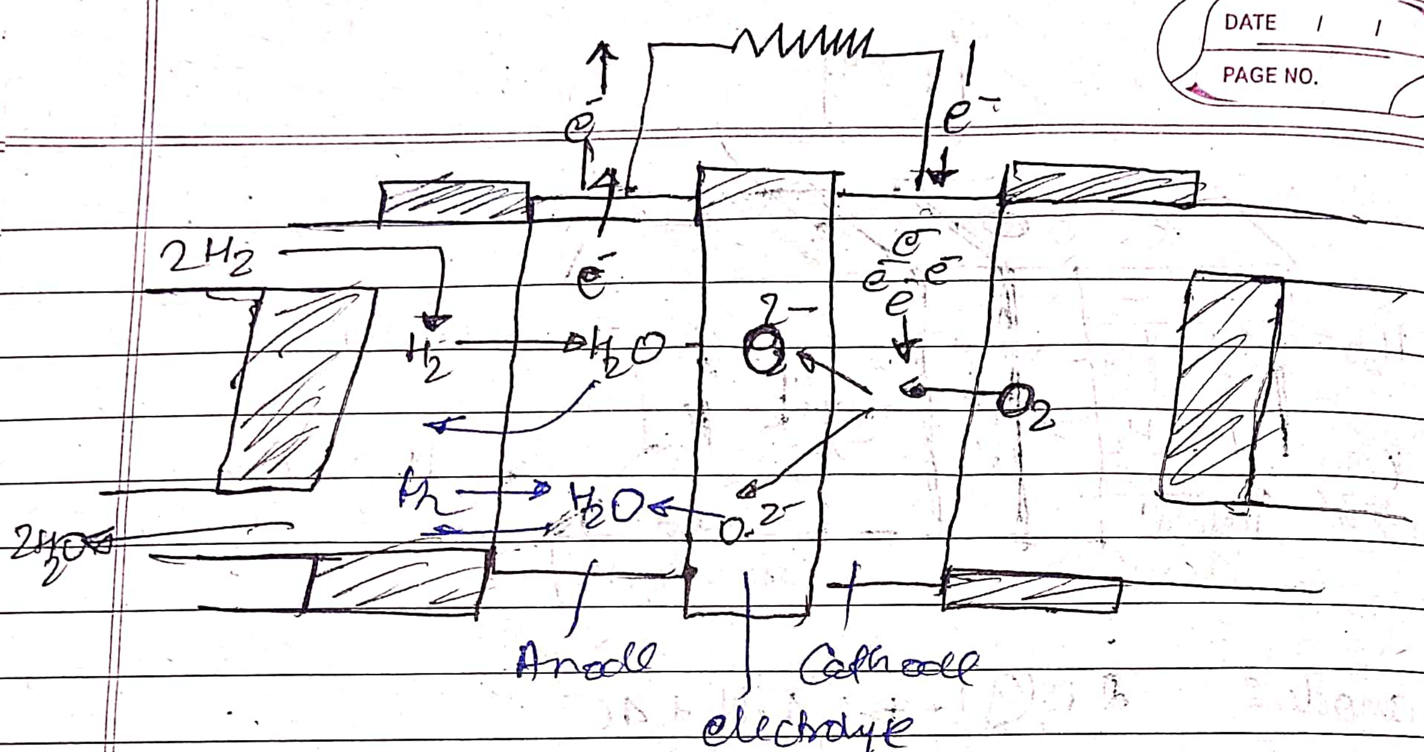


anode: $2H_2(g) \rightarrow 4H^+ + 4e^-$

cathode: $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(g)$

overall $2H_2(g) + O_2 \rightarrow 2H_2O(g)$

The overall rxn ~~Q~~represents an essentially pollution - free conversion of Hydrogen & oxygen to water which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23V under standard conditions. in practice the device achieves only about 0.9V. one of the major barriers to achieving greater efficiency is the fact that $4e^-$ reduction of $O_2(g)$ at cathode is intrinsically rather slow, which limits the current that can be achieved. All major automobile manufactory have major research programs involving fuel cells: one of the most important goals in the development of a better catalyst for the reduction of $O_2(g)$.



A fuel cell requires an external supply of reactants as pdt of rxn are continuously removed.