# UBA49-ENGINEERING CHEMISTRY CONCEPT MAPPING

# CHEMISTRY OF SEMICONDUCTORS

## Definition

Semiconductor
- @ Low Temp → Insulators — No free electrons
- @ High Temp → Conductors — free electrons.

## Primary Classifications

**Elemental / Intrinsic (Pure) @ RT**
* Electron - Hole pair created
* Low current cond.

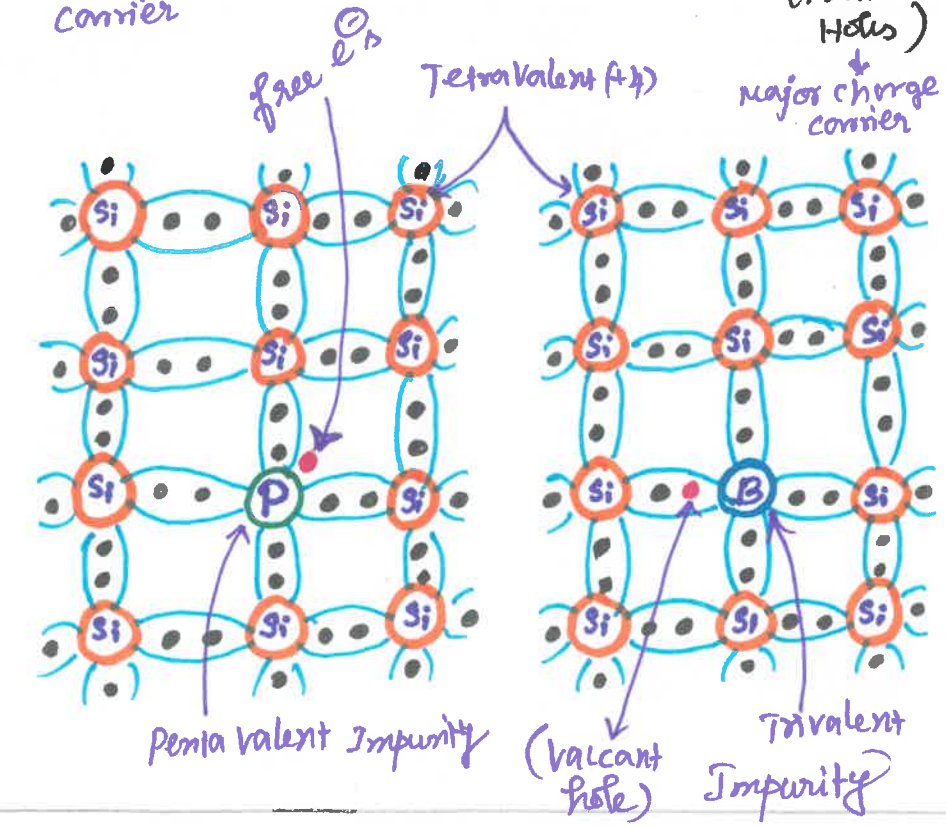
Eg: Si, Ge

**Compound / Extrinsic (Impure)**
* Electron - Hole pair created by adding Impurities (Dopping)
* High Current Cond.

Eg: GaAs / GaP

Major charge carrier ← N-type (negative electron)

P-type (Positive Holes) — Major charge carrier

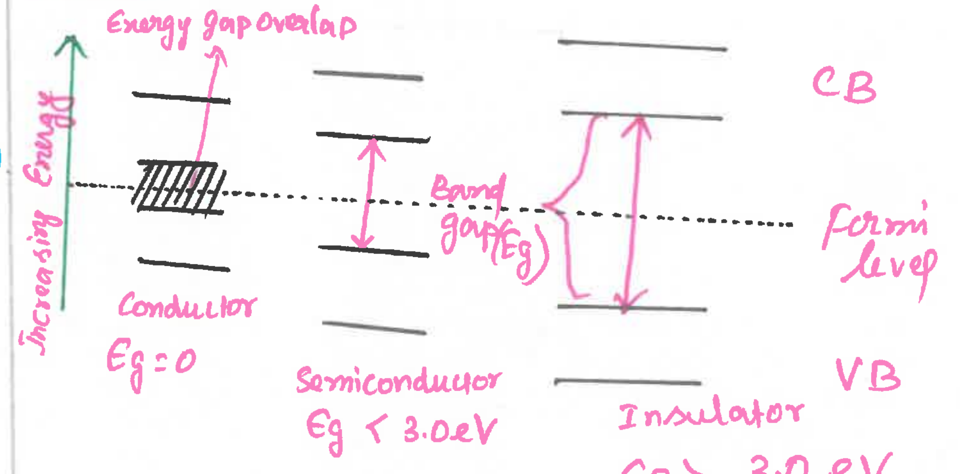


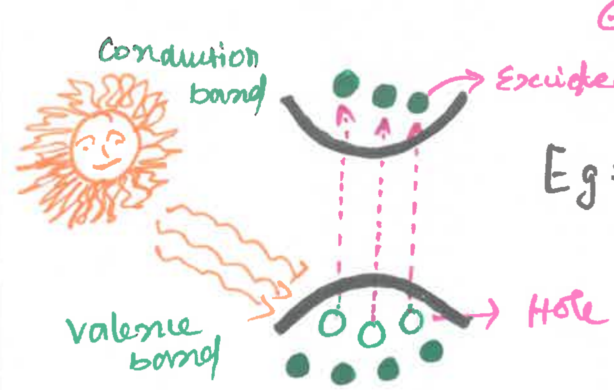

## Elements of Semiconductors

| II | III | IV | V | VI |
|---|---|---|---|---|
| | B | C | N | |
| | Al | Si | P | S |
| Zn | Ga | Ge | As | Se |
| Cd | In | Sn | Sb | Te |
| Hg | Tl | Pb | Bi | |

- → Elemental
- → Binary SiGe, SiC
- → Binary - InP, GaAs
- → Ternary Eg: HgCdTe.
- → Quaternary Eg: InGaAsP
- HgTe, CdSe

## Band Gap




$E_g = h\nu = \frac{hc}{\lambda}$

$\therefore \nu = \frac{c}{\lambda}$

- Find the room temperature electrical conductivity of silicon that has been doped with $1.0 \times 10^{23}\ m^{-3}$ of arsenic atoms. Assume values for electron and hole mobilities of $0.065 \times 0.22\ m^2/Vs$, respectively.

$\sigma = n * e * \mu_n$ $= 1.602 \times 10^{-19} C * 1.0 \times 10^{23} e/m^3 * 0.065\ m^2/Vs$

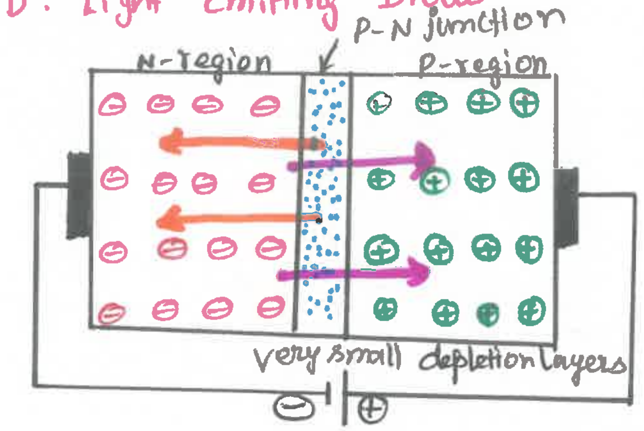
$\sigma$ = Electrical Conductivity $= 1.602 \times 10^{4}\ C/m^3 * 0.065\ m^2/Vs$

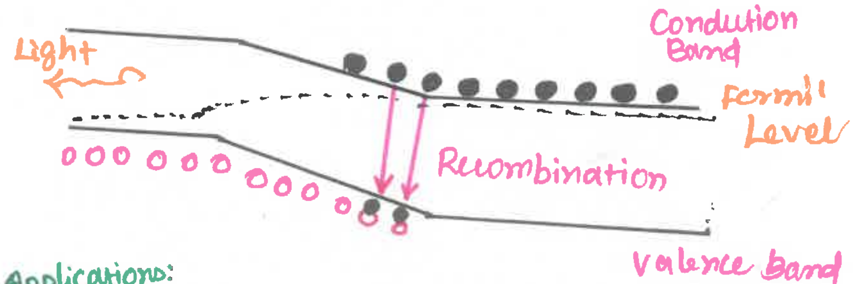
n: Electron concentration $= 1.0413 \times 10^{3}\ S/m$

e: Elementary Charge ($\sim 1.602 \times 10^{-19} C$) $= 1041\ S/m$

## SEMICONDUCTORS IN OPTICS

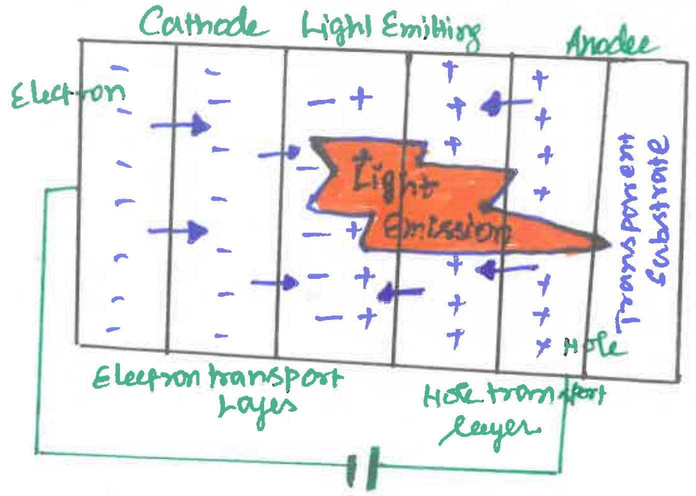
**LED: Light Emitting Diode**




Applications:
- → Sensors, Mobiles
- → Traffic signals etc.,

**OLED: Organic Light Emitting Diode**




Electric Current ⇒ Organic compound ⇒ Light.

Advantages:
* less power consumption
* Thin display
* low cost ; Safe Environment.

Disadvantages:
* less light span
* Easily damageable

## PERODIC TRENDS:

Relationship between periodic trends and metallic character

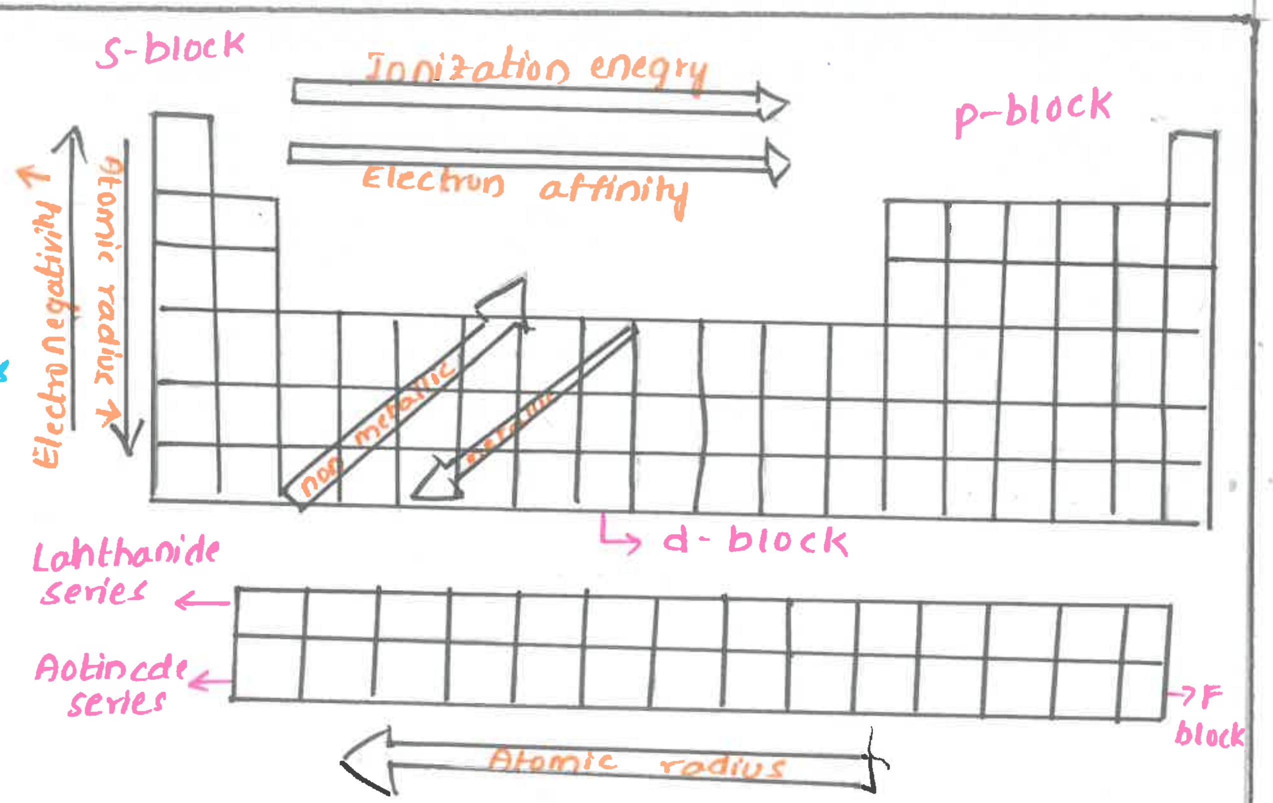
Across A period

Metallic character decreases

Ionization Energy Increases: Elements less likely to lose electrons

Electronegativity Increases: Element more likely to gain electrons

Atomic Radius Decreases: Smaller atomic size makes it harder to lose electrons.




Down a Group

Metallic character Increases:

Atomic Radius : Larger atomic radius single makes it easier to lose electrons

Ionization enegry decreases: Elements more likely to lose electrons

Electro Negativity decreases: Elements less likely to gain electrons

### ATOMIC RADIUS

Outer most shell

Nucleus ($e^-$, proton & Neutron)

* Distance between Centre of Nucleus, outermost shell

Across the period

From Left to Right:

* Atomic no ↑
* no. of proton ↑

Nuclear charge } outermost shell pull

Atomic radius ↓

Top to bottom:

* No. of shell increases
* outermost shell away

Atomic Radius ↑

### IONIZATION ENERGY

* Removal of an $\bar{e}$

$\boxed{Metal + I.E \rightarrow M^+ + \bar{e}}$

From left to right:

* Atomic size ↓
* Electrons are tightly
* Require lot of enegry to remove an $\bar{e}$

Ionization energy ↑

Top to bottom:

* Atomic size increases
* outmost shell away from the centre of nucleus
* It Requires less amount of enegry of $\bar{e}$

Ionization energy ↓

### ELECTRONEGATIVITY

* Attraction of $\bar{e}$

$\boxed{Atom + \bar{e} \rightarrow A^- + E\uparrow}$

From Left to Right:

* Atomic size ↓
* Attraction of $\bar{e}$ toward nucleus ↑
* So, greater affinity of $\bar{e}$ towards the nucleus

Electronegativity ↑

Top to bottom:

* Atomic size ↑, Lesser attraction of $\bar{e}$
* So, Lesser affinity of $\bar{e}$

Electro negativity ↓

### ELECTRON AFFINITY

* Ability to hold the $\bar{e}$

$\boxed{C + \ddot{O}: \rightarrow CO_2}$

From left to right:

* Atomic size ↓
* outmost shell pull closer
* Increased attraction of $\bar{e}$

Electron affinity ↑

Top to bottom:

* Atomic size ↑

Lesser attraction of $\bar{e}$

* Increased outermost

Electron affinity ↓

### METALLIC CHARACTER

* How atom readily lose an $\bar{e}$

$\boxed{Na \rightarrow Na^+ + \bar{e}}$

From left to right:

* $\bar{E}$ are tightly held in out-most
* Hard to remove an $\bar{e}$

Metallic character ↓

Top to bottom:

* outmost shell away from centre of radius
* Easy to remove an $\bar{e}$ from outmost

Metallic character ↑

# Types of Semiconductors

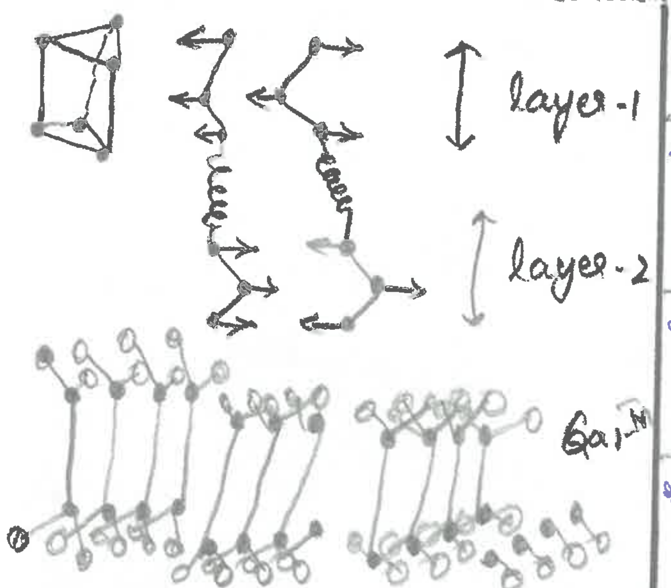
## Metal Oxide Semiconductors (MOS)

Most Oxides are good insulators

Ex - $CuO$, $Cu_2O$, etc.

Metal + Oxygen ⟶ Metal oxide
Basic in nature

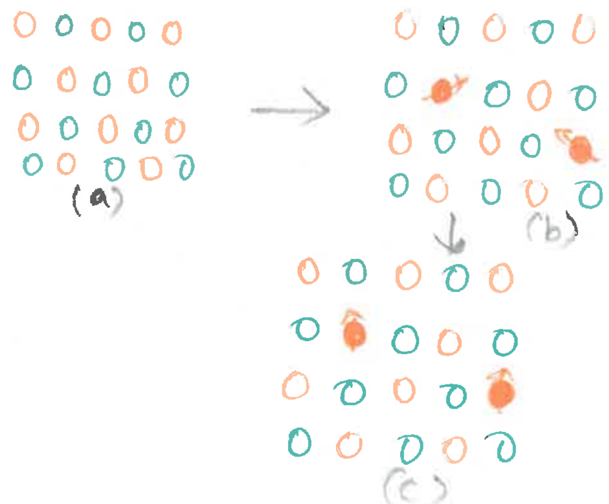
* Contain an anion of oxygen in the Oxidation state of '-2'
* II - VI compound Zinc Oxide ($ZnO$) having application as a transducer and as an ingredient of Adhesive tapes
* $CuO$ and $Cu_2O$ showed Super-conductivity.
* $La_2CuO_4$, Eg of about 2eV is called as high-Tc Super-conductor




for this discovered thing, Bednorz and Muller recieved the physics Noble prize in 1987.

## Magnetic Semiconductors

* In Corporating Mechanism into existing Semiconductor Structure by a Magnetic dopant [Cr, Mn, Fe]
* the Exchange coupling between these dopants leads to magnetic Properties




| | |
|---|---|
| * Ferromagnetic ↑↑↑↑↑↑↑↑ | Below Tc, spins are aligned parallel in magnetic domains |
| * Antiferromagnetic ↑↓ ↑↓ ↑↓ | Below $T_N$, Spins are aligned in Antiparallel in magnetic domain |
| * Ferrimagnetic ↑↓ ↑↓ ↑↓ | Below Tc, Spins are aligned anti Parallel but do not cancel |

## Colours & Semiconductors

→ Colour due to $\boxed{\text{Light}}$ → $\boxed{\text{Spectrum}}$ → $\boxed{\text{Visible Region}}$

$\boxed{\text{Spectrum}}$ ← $\boxed{\text{Bundle of Radiations}}$ → $\boxed{\text{Each radiation having own wave length}}$ → $\boxed{\text{Visible 370 - 720 nm}}$ ⟶ $\boxed{\text{Part of light}}$

→ Colour Appearance

→ [When hit / pass light on] The Surface of material

Transmission, Absorption, Emission, Refraction

* With Respect material λ value will change

$E = Mc^2$ - Light - photon - $h\nu$

$E = hc/\lambda \Rightarrow E_g = hc/\lambda$

Visible wavelength 370-720 nm

Respective Eg Range 1.6 - 3eV

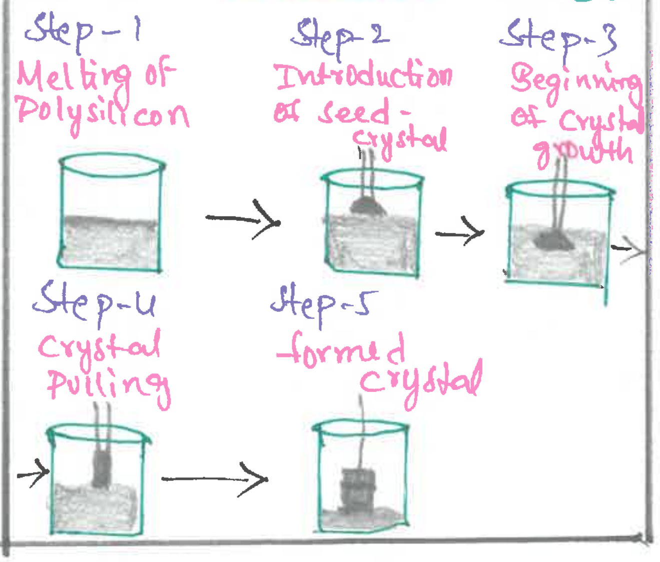
* Semiconductors in this band gap region will Appear in the respective colour.

| λ (nm) | Eg (eV) | colour |
|---|---|---|
| ~380 - 450 | ~ 2.95 | violet |
| ~450 - 485 | ~ 2.64 | Blue |
| ~565 - 590 | ~ 2.14 | Yellow |
| ~625 - 740 | ~ 1.77 | Red |

Example

1) Si - light ⟶ M → All visible radiations are absorbed → Appear as Black
100% Absorbance ← 0% Transmission
2) $TiO_2$ → 100% Transmission 0% Absorption → white colour Appears
3) Gaps - Eg = A = are

## Silicon Crystal Synthesis By CZOCHRALSKI Process



# SOLAR CELL



(i) RENEWABLE → WIND, SOLAR, HYDRO ETC...
(ii) NON-RENEWABLE → MINERAL GAS, COAL, PETROLEUM

LIGHT ENERGY (PHOTONS) ⟶ ELECTRICAL ENERGY (electrons)

SOLAR CELL DEPENDS ON :-
* intensity of sunlight
* wavelength of sunlight
* Type of semiconducting material

## CLASSIFICATION OF SOLAR CELL

### FIRST GENERATION SOLAR CELLS.

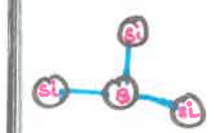
* Developed in 1954

MONO CRYSTALLINE SILICON SOLAR CELL
→ $e^-$ flow is easy and high efficient
→ Process pure and expensive
→ long life and uniform lattice

POLYCRYSTALLINE SILICON SOLAR CELL
→ $e^-$ flow is not easy and low efficiency
→ Process little defect and inexpensive
→ Short life and non-uniform lattice

CONSTRUCTION:-


P-type




N-type


working mechanism
Semiconducting material
↓
Absorbed sunlight
↓
$e^-$ is linked liberated
↓
move around within material
↓
Produce DC current
↓
AC current

* Band gap: 1.12 eV (pure si)
* High efficiency ~ 91%.
* Used to prepare Silicon wafer
* Expensive
* Heavy weight

### SECOND GENERATION SOLAR CELL.

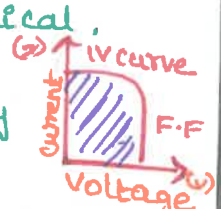
* Developed in 1970
- Amorphous silicon (a-si)
- Cadmium Telluride (CdTe)
- Copper iridium gallium selenide (CGIS)

CONSTRUCTION


Very thin absorbing layer.

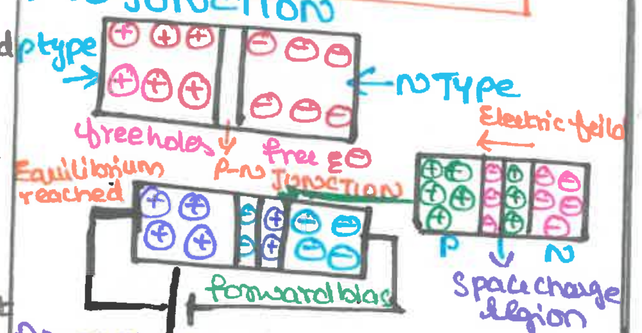
ADVANTAGES
* Low production cost
* Small amount required area
* Very thin film
* More Economical

DISADVANTAGE
* Not user friendly
* Cd is Toxic
* Te is not Easy abundant




PCE(%) = ISC x Voc x F.F

P-N JUNCTION




Amorphous si
* No-long range crystalline order
* low temperature process
* Doping become limited
* Si-H band gap 0.7 eV

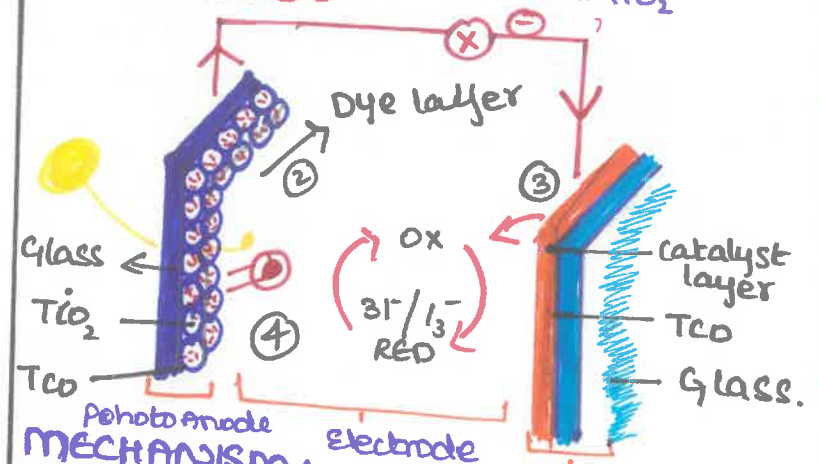
### THIRD GENERATION SOLAR CELL.

* Dye-sensitized solar cell (DSSC) 16-18%
- organic solar cell - 16% - 18%
- polymer solar cell - 18%
- Pervoskite solar cell - 25%
* Developed in 1972

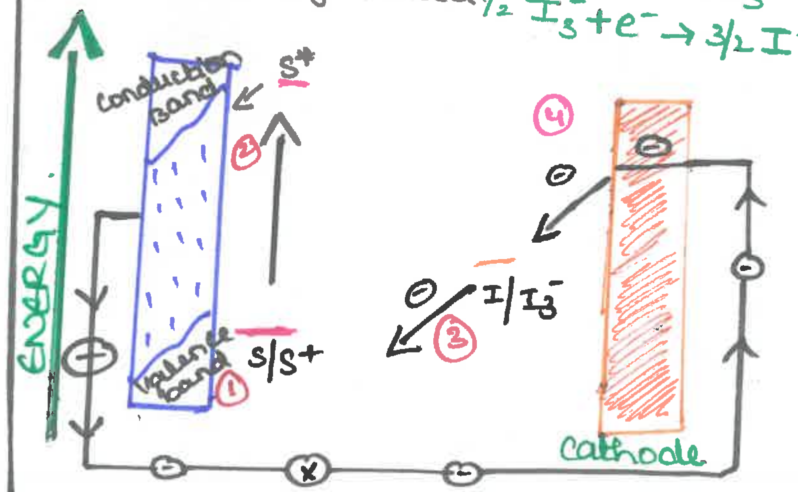
DYE-SENSITIZED SOLAR CELL

KEY COMPONENTS:-
SEMICONDUCTOR: $TiO_2$ (Anode)
SENSITIZER: N719 Dye
REDOX MEDIATOR: $I_3^-/I^-$
COUNTER Electrode: Platinium
mechanical support: FTO GLASS coated with $TiO_2$

CONSTRUCTION:-




MECHANISM:-
Step1: Photo excitation $S \xrightarrow{h\nu} S^*$
Step2: Electron injection $S^* \longrightarrow S^+ + e^-$
Step3: Dye regeneration $S^+ + 3/2\, I^- \rightarrow S + 1/2\, I_3$
Step4: Iodine regenerated $1/2\, I_3 + e^- \rightarrow 3/2\, I^-$




### WORKING:-
light pass through anode
↓
Excited dye molecule
↓
excited molecule injected into the $TiO_2$ layer
↓
Electron layer flows through circuit to Pb Electrode and flow into iodine
↓
$e^\ominus$ back to dye molecule
↓
DC ⟿ AC current

ADVANTAGES:-
* less Expensive
* less fabrication process.

DISADVANTAGE:-
* low Efficiency
* leakage of Electrolytes
* Poor-device stability

Application of SOLAR CELL:-
→ Domestic power supply
→ Electric power generation in space
→ used in vehicles
→ water heating
→ used in water supply
→ Drying agriculture product

FUTURE APPLICATION
ORGANIC SOLAR CELL:-
* Photosynthesis in plants
* use of light-sensitive dyes
* cost of manufacture decreased by 60%.

NEW ALLOYS:-
* In, N, Ga
* Convert full spectrum

# ELECTRO CEMISTRY & STORAGE DEVICES

## TERMINOLOGY

Current :- Flow of electrons

electrode :- material /metallic rod| bar| strip

Anode :- Loss of electrons (oxidation)

Cathode :- Gain of Electrons (Reduction)

Electrolyte :- Salt solution [$CuSO_4$, $ZnSO_4$]

* Conductive medium * strong & weak electrolyte

Electrode potential :- tendency to lose (or) gain electrons (V).

standard electrode potential :- Electrode potential measured in 1M of solution of 25°c

conductance :- solution - passage of Electricity

Types of Conductance :-

specific conductance :- conductance of solution b/w two electrods (1cm³) with 1cm apart [$sm^{-1}$]

$$\boxed{R = \rho \frac{l}{A}}$$

molar conductance :- conductance of all ions produce by 1 M electrolyte [S $cm^{-1}$ $mol^{-1}$]

$$\boxed{\begin{array}{l} m = k \times V \\ m = k \times \frac{1000}{c} \end{array}}$$

equivalent conductance

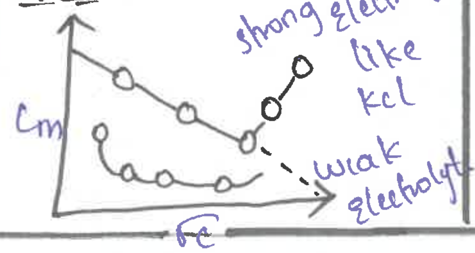
conductance of all ions produce of 1 geql of electrolyte

$$\boxed{\begin{array}{l} \lambda = k \times V \\ \lambda = k \times \frac{1000}{N} (\Omega^{-1} cm^{-1} eq^{-1}) \end{array}}$$

effect of dilution :-

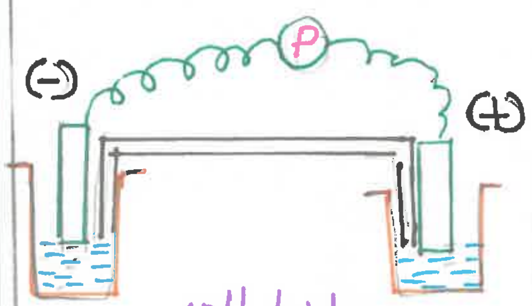
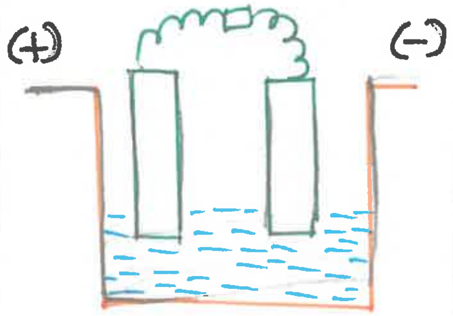
$$\lambda_c = \lambda_0 - [82.4 / (DT)^{1/2} \eta + 8.20 \times 10^5 / (DT)^{3/2} \lambda_0]$$

Graph :-




## TYPES OF CELLS

CELLS
- Electrochemical cell
- Electrolytic cell

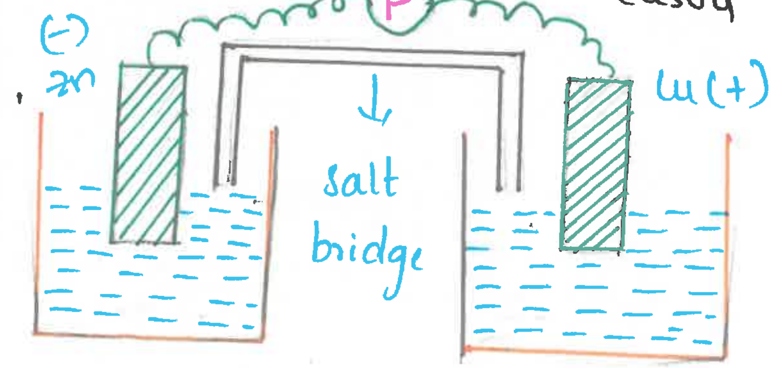
| ELECTROCHEMICAL CELL | ELECTROLYTE CELL |
|---|---|
|   |   |
| * chemical Energy to electrical Energy | * electrical energy to chemical Energy |
| * spontaneous | * Non - spontaneous |
| * Two half cells with same (or) different electrode & electrolyte. | * single cell contains same electrolyte. |
| * Anode :- -Ve cathode :- +Ve. | * current flows from cathode to anode. |
| * current flows from anode to cathode | * salt bridge is not required. |
| * salt bride is required. | |

## GALVANIC CELL

* Electrochemical cell

* Anode : Zn electrolyte : $ZnSO_4$

Cathode : Cu $CuSO_4$




Cell reactions :-

Anode : $Zn \rightarrow Zn^{2+} + \cancel{2e^-}$ (oxidation)

cathode : $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

$$\overline{Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu}$$

Zn ↓ $-E^* = -0.76$

$E^* = +0.34$ ↑ Cu.

CELL REPRESNTATION :-

$Zn | Zn^{2+} || Cu^{2+} | Cu$
(s) (aq) (aq) (s)

↓

Phase boundary

Applications :-
- Radio
- Torch
- Hearingaids.

## ELECTROCHEMICAL SERIES:

Arrangement - Electrodes - increasing order - Reduction potential (298 K, 1M)

Reference

-ve | +ve

Oxidising agents ⟵⟶ Reducing agents

| | | |
|---|---|---|
| $Li/Li^+$ | $Li^+ + e^- \rightarrow Li$ | $-3.00\,V$ |
| $K/K^+$ | $K^+ + e^- \rightarrow K$ | $-2.12\,V$ |
| $Ca/Ca^{2+}$ | $Ca^{2+} + 2e^- \rightarrow Ca$ | $-2.87\,V$ |
| $Na/Na^+$ | $Na^+ + e^- \rightarrow Na$ | $-2.7\,V$ |
| $Al/Al^{3+}$ | $Al^{3+} + 3e^- \rightarrow Al$ | $-1.66\,V$ |
| $Zn/Zn^{2+}$ | $Zn^{2+} + 2e^- \rightarrow Zn$ | $-0.76\,V$ |
| $Fe/Fe^{2+}$ | $Fe^{2+} + 2e^- \rightarrow Fe$ | $-0.44\,V$ |
| $Cd/Cd^{2+}$ | $Cd^{2+} + 2e^- \rightarrow Cd$ | $-0.403\,V$ |
| $Ni/Ni^{2+}$ | $Ni^{2+} + 2e^- \rightarrow Ni$ | $-0.236\,V$ |
| $Sn/Sn^{2+}$ | $Sn^{2+} + 2e^- \rightarrow Sn$ | $-0.14\,V$ |
| $Pb/Pb^{2+}$ | $Pb^{2+} + 2e^- \rightarrow Pb$ | $-0.126\,V$ |
| $Pt/H_2/H^+$ | $2H^+ + 2e^- \rightarrow H_2$ | 0.00 Std |
| $Cu/Cu^{2+}$ | $Cu^{2+} + 2e^- \rightarrow Cu$ | $+0.337\,V$ |
| $Ag/Ag^+$ | $Ag^+ + e^- \rightarrow Ag$ | $+0.79\,V$ |
| $Hg/Hg^+$ | $Hg^+ + e^- \rightarrow Hg$ | $+0.92\,V$ |
| $Cl_2/Cl^-$ | $Cl_2^- + e^- \rightarrow Cl_2$ | $+1.359\,V$ |

→ 1.1 Volt

## Applications / Uses / Significance:

1. Construction of a cell:

$E^\circ\,cell = ER^\circ - EL^\circ$

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

2. Reaction Feasibility ($E^\circ$ value):-

$E^\circ\,cell = +ve$ ; Spontaneous reaction

$E^\circ\,cell = -ve$ ; No reaction

Lower reduction potential } replaces higher reduction potential

3. Hydrogen Displacement reaction:

Metal above - Site → displaces $H^+$ of acids

Eg:- $Zn + H_2SO_4 \rightarrow ZnSO_4 + H^+$

$E^\circ_{Zn} = -0.726\,V$

$Ag + H_2SO_4 \rightarrow$ No reaction

$E^\circ_{Ag} = 0.8\,V$

4. Determination of Equilibrium constant ($E_{eq}$):-

$-\Delta G^\circ = nFE$ , $-\Delta G^\circ = RT\ln K$

$RT\ln K = nFE$

$2.303\,RT\log K = nFE$

$\log K = \frac{nFE}{2.303\,RT}$

5. Behaviour of Metal:-

Prediction : Oxidation / Reduction

Higher- Reduction — Lower Reduction

$\frac{1}{2}F_2 + e^- \rightarrow F^-$ — $Li \rightarrow Li^+ + e^-$

$E^\circ_F = +2.8\,V$ — $E^\circ_{Li} \Rightarrow 0.3\,V$

6. Displacement of Metal:-

from electrochemical series replaces

Higher metal → Lower metal

Eg: $2Li^+ + ZnSO_4 \rightarrow Li_2SO_4 + Zn^{2+}$

$Mg + 2AgNO_3 \rightarrow Mg(NO_3)_2 + 2Ag$

Anode : Oxidation : Lose of $e^-$

Cathode : Reduction : Gain of $e^-$

## DETERMINATION OF SINGLE ELECTRODE POTENTIAL:-

→ Nernst Equation (1889)

→ Unknown Temperature / pressure / concentration

Related

- Electrode Potential + concentration of Metal ions

(Work done Max) (Maximum electricity)

$W_{max} = W_{ele}$

$W_{max} = -G$

Electrical Energy = Volt x coulomb

$W_{max} = W_{ele} = -nFE$

n - no. of electrons

F - Faraday

E - Volts or Energy

$\Delta G = -nFE$

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

Reversible Electrode Reaction

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

$K_c = \frac{[M]}{[M^{n+}]}$

$K_c$ (Eq constant) & $\Delta G$ (Change is free energy)

Related as

$\Delta G = \Delta G^\circ + RT\ln K_c \rightarrow ①$

$① \div -nF$

$\Rightarrow \frac{\Delta G}{-nF} = \frac{\Delta G^\circ}{-nF} + \frac{RT\ln K_c}{-nF}$

$\frac{\Delta G}{-nF} = \frac{\Delta G^\circ}{-nF} + \frac{RT\ln[M]}{-nF} - \frac{RT\ln[M]}{-nF}$

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

$\because [M] = 1$

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

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

E - Electrode potential

$E^\circ$ - Standard Electrode potential

n - no. of electrons

R - Gas constant

F - Faraday

[C] - conc. of $M^+$ ions

T - Temp (298 K)

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

$E = E^\circ - \frac{0.0591}{n}\log\frac{[Product]}{[Reactants]}$

Applications:-

* To determine the electrode potential.
* To predict corrosion behaviour.

# ELECTRODES

→ Conductor- forms electrical contact- non metallic part - Circuit.

1. Reference electrode

Constant- potential

Primary Reference electrode

Eg:- Standard Hydrogen Electrode

Secondary Reference Electrode

Eg:- Calomel

Ag-AgCl

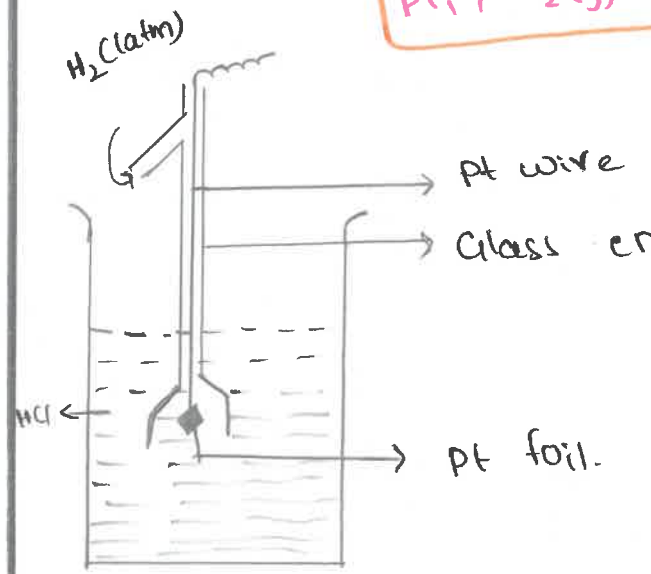
2. Indicator Electrode

Charge in potential with the change in concentration

## → Primary Reference Electrode:

Standard Hydrogen Electrode

$\boxed{Pt, H_2(g)\ (1atm) \mid H^+\ (1M)}$




Reaction:-

At anode:

$H_2(g) \rightleftharpoons 2H^+_{(aq)} + 2e^-$

At cathode:

$2H^+ + 2e^- \rightleftharpoons H_2(g)$

* Standard Hydrogen potential = 0V
* pressure : 1atm
* Temp = 298K
* Electrolyte HCl

Applications:

1. Reference - Electrode potential measurement

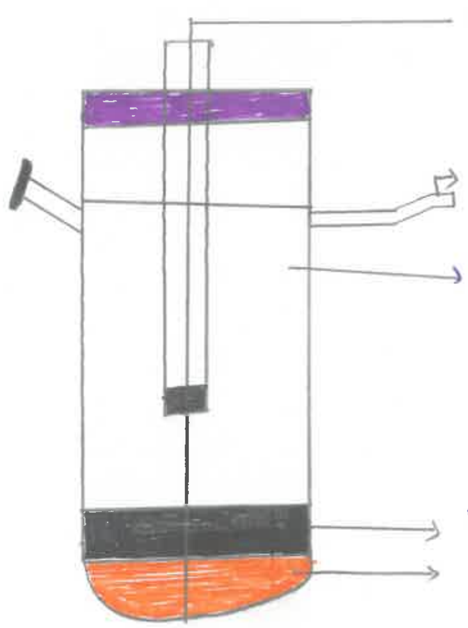
Disadvantages

1. Not easy-transportation
2. Difficult- get- pure hydrogen

→ Secondary Reference Electrode:

* Saturated Calomel Electrode

$Hg_{(l)}, Hg_2Cl_{2}(s) \mid KCl\ (sat)$




Reaction:

Anode :- $2Hg_{(s)} + Cl^-_{(aq)} \rightleftharpoons Hg_2Cl_2 + e^-$

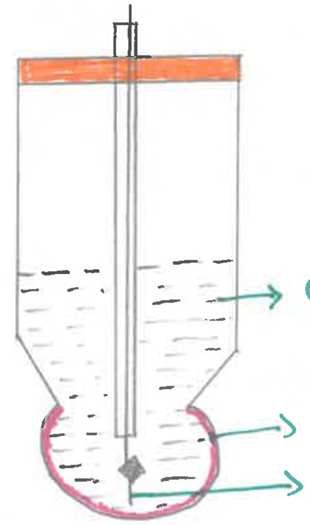
cathode:- $HgCl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$

* potential - Sat KCl: 0.2422V

→ Advantages

1. Easy to setup
2. Easy to transport
3. long self life, Reproducability of emf
4. low Temp. co-efficient can be used in variety of solutions
5. $E^\circ$ value is accurate

→ Ion Selective Electrode




$Ag_{(s)}, AgCl_{(s)} \mid HCl\ (0.1M) \mid glass$

$$\boxed{\therefore\ pH = \frac{E_{cell} - 0.2422 + E_G^\circ}{0.0591}}$$

Advantages

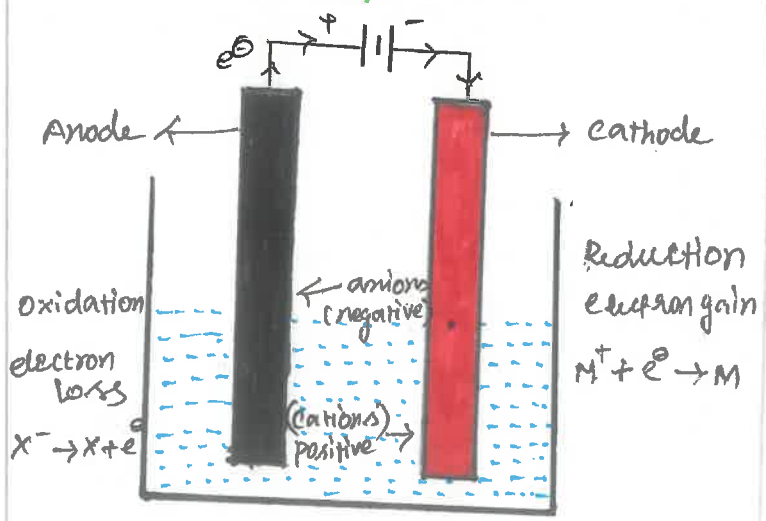
* Easy to Construct
* Accurate results
* Not easily poisones
* Equilibrium quickly attaines
* Can be used in various solutions

Disadvantages

* Glass has high resistance
* can't be used in high alkaline, ethanol, acetic acid.

## BATTERIES

* Chemical energy into electrical energy.
* A battery consists of number of anodes, cathodes and electrolytes or a combination of two or more cells.




### BATTERY

| Primary | Secondary | Fuel cell (or) Flow battery |
|---|---|---|
| * Non reversible | * Reversible | * Non-reversible |
| * Galvanic | * Galvanic discharging | * Galvanic |
| Eg: Lechlanche or Dry cell | Lead-Acid | $H_2O_2$ or $CH_3OH - O_2$ |

### Requirements of a battery

* It should have more storage capacity
* It should be light and compact
* It should be capable of recharged.
* It should be cheaper
* It should be constant voltage

## DRY CELL (or) LECLANCHE'S CELL

Anode : Zn

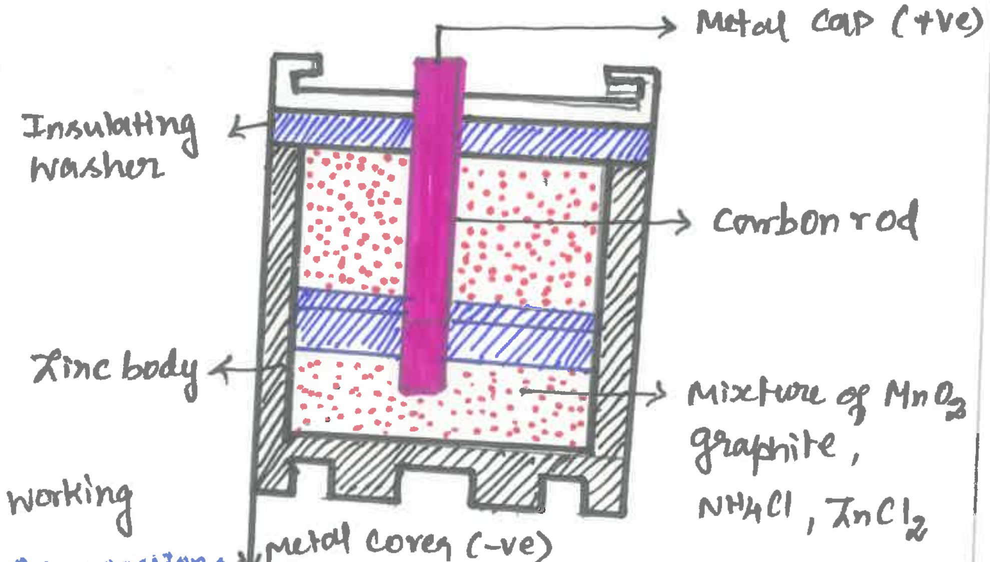
Cathode : Carbon rod graphide

Electrolyte: $NH_4Cl$, $ZnCl_2$, $MnO_2$, Starch

Cell representation

$$\underbrace{Zn \mid Zn^{2+}}_{\text{Anode}} \; \underset{\text{Salt bridge}}{||} \; \underbrace{\underset{+ NH_4Cl}{MnO_2} \mid MnO_2 \mid MnO(OH)_3}_{\text{cathode}}$$

oxidation    Reduction




working

Cell reactions

Anode : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{\ominus}$

Cathode : $2MnO_{2(s)} + H_2O + 2e^{\ominus} \longrightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$

Acid base reaction between $OH^{\ominus}$ and $NH_4^{\oplus}$

$$NH_4^{\oplus}{}_{(aq)} + OH^{\ominus}{}_{(aq)} \longrightarrow NH_{3(g)} + H_2O_{(l)}$$

Reaction of $NH_{3(g)}$ and $Zn^{2+}$ from $ZnCl_2$.

To form complex ion $[Zn(NH_3)_2Cl]$

Two electrodes:

$$2MnO_{2(s)} + 2NH_4^+{}_{(aq)} + 2e^{\ominus} \longrightarrow [Zn(NH_3)_2]Cl_{2(s)}$$

Applications: Transistor; Radios; Calculator and Flash light.

## LEAD STORAGE CELL

Anode: Pb

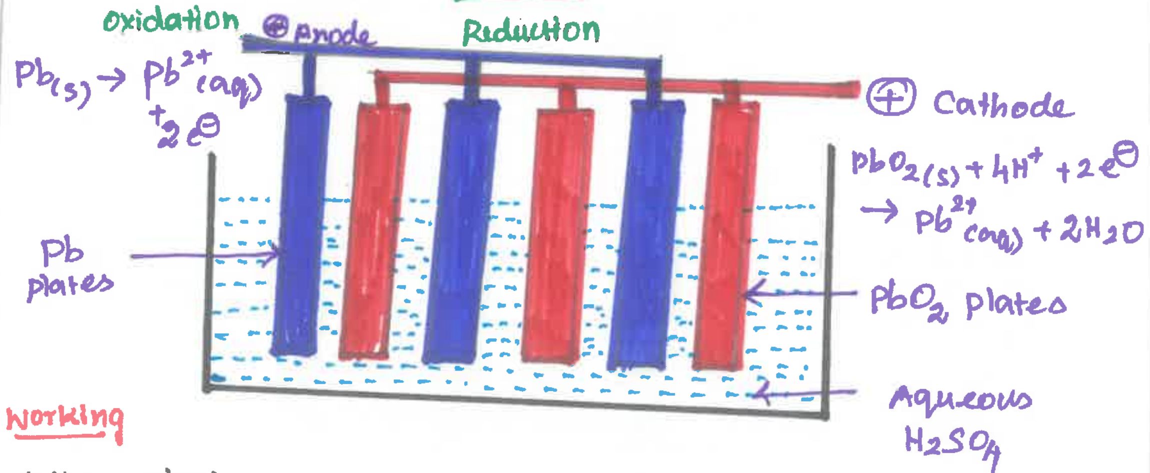
Cathode: $PbO_2$

Electrolyte: dil. $H_2SO_4$ (aqueous)

Cell representation:

$$\underbrace{Pb \mid PbSO_4}_{\text{Anode}} \; \underset{\text{Salt bridge}}{||} \; dil.H_2SO_4 \mid \underbrace{PbO_2 \,||\, PbSO_4}_{\text{Cathode}}$$

oxidation    Reduction




Working

Cell reaction:

Anode: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightleftharpoons PbSO_{4(s)} + 2e^{\ominus}$

cathode: $PbO_{2(s)} + 4H^+ + SO_4^{2-} + 2e^{\ominus} \rightleftharpoons PbSO_{4(s)} + 2H_2O$

Discharging:

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightleftharpoons 2PbSO_4 + \text{energy} + 2H_2O$$

Charging:

$$2PbSO_{4(s)} + 2H_2O + \text{Energy} \rightleftharpoons Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4$$

Advantages:

* Made easily
* produce high current.

Disadvantages:

* It causes environmental hazards.

## LITHIUM ION BATTERY [LIB]:

- Rechargeable.
- Li ion move inside the cell.

EMF = 3.2 to 3.7 V

ANODE : Lithium-metal Oxide [$LiCoO_2$, $LiMN_2O_4$, $LiFePO_4$ etc]

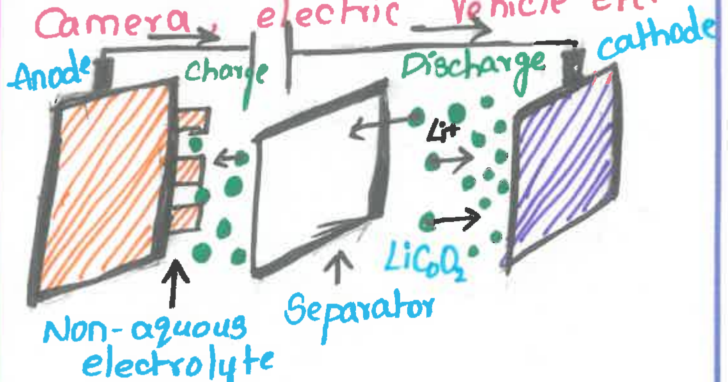
CATHODE : Carbon [Graphite].

ELECTROLYTE : Non-Aqueous [Flamable] Carries $Li^+$ b/w electrodes

Eg: Lithium hexafluoro phospate, mixture of ethylene carbonate, Dimethyl Carbonate, Polycarbonate.

Separator : Block the flow of $e^-$ [porous polymer film]

Application : Laptop, mobile phone, Camera, electric Vehicle etc.




MECHANISM:

Discharge: $Li^+$ move from anode → Cathode through electrolyte

- Insert in cathode.
- $e^-$ flow Anode → Cathode in outside Circuit.

Charging : $Li^+$ move cathode → anode.

- Insert cathode at Anode
- $e^-$ flow cathode → anode in outside circuit.

DISCHARGE HALF CELL:

CATHODE : $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

ANODE : $LiC_6 \rightarrow C_6 + Li^+ + e^-$

$LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$.

**Advantages:**

- Light weight
- Long Life
- High Capacity
- Low self discharge

**Limitations:**

- Thermal runaway
- Degrate at high temp
- No Rapid change
- Sensitive for moisture & high temp

## LITHIUM SULPHUR BATTERY [LSB]

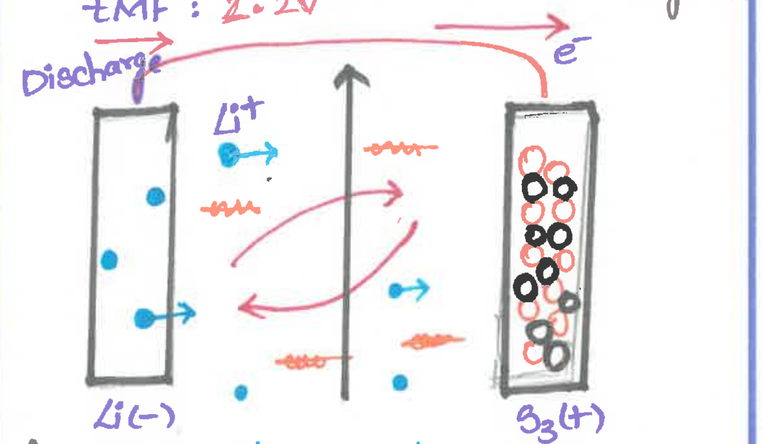
- Rechargable
- Cheaper than LIB
- High specific Energy
- Multistep mechanism.

ANODE : Lithium

CATHODE: Sulphur (or) Sulphur Carbon

ELECTROLYTE : polysulphides (liquid Organic)

EMF : 2.2V




ANODE : $2Li \longrightarrow 2Li^+ + 2e^-$

CATHODE : $S + 2e^- \longrightarrow S^{2-}$

$2Li + S \longrightarrow 2Li^+ + S^{2-}$

MECHANISM:

- $S^{2-}$ ions react with $S \rightarrow$ polysulphide.

$S^{2-} + nS \longrightarrow [S_{n+1}]^{2-}$

Recharging :

- The reaction will be reverted.

$Li_2S$ + Electricity $\longrightarrow 2Li^+ + S^{2-} \rightarrow 2Li + S$

Advantages → Light weight, Low cost

- Safer than LIB.

Application → Energy storage, Electric vehicles.

## FUEL CELLS

- Converts chemical energy into directly electrical Energy.

### Hydrogen - Oxygen fuel cells

- Similar to galvanic cell 2-half cell reaction

Electrodes : porous graphite + platinum silver or metal oxide.

Electrolyte : NaOH, KOH, $H_2SO_4$

NaOH or KOH → Alkalyne fuel cells

$E_{cell}$ = 1.5V

ANODE : $2H_{2(g)} + 4\,OH^-_{(aq)} \rightarrow 4H_2O + 4e^-$

CATHODE : $O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$

$2H_2 + O_2 \longrightarrow 2H_2O$

**Advantages**

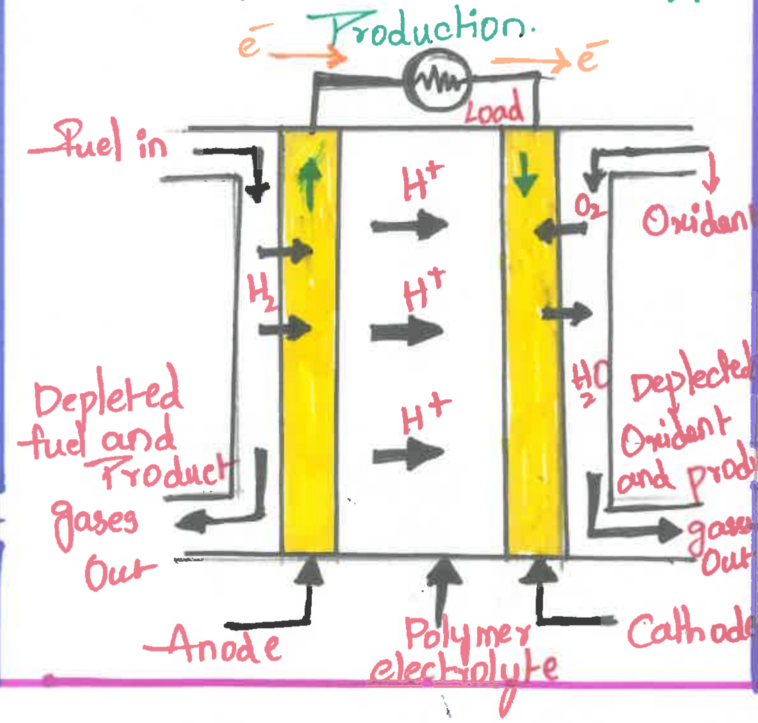
- It can be used in remote location

**Disadvantages**

- Low Life
- easily poisoned by $CO_2$.

Applications:

Space crafts, vechicles, energy production.




### Methanol - Oxygen fuel cells

- Operating range 50°c to 120°c.

Electrodes: platinum or Ruthenium based materials.

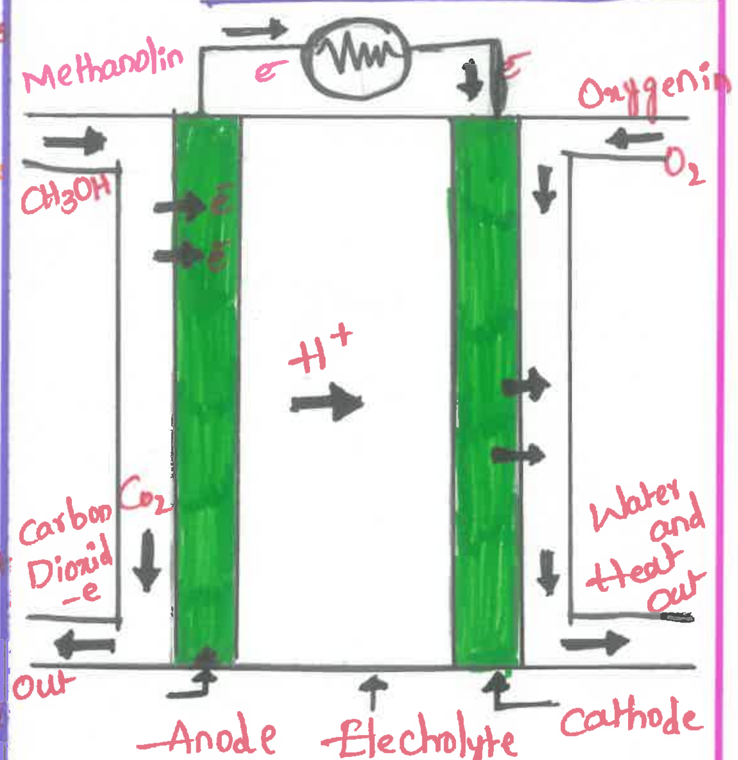
Electrolyte : polymer membrane (Dupont's Nafion®)

$E_{cell}$ = 1.18V

ANODE : $CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$

CATHODE : $3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

$CH_3OH + 3/2O_2 \longrightarrow 2H_2O + CO_2$




Advantages : Low carbon emission and good solubility water.

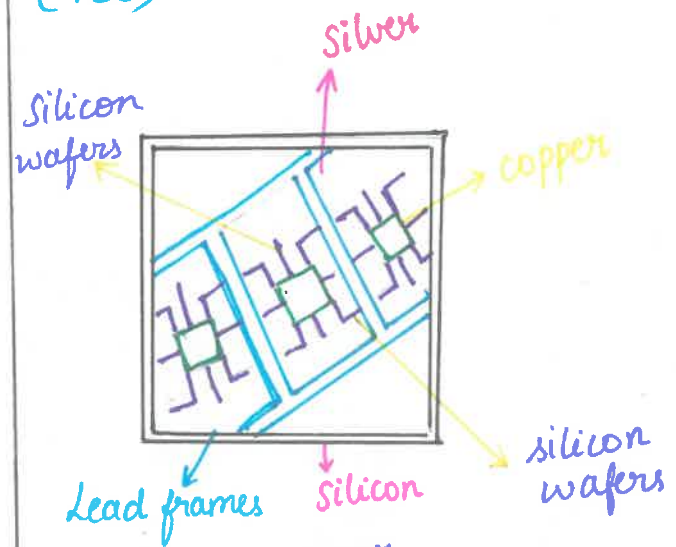
Application : Military and vehicles, sensors, Information Technology.

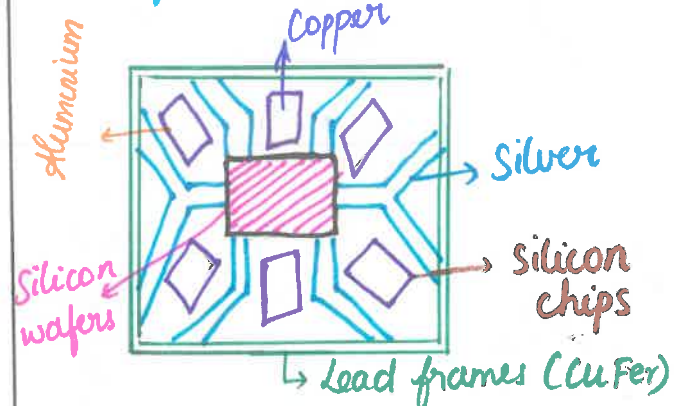
# CORROSION OF ELECTRONICS

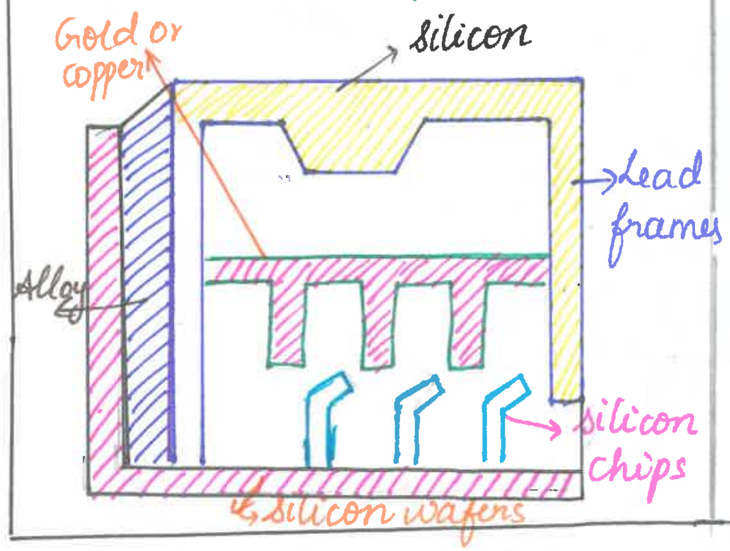
## COMPOSITION OF ELECTRONIC SYSTEMS:-

* Integrated circuits (ICs)
* Printed circuit Board
* Computer Hard Disc

## CHEMISTRY OF INTEGRATED CIRCUITS (ICS)



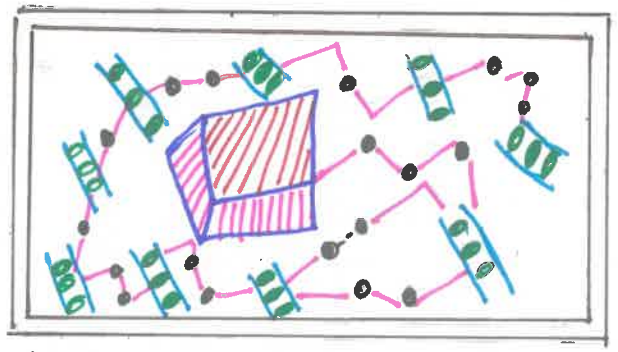




## PRINTED CIRCUIT BOARD

* Copper
* Ni - P (ELNI)

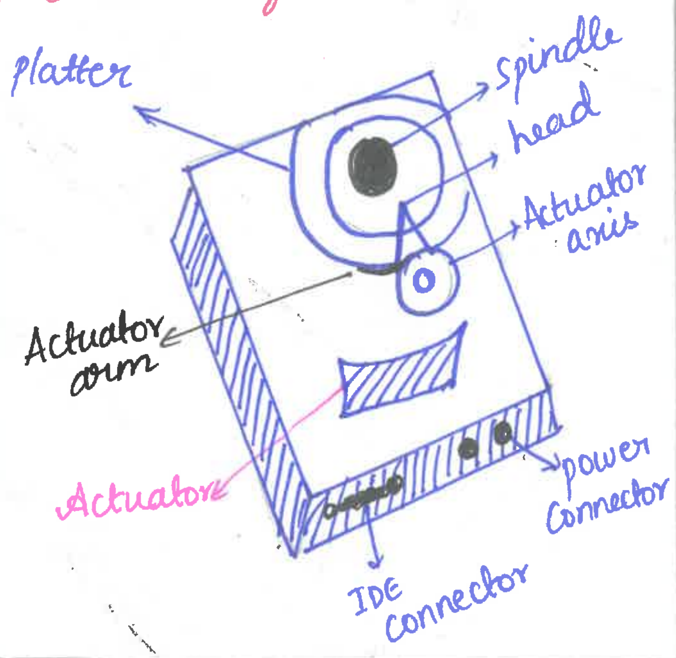
Uses of Engineering Process

* Produce a PLB
* Solderability
* Good connectivity



## COMPUTER HARD DISC (CHD)

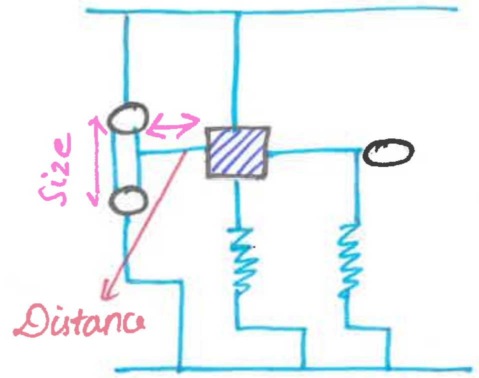
* Round disc platter
* Magnetic recording media
* Aluminium electro plated with nickel.
* Cobalt alloys



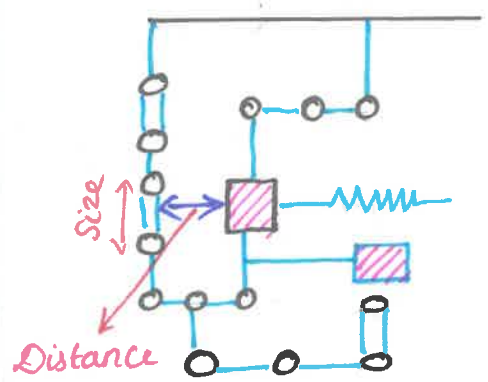

## CAUSES OF DEVICE CORROSION

Demand for miniaturization

Before miniaturization




After miniaturization




### MULTIPLICITY OF MATERIALS USED:

* Integrated circuit
* Printed circuits Board
* Switches
* Magnetic Recording media
* Packaging and Shielding parts
* Connectors

### CORROSIVE RESIDUES

* Process related residue
* Service related residue

## PRODUCTION SERVICE RELATED CORROSION

Process related residues

* chemical contamination
* Fluxing agents
* Etching medium
* Plating bath Residues
* Additives
* Soldering materials

Service related residues

* Aggressive ions - $Cl^-$ $SO_2$ (g)
* water layer
* Relatively low humidity
* Composition of moisture
* Temperature

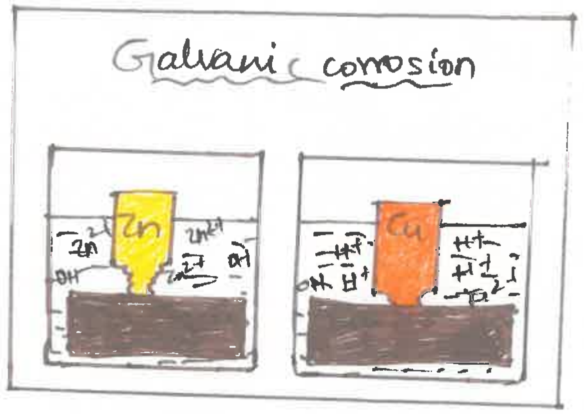
### FRETTING CORROSION RESIDUES

* Gaseous pollutant
* Contact physics
* Contact chemistry
* Additives materials
* Composition of moisture
* Miniaturization
* Electrical contact degradation

# Major forms of Corrosion observed in Electronics

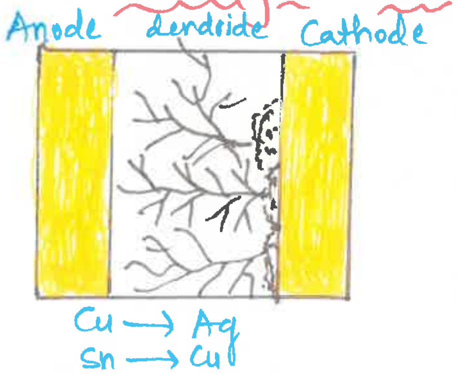
## 1. Galvonic Corrosion :-

* Materials Varied :- electrochemical potential (ENIG in PCB)



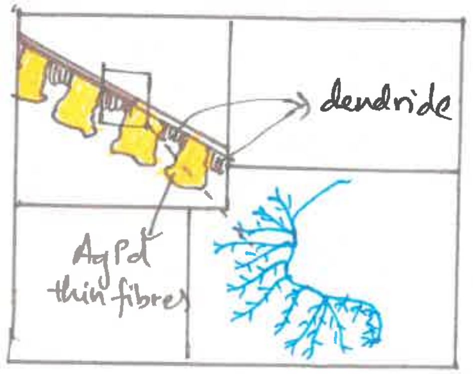

* Corrosion on connectors and switches
* Corrosion (product) high resistance
* $E^\circ_{Zn} = -0.76\,V$
  $E^\circ_{Fe} = -0.44\,V$
  $E^\circ_{Cu} = +0.34\,V$

## 2. Electrolytic metal migration:



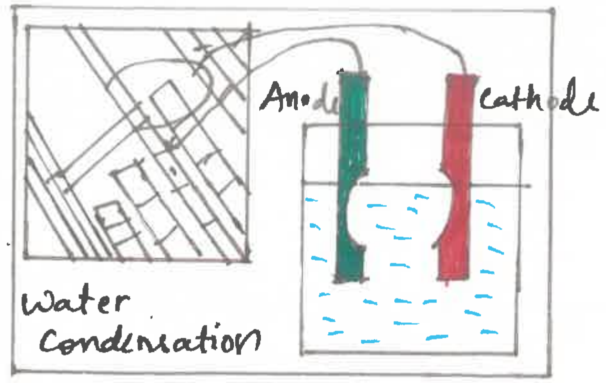

* Potential gradient- two connectors
* In Humid environment
* Metal ion migration Anode → Cathode
* Metal hydride formation at cathode
* Dendride formation.
* Metals : Cu, Ag, Sn, Pd etc.

## 3) Anodic Corrosion :



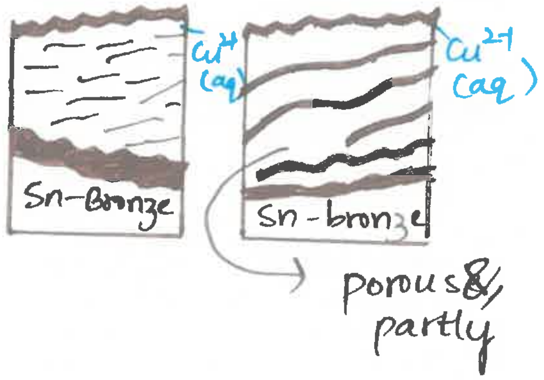

* $H_2S$ cause corrosion (even below 50ppb)
* On Ag-Pd thin fibre
* Dendride formation from cathode → Anode
* Irreversible

## 4) Cathodic Corrosion :



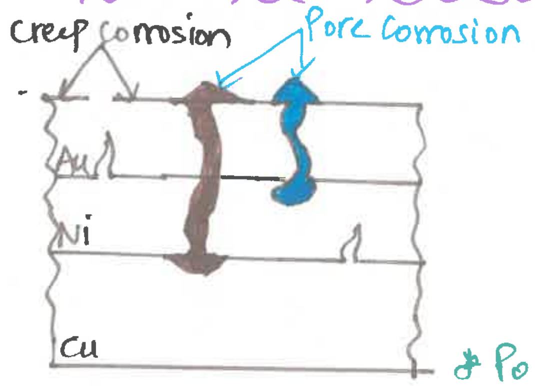

* Less noble metals corrosion in acidic and Alkaline (Al, Zn)
* Cathodic oxygen reduction → $OH^-$
  $OH^-$ → change the pH

## 5) Atmospheric Corrosion :




* Above critical relative humidity
* Gaseous or solid pollutants
  Ni/or Pb or Sn $\xrightarrow[\text{humidity}]{70\%}$ sulphates
* Gaseous pollutants $\xrightarrow[PE]{Pd}$ resinous solids
* Mechanical effect : Dust
* Chemical effect : Pollutants from industries
* Oilly pollutants: Aerosis (solids will be trapped)

## 6) Pore & Creep Corrosion :

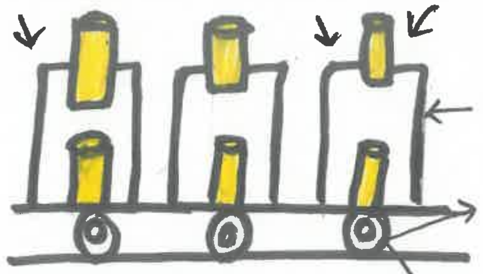


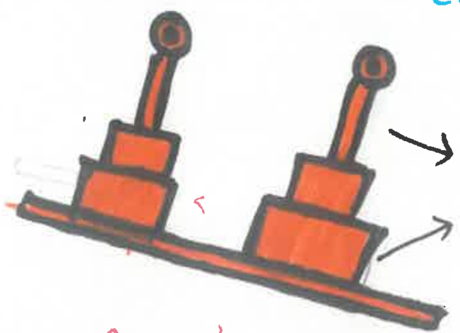

* Corrosion on non-uniform noble metal coating (ENIG)
* Ni, Cu $\xrightarrow[\text{interaction}]{S, Cl\ etc}$ Corrosion [through galvanic cell formation]

**Pore**
* Pollutant interaction Core metals (Ni, Cu)
* Synergatic effect of $Cl^-$, oxides, sulphates

**Creep**
* Reactive metal next to noble metal layer.
* Corroded product creep out on Au surface
  eg:- $CuSO_4$, $NiSO_4$

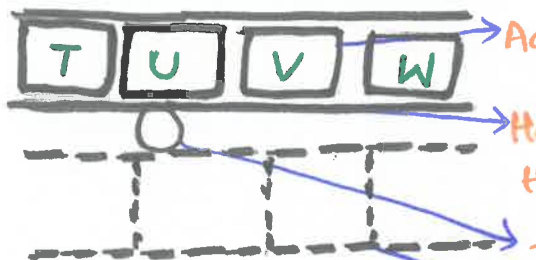
## Electrical contact degradation




### Mechanism of Degradation of electric contacts

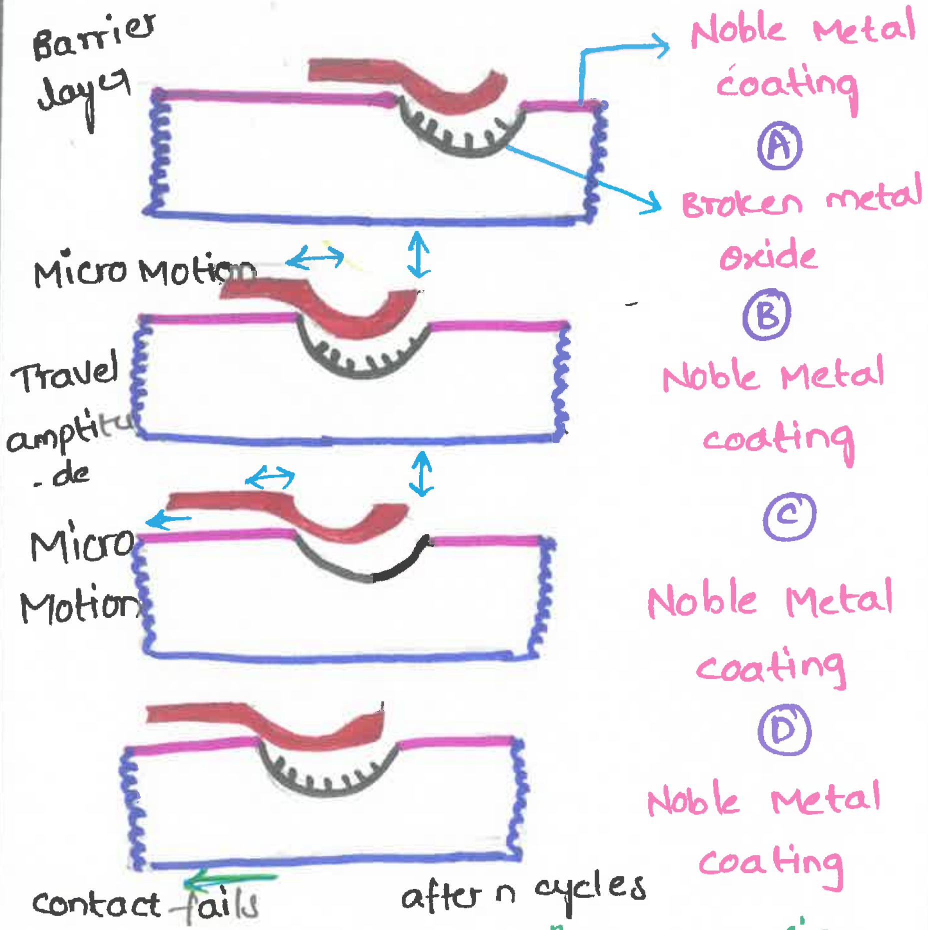
contact physics




contact chemistry

$NH_2$ IC PCB $SO_2$ $H_2S$ $O_3$ $NO_x$

## Fretting Corrosion




### Factors influencing fretting corrosion

* Distance
* Amplitude
* Equilibrium position
* Movement

### Displacement frequency :-

* Repeating event
* vibrations
* logical differences

Both External forces ⇄ Relative Movement electrical contacts.

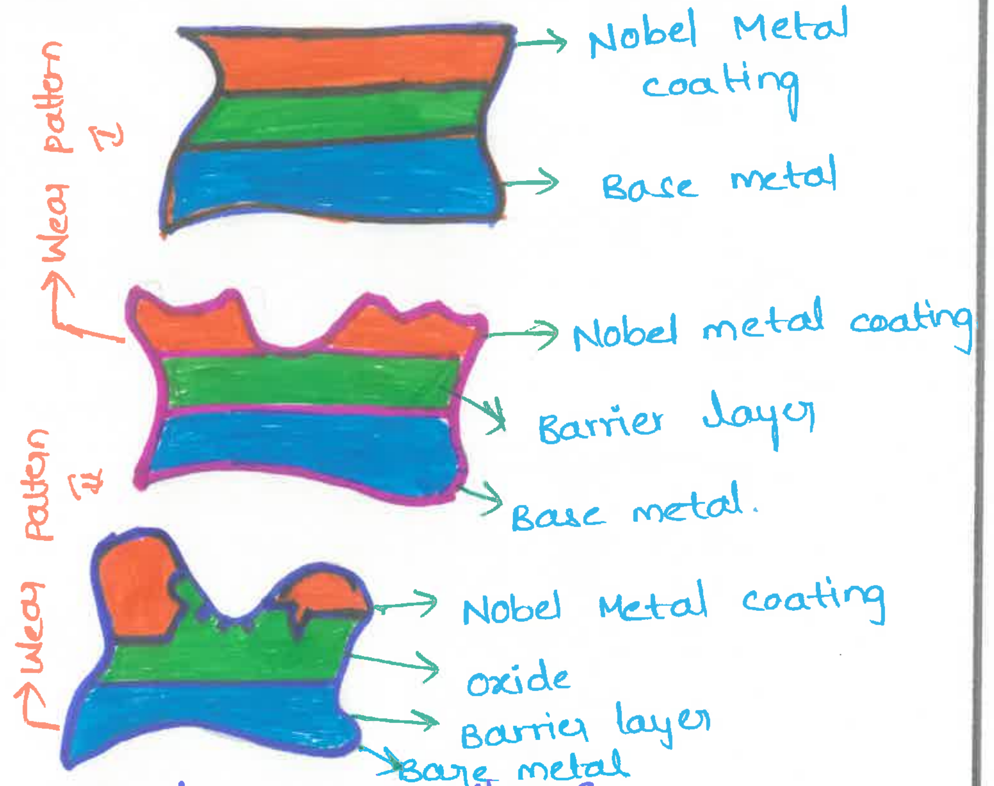
## Causes and development of fretting corrosion :-

Stage -wise process

fretting wear

* Relative Motions
* Thermal expansions
* Mating of contacts
* Mechanical vibrations

### Wear pattern of electrical contacts :-



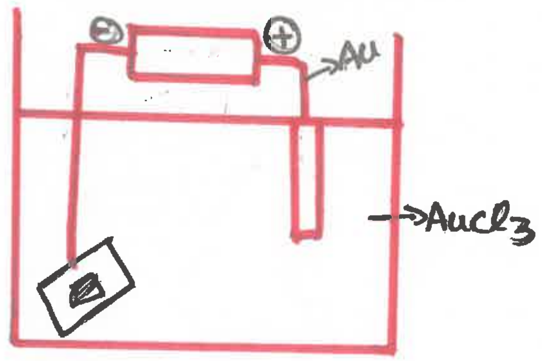

### Methods of protection :

* Gold plating Materials
* passivation
* PTFE
* self-assemble
* Molecules
* PEPE (perfluoropoly ether)

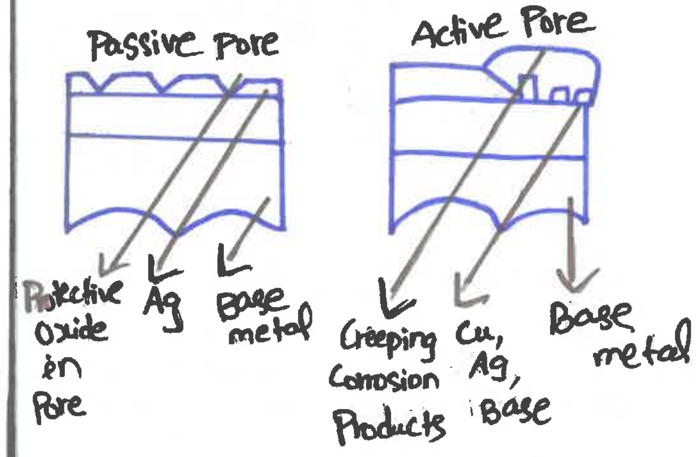
## Methods of Protection:-

* Gold Plating
* Corrosion Protection of computer hardware using PFDE.
* PTPE method (Greasing)
* Passivation.

## Features of Gold Plating

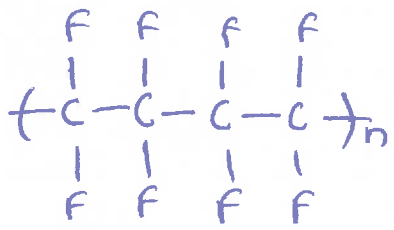



* Hardness
* Imporved wear resistance.
* Improved Coatings
* Improved surface perfection.




## PTFE:-

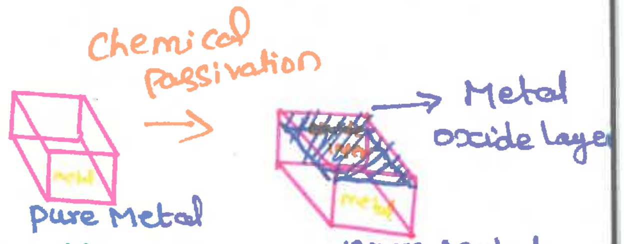
* Reduced friction.
* Additional life time.
* Electrical Contacts
* Contact resistance



## Passivation:-

⇒ Passivation forms an exterior layer on metal surfaces, preventing Corrosion by blocking exposure to air and water.

⇒ This protective layer stops oxidation safeguarding metals like iron and its alloys.



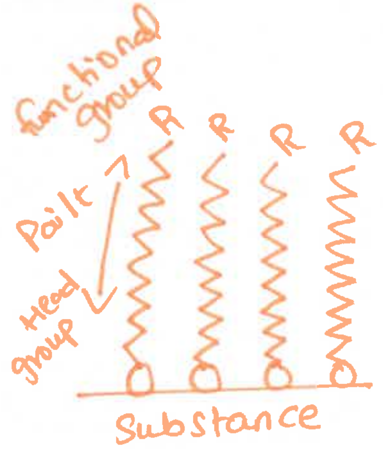

These thin layers

* Enhance water oxidation reaction kinetics.
* Reduce charge recombinational surface states.

* Protect metal surface from chemical corrosion.

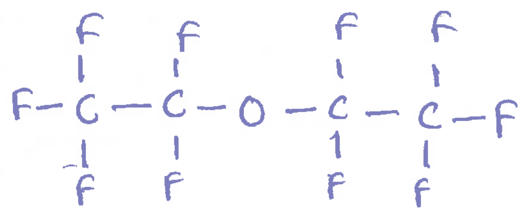
## Self Assembled molecules

* Bi or multifunctional materials
* different functionality.
* Attached with metals
* electrically conductive surface.
* oxidation.




## PFPE (perfluoropoly ether)

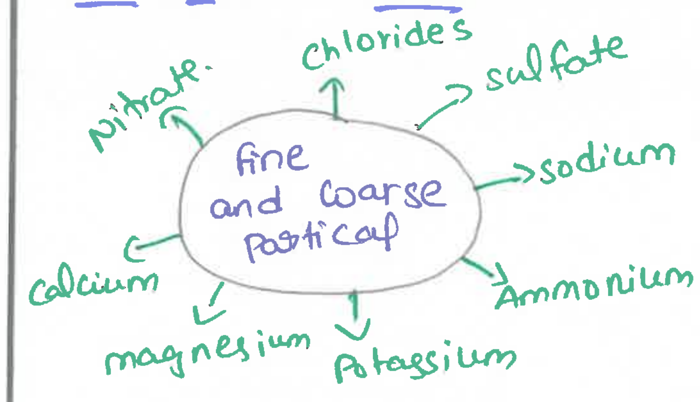
⇒ long chain polymer.
⇒ Branched and lines
⇒ Structure inertness
⇒ High temperature performance



* Non-flamable
* Non-toxic
* Low vapor pressure.

## Environmental Contamination

### Atmospheric Pollutant




### Gas Contaminents

$H_2S$, $SO_2$, $SO_3$, $Cl_2$, $NO_x$, HF, $O_3$, $NH_3$

### According to ISA

(Instrument System & automation society)

| ISA category | $G_1$ | $G_2$ | $G_3$ | $G_4$ |
|---|---|---|---|---|
| $H_2S$ | <3 | <10 | <50 | >50 |
| $SO_2$, $SO_3$ | <10 | <100 | <300 | >300 |
| $Cl_2$ | <1 | <2 | <10 | >100 |
| $NO_x$ | <50 | <125 | <1250 | >1250 |
| HF | <1 | <2 | <10 | >10 |
| $NH_3$ | <500 | <1000 | <25000 | >25000 |
| $O_3$ | <2 | <25 | <100 | >100 |

* Effect of Environmental contamination:
  Breathing problems, Heart diseases, and Some types of Cancer.

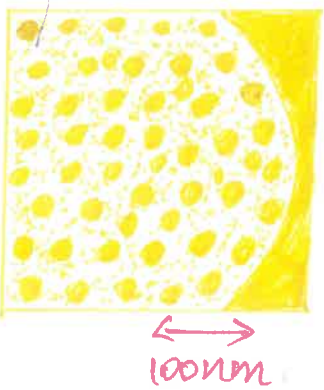
# NANOSTRUCTURES AND COMPOSITES

**Definition:**

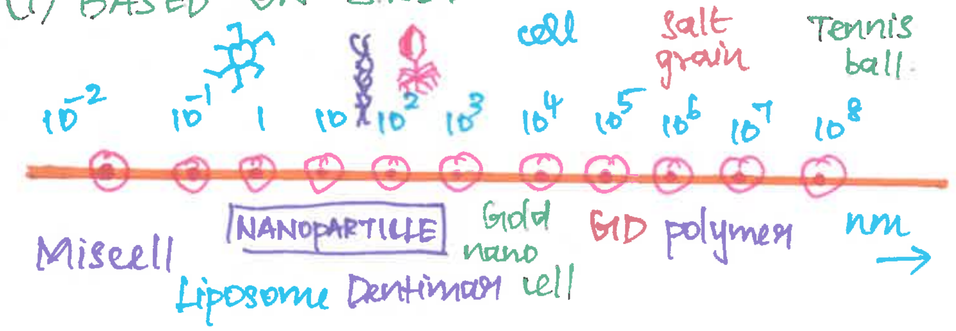
Nanostructure is a structure of intermediate size between Microscopic and Molecular structures.

**Classification of NSMs:-**

- Based on size
- Based on shape
- Based on Dimension




(i) BASED ON SIZE:-




Poly:- Long chain

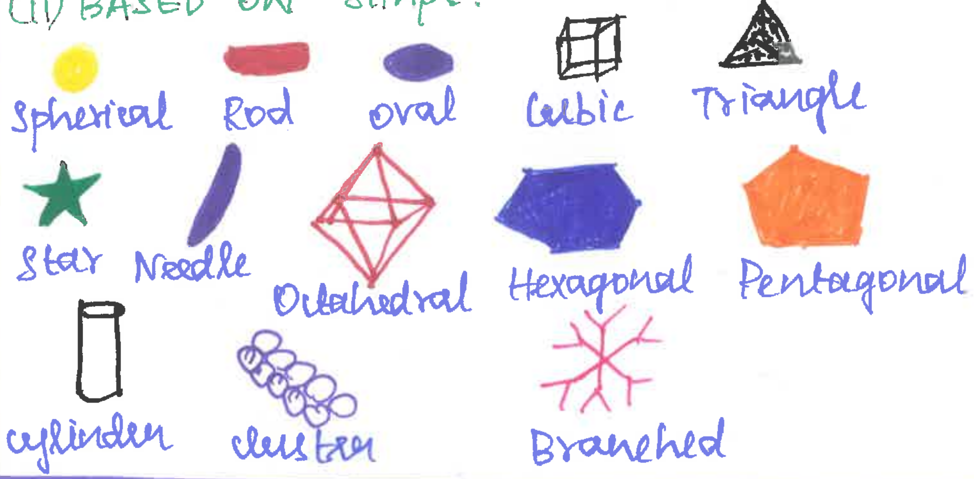
Macro:- 100 – 10,000 $A^{o}$

Micro:- less than 100 $A^{o}$

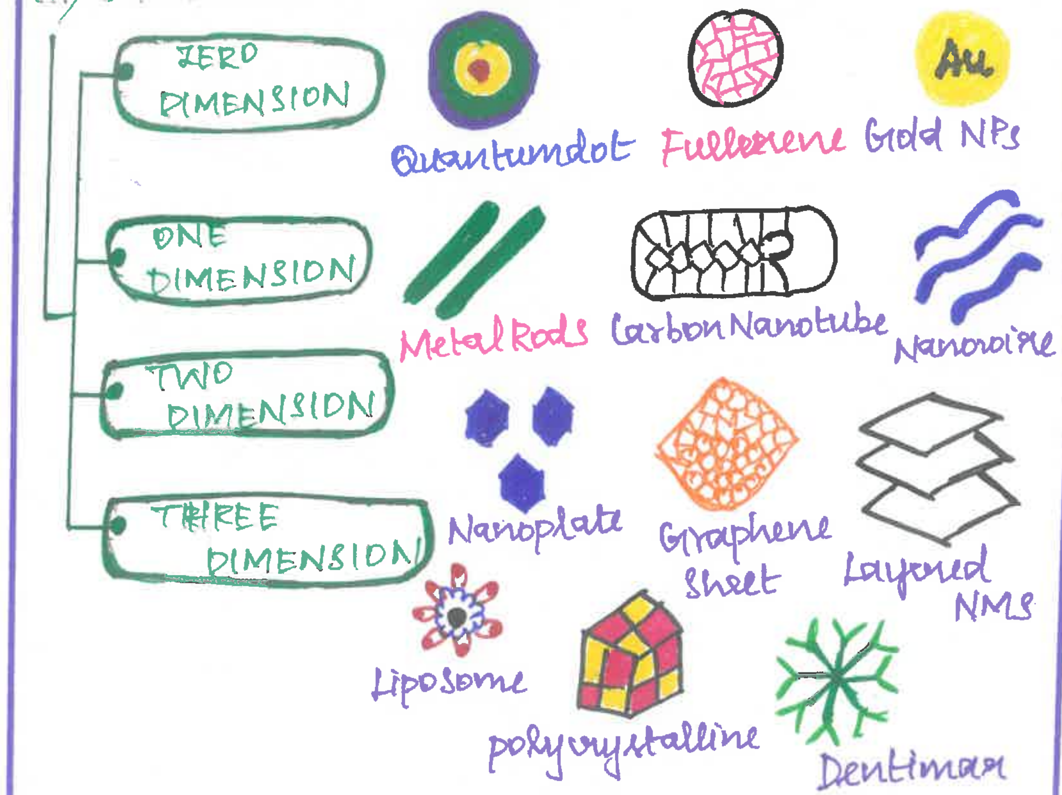
Nanomaterial:- $10^{-9}$ m

Examples:- Au, Ag, CNT, GO

(ii) BASED ON SHAPE:-

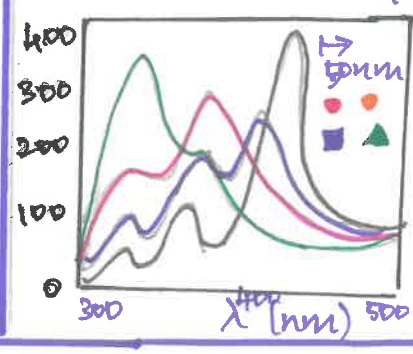


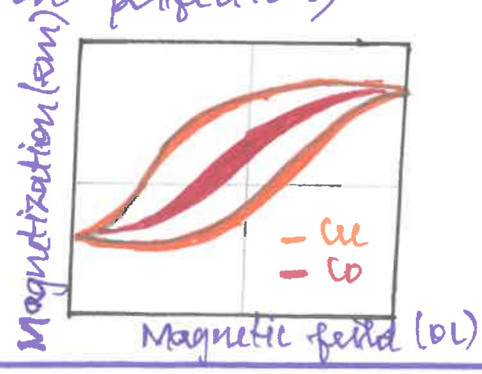

(iii) BASED ON DIMENSION:-



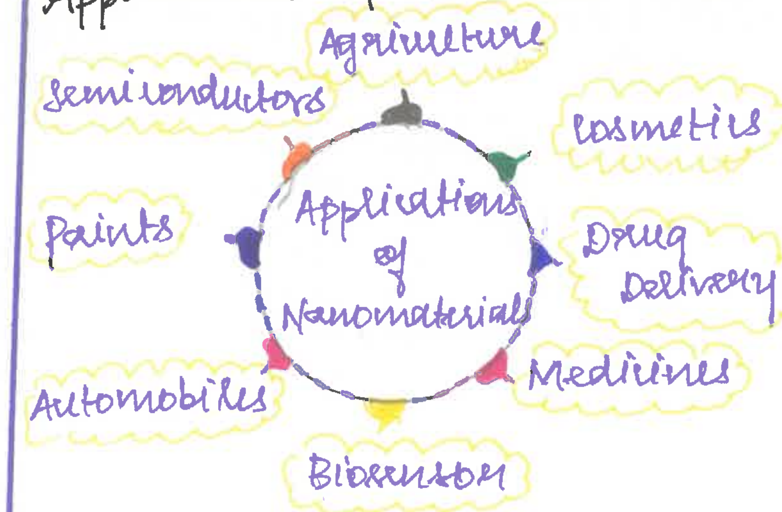

**Properties of Nanomaterials:-**

- Reduced Melting point (↑ with lattice size ↓)
- Ultra hard (↑ with reduced defects)
- Optical (blue shift due to ↑ Eg)
- Electrical conductivity (↓ with reduced Dimension, ↑ with better order)
- Magnetic (ferromagnetism > super paramagnetism)
- Self purification (Enhanced diffusion of impurity)
- Chemical stability (Depends on perfection)



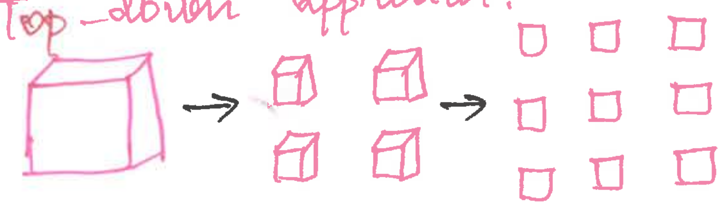

**Applications of Nanomaterials:-**




**Possible Approach of NMs:-**

Top-down approach
Bottom-up approach

Top-down approach:



Bottom-up Approach:

**Synthesis Methods:-**

| Chemical Methods | Physical Methods |
|---|---|
| Sol-gel Method | Ball milling |
| Condensation method | Thermal decomposition |
| Sol method | plasma Arch |
| Hydrothermal method | Electron beam (PVD) |
| Solvothermal method | Sputter deposition. |

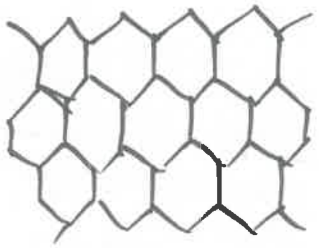
## Allotropes of Carbon

* Variable Oxidation states
Coordination number

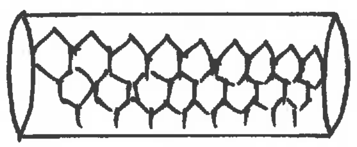
Ex: Diamond, graphite, Lonsdalite, Q- Carbon
Linear acetylenic carbon
Amorphous carbon fullerences
Carbon nanotubes

**Carbon Nanomaterials:**

Graphene

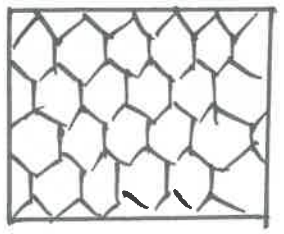


CNT



Fullerenes

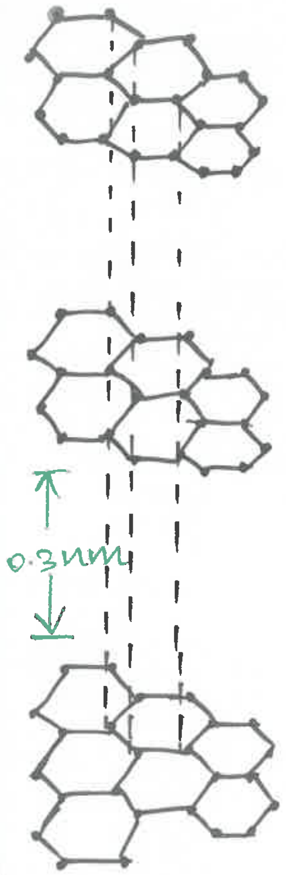
Graphene Nanocomposites



• $FeF_3$
$FeF_3$/graphene nanocomposites

## Graphene

* One atom thick planar sheet
* 2-D crystalline
* C-C 1.42 Å
* Interplanar spacing (3.35Å)
* Completely transparent
* Dense (Helium can pass)




### Properties of Graphene

* Structural
select repair holes
* Chemical
reactive
* Electronic
semi-metal or zero gap
* Electrical - high electron mobility conducts
* Optical
* Absorbs ≃ 2.3% of white light
High capacity
* Thermal - Thermodynamically stable
* Mechanical - strongest material
Breaking strength (100 times than steel)

**Other forms of graphene**

* Nanostripes (Spintrontes)
* Graphene oxide (GO)
* Soluble fragments of graphene
* 3-D graphene
* Bilayer graphene

## Carbon Nanotubes (CNT's)

→ CNTs - tube shaped materials
→ Made of carbon
→ Members of the fullerene structural family

**Classification**

i) Single walled Carbon Nanotubes (SWCNT's)
ii) Multi walled carbon Nanotubes (MWCNT's)

**SWNT's**

→ Special class of carbon materials
→ 1-D materials
→ Sheets of graphene - rolled up to form hollow tubes
→ Minimum diameter - 1 nm
→ Band gap - 0-2 eV

**MWNT's**

→ Elongated cylindrical nano objects made of Sp-2 Carbon
→ Diameter - 3-30 nm
→ Multiple rolled layers
→ Interlayer distance - 3.4 Å

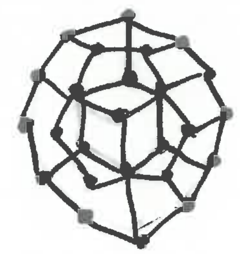
To describe structure of MWNT's:

Russian doll model
CNT contains another CNT inside it

Parchment model
Single sheet of graphene rolled over itself

## Fullerenes

$C_{20}$



$C_{28}$

→ A fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid or tube
→ Spherical fullerenes are also called buckyballs cylindrical the existence of C60, C70, C76 & C84

**Properties of fullerene**

Aromaticity: "Superaromaticity" that the electrons in the hexagonal rings donot delocalize over the whole molecule
Chemistry: Fullerenes are stable, but not totally unreactive

**Nano peapods**

Carbon peapod is a hybrid nanomaterial consisting of spheroidal fullerenes encapsulated within a carbon nanotube

**Applications**

→ Nanoscale laser
→ Single electron transistors

## FABICATION OF GRAPHELE:-

### Chemical vapour Deposition (CVD)

L CVD involves Dissociation, chemical Reactions of gaseous Reactants.

**Advantages:-**

* High quality graphone
* Absence of Impurities.

**Important components of CVD:-**

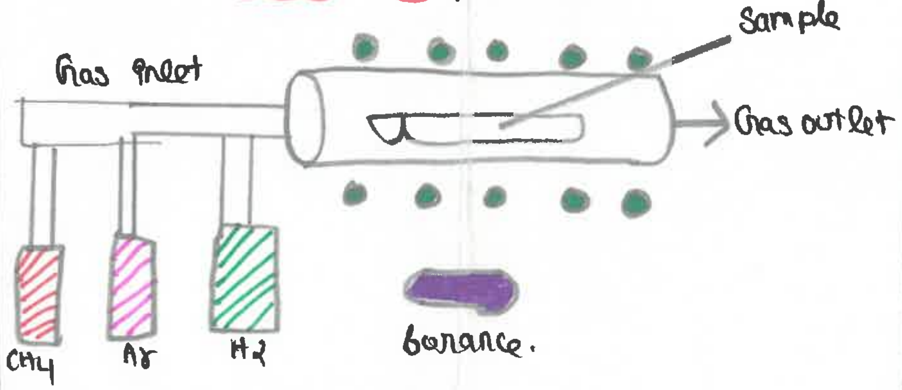
* chemical vapour precussion supply system
* CVD Reactions.
* Hot-wall Reaction
* Cold-wall Reactor.

The efficient gas handling system

Types of CVD }-
- Atmospheric pressure chemical vapour deposition (APCVD)
- Low pressure chemical vapour Deposition (LPCVD)

* Metal-organic chemical vapour Deposition
* Laser chemical vapour Deposition (LCVD)
* plasma enhanced chemical vapour Deposition (PECVD).

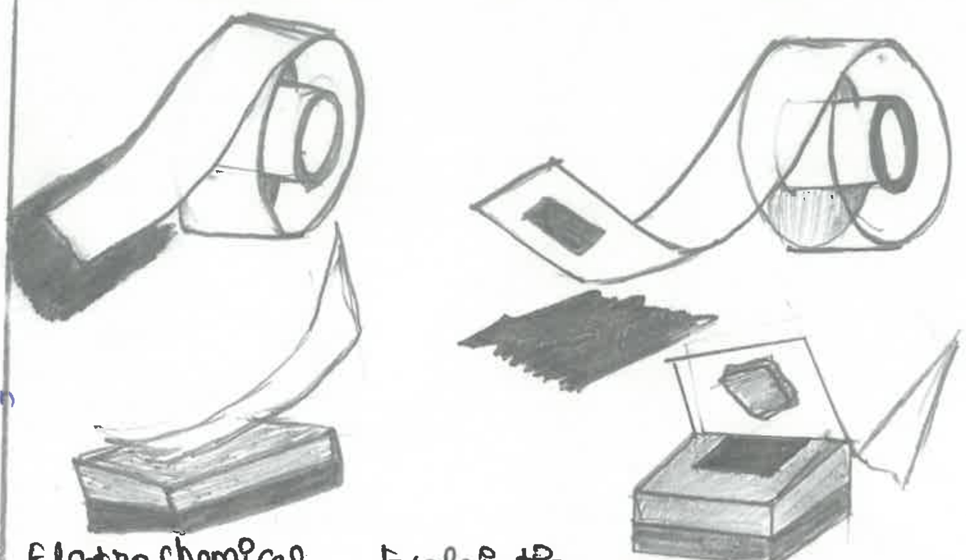
### Chemical vapour Deposition.




↳ Precusor - Hydrocarbons
↳ quite conformal
↳ versatile
↳ High purity & Density
↳ Hot & cold wall reactors
↳ carrier gas - Ar & $H_3$

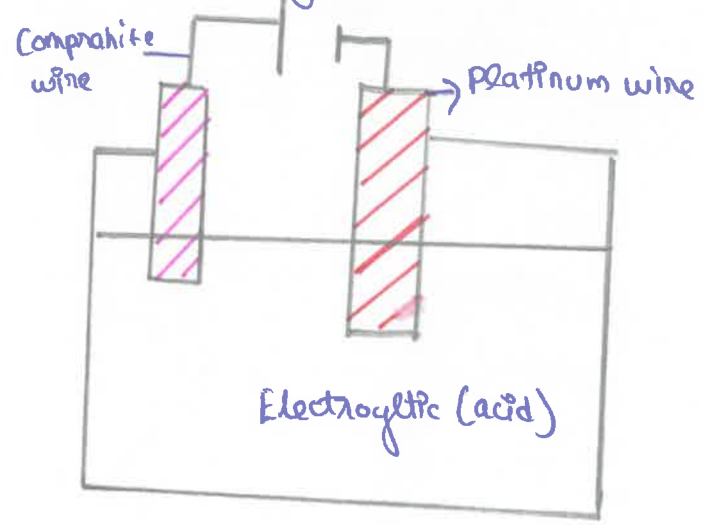
### Mechanical Exploition

* Scotch tape
* Se/$SiO_2$ wafer
* Impurity
* Limitations & skilled labour
* Highly ordered pyrolytic



### Electrochemical Exploiation:-

* Eco-friendly and high yield
* ordinary environment
* Precusor - graphite & HOPG.




* Cu on pt electrode
* Easy to operate
* Scalable.
* Impurities - unwashed salts.

### Application of Graphene:-

* Mechanical Strength, building materials mobile Device.

## Nano Composites

A fascinating class of materials that combine organic polymers & inorganic particles, contains,

⇒ Multiphase solid material (one / two / three dimensions)

⇒ Nano phase (< 100 nm) can be

1. Nanoparticles
2. Nanotubes / rods
3. Lamellar / fibrillar (CNT)

## Classification of Composites

**Matrix**

⇒ Metal
⇒ Ceramic
⇒ Polymer

1. Thermosets
2. Elastomers
3. Thermoplasts

**Reinforcing phase**

⇒ Material
⇒ Architecture

Continuous

Discont.
1. particle
2. Short fibre

## Classification of Nano Composites

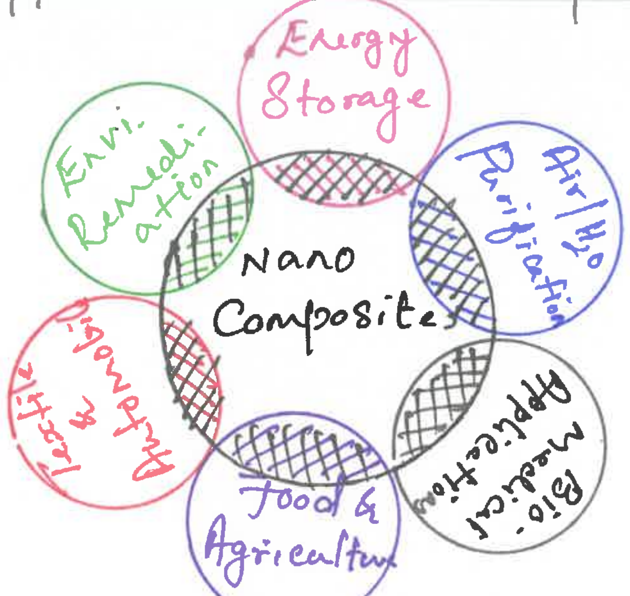
**Polymer Based**

1. Polymer / ceramic
2. Inorganic / organic polymer
3. Polymer / Layered silicates
4. Inorganic / organic Hybrid

**Non-polymer Based**

1. Metal Matrix nanocomposite
2. Ceramic nanocomposite
3. Ceramic / ceramic nanocomposite

## Applications of Nano composites



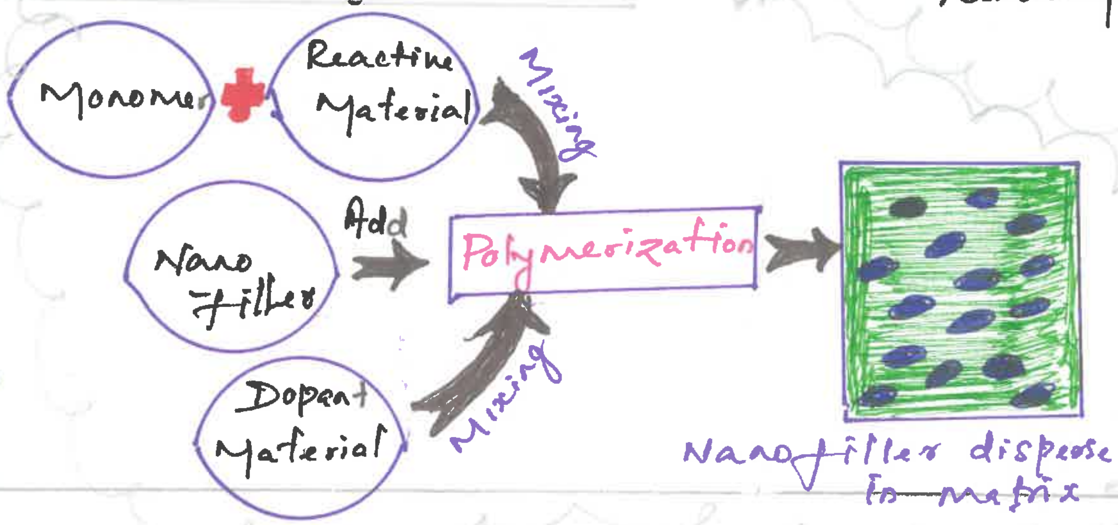

## Graphene - Polymer Nano Comp.

A layer of carbon atoms in a hexagonal lattice, incorporated into polymer matrix

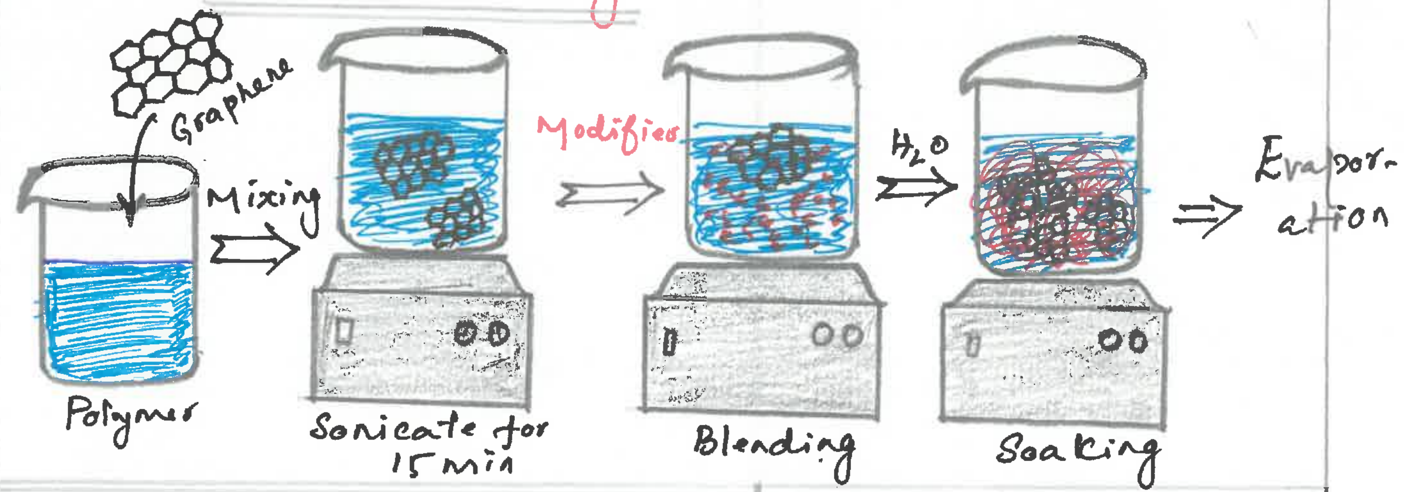
**Synthesis of Graphene - polymer Nano Composites**

⇒ Solution Casting
⇒ Melt Blending
⇒ In situ Polymerisation
⇒ Electrospinning
⇒ 3D Printing

## In-Situ Polymerization

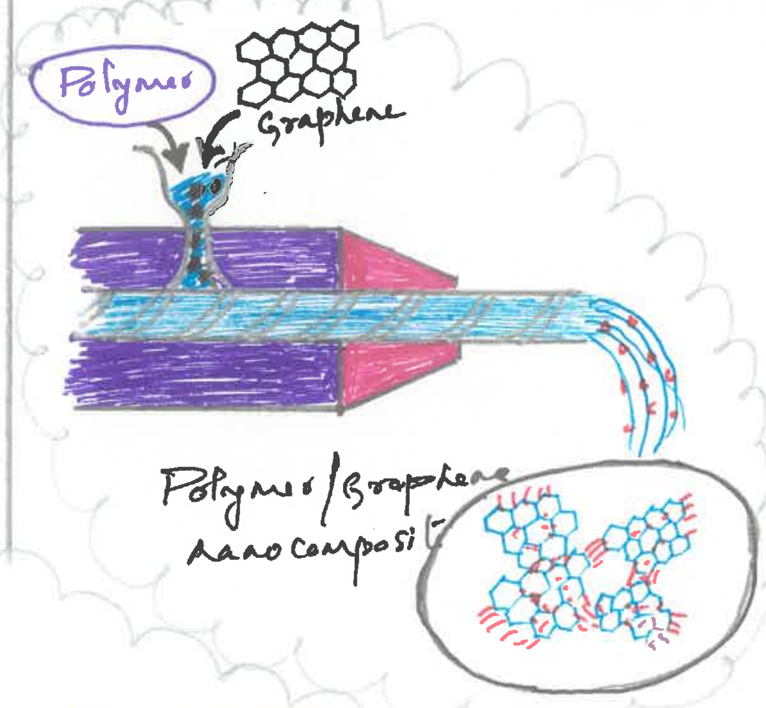



## Solution Casting




## Melt Blending / Mixing

⇒ High temp. & Shear forces
⇒ Easy dispersion / intercalation
⇒ Applicable to polar & non-polar polymers
⇒ Scaled-up to Industrial level

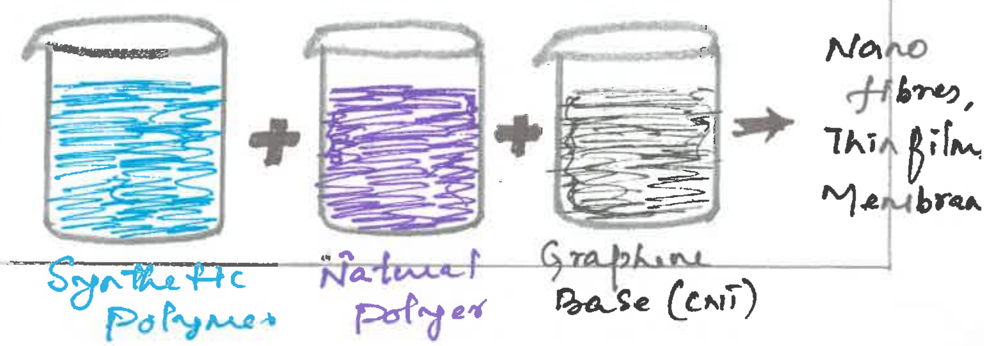



## Applications of polymer Nano composites


## Applications of Non-polymer Nano composites

⇒ Automobiles
⇒ Electronics
⇒ Energy Generation
⇒ Biosensors
⇒ Env. Remediation

## Synthesis of Graphene Infused Polymers



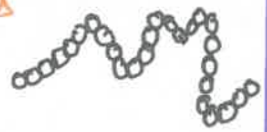
## Polymer & its calassifications:-

polymer – very high molecular weight.

Many units of monomers covalently bonded toagther to form a long chain. [or macromoleaule]

monomer $\xrightarrow[\text{(covalent bonds formed)}]{\text{Polymerisation}}$ polymer

O



mono-mer / single part
oligo-mer / few parts

From the Greek words:
'poly' meaning 'many'
'meros' meaning 'parts'

[eg]

$nH_2C=CH_2 \longrightarrow \{CH_2-CH_2\}_n$

$n\ H_2C \overset{O}{—} CH_2 \longrightarrow \{CH_2-CH_2-O\}_n$

* polymer production is 368 million metric tons in per annum (>> all other synthetic chemicals combined.
* more than 50% of Industrial chemists works on Polymer related projects.
* polymer will play a crucial roles in current and future technologies.


## classification of polymer

1. Based on origin
   * Natural
   * Synthetic

a) Natural polymer
* Naturally eccurs

Eg: Starch, cellulose, proteins, natural rubbers.

b) Synthetic polymer
* prepared artificially in lab.

Eg:- polyethylene (PE), nylon, polyvinyl chloride, terylene.

2. Based on monomer Composition:-

a) Homopolymer – only one type of monomer.

$nA \longrightarrow (A)_n$

$nCH_2=CH_2 \longrightarrow \{CH_2-CH_2\}_n$

Ethylene — polyethylene

b) copolymer – more than one type of monomer.

$nA + mB \longrightarrow A-A-B-B-A-B$

$n\{CH_2-CH=CH-CH_2\}_n \{CH_2-CH\}_m$ (with $C_6H_5$ on CH)

styrene — butadiene — rubber

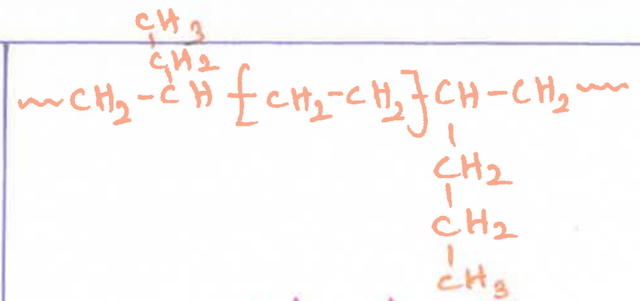
3. Based on chain structure.

a) linear
* long and straight chains
* no branches
* well packed and high densities

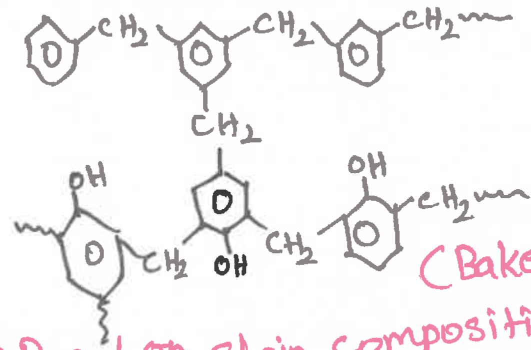
Eg:- Polyethylene, nylon.

b) Branched Polymer
* linear chains with side chains
* irregularly packedged and low densities.

Eg:- low density polyethylene [LDPE].



c) cross linked polymers:
* Three dimensional network
* Bi and Tri functional monomer used.
* Strong covalent bond, hard, brittle



(Bakelite)

4. Based on chain composition:

a) Homochain: all carbon atoms in back bone.

eg:- PVC

b) Hetero chain: contains N, S, O

eg: nylon, terylene.

5. Based on polymerisation:-

a) Addition polymers:-
obtained is addition of monomers
n(monomer) → polymer.

M.W of polymers = n × M.W of polymer

eg:- pvc, polyethylene.

b) condensation polymers:-
* condensation polymer of two or more monomers.
* Simple molecules eliminated.

$nHO-R-OH + n\ HOOC-R-COOH$
$\downarrow$
$\{O-R-O-\overset{\underset{\|}{O}}{C}-R-\overset{\underset{\|}{O}}{C}\}_nO + nH_2O$

ester

6. Based on chemical composition

a) organic polymer:
backbone composed of C, N, O, S

Eg:- pvc, nylon 66

b) Inorganic polymer:
No carbon is back bone.

Eg: Phosphazene, Silicon rubber.

7. Based on molecular forces.

a) Elastomers:
* weakest intermolecular forces.
* elastic behaviour.

Eg:- natural rubbers.

b) Fibres:
* chains held together by strong intermolecular forces.
* High tensile strength

eg:- nylon 66, polyester, silk

c) Thermoplastics:
* linear long chain
* Soften on heating
* intermediate intermolecular force
* remoulded agin

eg: PVC, teflon

d) Thermosetting plastics:
* hard and rigid
* cannot be reshaped

eg: bakelite, melamine

classification system for polymers enhances understanding of their properties, Processing techniques and applications across industries such as consumer goods, packaging, aerospace, and automotive sectors.

# PLASTICS

* high molecular weight organic materials
* moulded into shape by applying heat and pressure
* intermediate intermolecular force between elastomers and fibres

## ADVANTAGES

* high strength/weight ratio
* low melting point
* easily moulded
* very good strength and toughness
* low co-efficient of thermal expansion

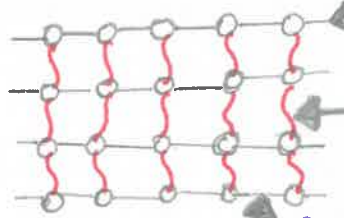
## DISADVANTAGES

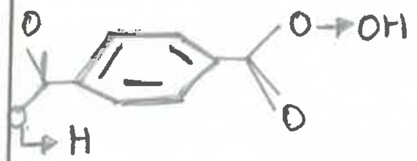
* Softness, brittle at low T
* Deformation under load
* low heat-resistant
* degrade upon exposure at heat and UV radiation

## PLASTIC CLASSIFICATION

i) Based on Structure

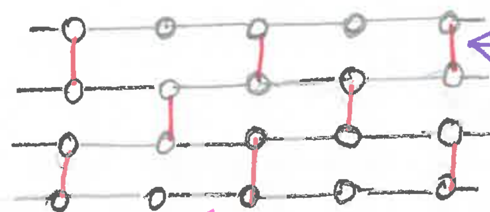
a) Thermoplastics
soften on heating, harden on cooling



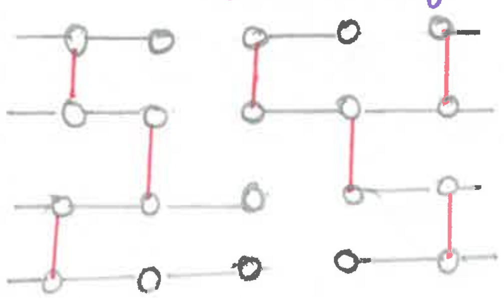



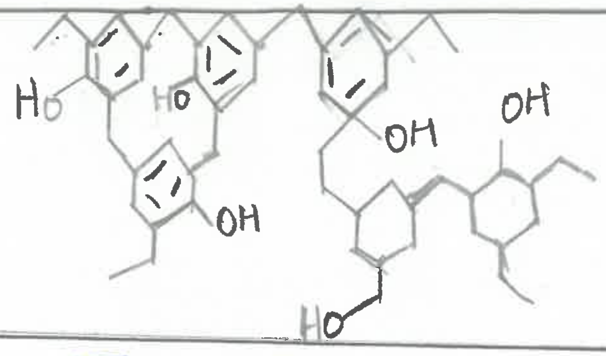

Ex: PVC, Polythene, PET

b) Thermosetting Plastics
harden on heating
cannot be softened again




↓ heating




eg: Bakelite, Polyster

| THERMOPLASTICS | THERMOSETTING PLASTICS |
|---|---|
| * Produced by additional polymerisation | * Produced by condensation Polymerisation |
| * Processed by injection moulding | * Produced by compression moulding |
| * linear long chain polymer | * cross linked three dimensional network structure |
| * weak vanderwaals force b/w polymer chains | * strong covalent bonds b/w polymer chains |
| * weaker, soft and less brittle | * strong, hard and more brittle |
| * Remoulded | * Scraps cannot be remoulded |
| * soluble in organic solvents | * insoluble in organic solvents |
| * Behave like metals & glasses | * Behave like cements & ceramic |

uses:

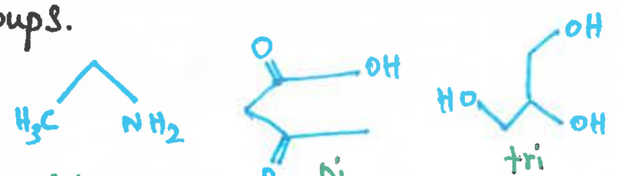
(a) polyethylene tetrapthalate
drinking bottle, microwave packaging
(b) polyvinyl chloride (PVC) Plastic bags, container lid
(c) polystyrene (PS)
food container, bottle caps, medicine bottles, straws
(d) HDPS - custom packing

uses:

(a) Epoxy resin
bonding, laminating, coating
(b) Bakelite
electrical insulator and Plasticware
(c) Polyurethanes: mattresses, car Parts, shoe soles, flooring
(d) Durbplast - making car parts

## Functionality

* It is the number of polymerizable groups.



Mono Di tri

**Degree of polymerization :-**

* Number of repating monomer units in the polymers.

Degree of polymerization (DP) = $\frac{MW}{MO}$

where :-

Mw – Avg molecular wt of polymers
Mo – Molecular weight of repating unit or monomer.

**Degree of polymerisation, DP :-**

Dp = mean number of monomer per polymer chain. e.g calculate the DP of a polystyrene chain with an Mn of 10,000.

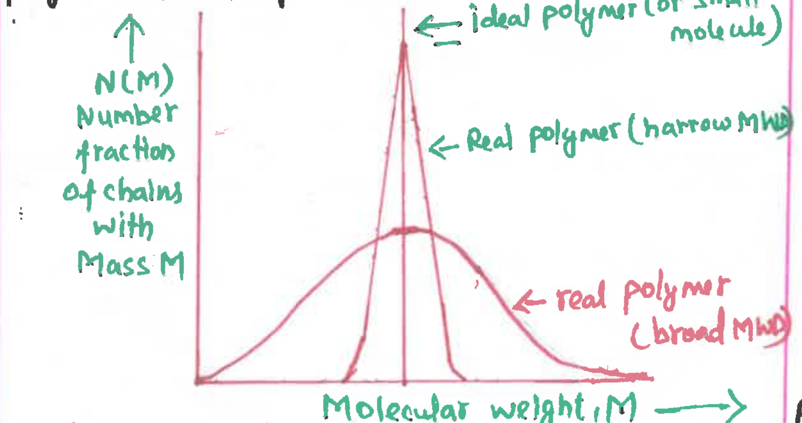
$Dp = \frac{10,000}{104} = 96.15 = 96$

* If Dp < 10, get, OLIGOMERS, not polymer

**Molecular weight of polymers :-**

problem :- polymers have different chain length

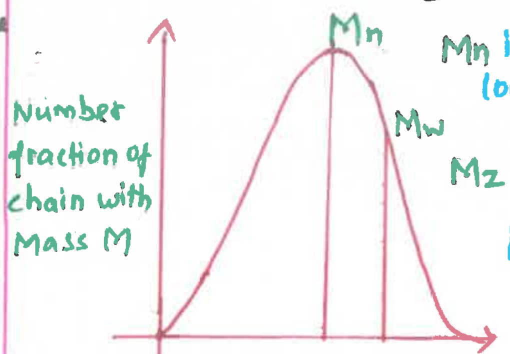
* Unlike small molecules, polymer are 'polydisperse' (no unique molecular weight)
* Hence need to measure the molecular weight Distribution (MWD).
* Define N(M) as the number fraction of polymers chains of molecular weight M.




**Molecular weight :-**

Number of average $(M_n) = \frac{\sum n_i M_i}{\sum n_i}$

weight - average $(M_w) = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$

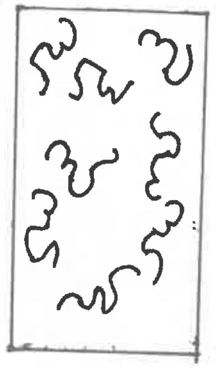



Mn is biased towards low mol. wt, species

Mz is seldom used

$M_n < M_w < M_z$

**8 mol 5000 Molecular weight :-**



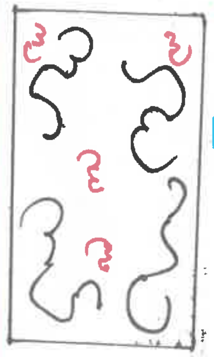
$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i} = \frac{8 \cdot 5000}{8} = 5000$

$\overline{M_w} = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{8 \cdot 5000^2}{8 \cdot 5000} = 5000$

$PDI = \frac{\overline{M_w}}{\overline{M_n}} = 1$

monodisperse (molecularly uniform)

**4 mol 9000 molecular weight, 4 mol 1000 molecular weight :-**



$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i} = \frac{4 \cdot 9000 + 4 \cdot 1000}{4+4} = 5000$

$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{4 \cdot 9000^2 + 4 \cdot 1000^2}{4 \cdot 9000 + 4 \cdot 1000} = 8200$

$PDI = \frac{\overline{M_w}}{\overline{M_n}} = 1.64$ polydisperse

**polydispersity index, PDI**

$PDI = M_w / M_n$

* a crude measure of the width of the MWD curve.
* If PDI < 1.20, near-monodisperse polymer (by living anionic polymerization)
* If PDI < 1.20 polydisperse polymer (PDI > 2.0 very often)

## Types of polymers.

**Addition polymers :-**

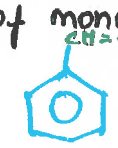
* Repeated addition of monomers molecules possessing double or triple bonds

**Homopolymers :-** Obtained from same monomers.

eg. polyethe

$n CH_2 = CH_2 \longrightarrow \sim[CH_2 - CH_2]\sim$
(ethane) (polyethane)

**copolymers :-** two diff units of monomers.

$n CH_2 = CH - CH = CH_2 + n$  $\longrightarrow$

1,3 Butadiene Styrene

$\sim[CH_2 - CH = CH - CH_2 - CH_2 - CH_2]_n\sim$ 

Butadiene - styrene copolymers [BUNA-S]

**Addition polymerization mechanism :-**

* Chain growth polymerization free radicals mechanism.

**(i). chain - initiation Step :-**

$C_6H_5 - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - C_6H_5 \rightarrow 2(C_6H_5\overset{O}{\overset{\|}{C}} - \dot{O}$

Benzyl peroxide

$\rightarrow 2\, (\dot{C}_6H_5$

phenyl free radical

$C_6H_5 + CH_2 = CH_2 \longrightarrow C_6H_5 - CH_2 - \dot{C}H_2$

**(ii) chain propagating step :-**

$C_6H_5 - CH_2 - \dot{C}H_2 + CH_2 = CH_2 \rightarrow C_6H_5 - CH_2 - CH_2 - CH_2 - \dot{C}H_2$

$\downarrow$

$C_6H_5 [CH_2 - CH_2]_n CH_2 - \dot{C}H_2$

**(iii) chain terminating Step :-**

$C_2H_5 [CH_2 - CH_2]_n CH_2 - \dot{C}H_2 +$
$C_6H_5 [CH_2 - CH_2]_n CH_2 - \dot{C}H_2$
$\longrightarrow C_6H_5 [CH_2 - CH_2]_n - CH_2 - CH_2 - CH_2 - CH_2 [CH_2 - CH_2]_n C_6H_5$

polythene

**Condensation polymers :-**

* condensation reaction between bifunctional and trifunctional monomers.
* Elimination of small molecules like $H_2O$, alcohol, HCl etc.

$n NH_2 - (CH_2)_6 - NH_2 + n HOOC - (CH_2)_4 COOH$
(Hexamethylene diamine) (Adipic acid)

$\downarrow$

$\sim[NH - (CH_2)_6 - NH - CO - (CH_2)_4 - CO]\sim_n + H_2O$
(nylon-6,6)

| Addition polymerization | Condensation polymerization |
|---|---|
| Must have atleast one multiple bond | Must have atleast two identical ordifferent functional group |
| No other byproduct is formed | By product such as $H_2O$ $CH_3OH$ are formed. |
| No of monomeric units decrease steadily. | monomer disappear at the early stage of reaction |
| polymer molecules weight is multiple of monomer molecular weight | polymer molecular weight need not be an integral multiple of monomer. |
| High molecular weight polymer is formed at once | molecular weight of the polymer rises steadily. |
| Longer reaction times gives higher yield. but have a little effect on molecular weight. | Longer reaction times are essential to obtain high molecular weight. |

# Importance of Addition Polymer -

## Polyethene -

1) Low-density Polythene [LDPE]

- $nCH_2 = CH_2 \xrightarrow[1000-2000\,atm]{350-370K} \sim[-CH_2-CH_2\sim]_n$

Traces of Oxygen

Properties -

- Chemically inert, tough, flexible, poor conductor of electricity.

Applications -

- Insulation of electric wire, squeeze bottles toys and flexible pipes.

2) High-density Polyethene [HDPE]

- $nCH_2 = CH_2 \xrightarrow[\text{Zeigler-Natta catalyst}]{333-343K / 6-7atm} \sim[CH_2-CH_2]_n$

Properties -

Chemically inert and tougher, harder.

Uses -

- Buckets, dustbins, bottles etc.,

3) LLDPE (Linear low-density poly ethylene)

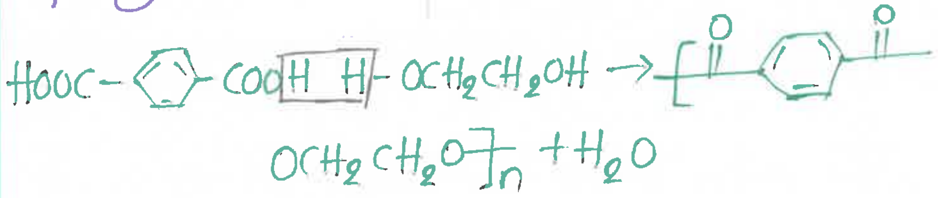
* copolymer of ethylene & 1-butene

Uses - making golf ball covers, orthopae

4) UHMWPE [ultrahigh molecular-weight polyethylene]

Uses - It is used in making surgical prostheses heavy duty liners

## Polyester



Brand names depending on the manufacturer and specific products.

Brand Names - Dacron, Terylene, PET.

Used in Clothing, home furnishings, and industrial textiles, including fleece and performance fabrics.

## Polyamide -

Hexamethylene diamine

$nHO-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-\boxed{OH + H}-\overset{H}{N}(CH_2)_6NH \rightarrow [\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-\underset{H}{N}(CH_2)_6\underset{H}{N}]_n + OH_2$

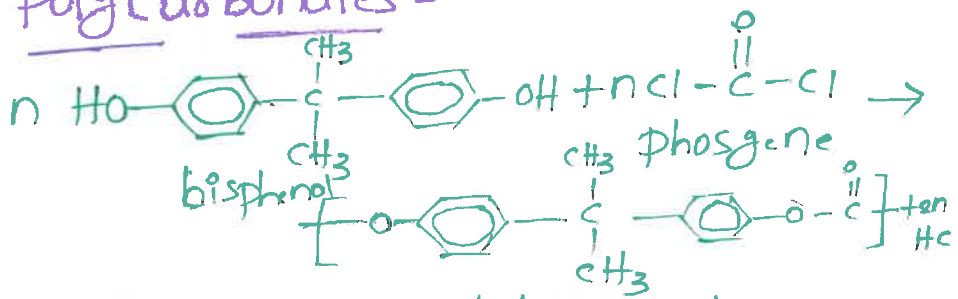
Adipic acid

Nylon

Brand name - Nylon, kevlar, Nomex, caprolon, Tactel, Derlon, Cordura.

used in textiles such as clothing sportwear, and lingerie due to its durability and elasticity.

## Poly Carbonates -

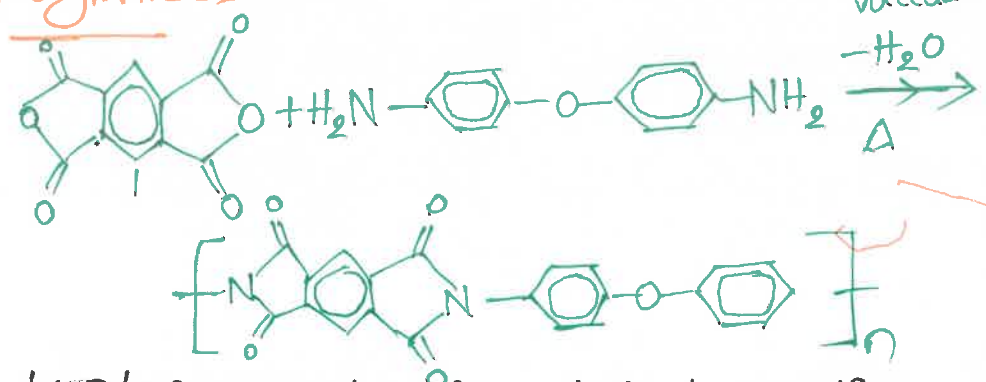



Polycarbonate

Brandname - Lexan, Makrolon, Calibre, Panlite, Tarflon.

Lexan by SABIC and Makrolon by Convestro are Prominent in automotive aerospace, electrical, medical applications

## Polyimides




Kapton, vespel, upilex, Apical, pyralin

Used in flexible printed circuits, aerospace application and electronic industries.

## Polyurethane -

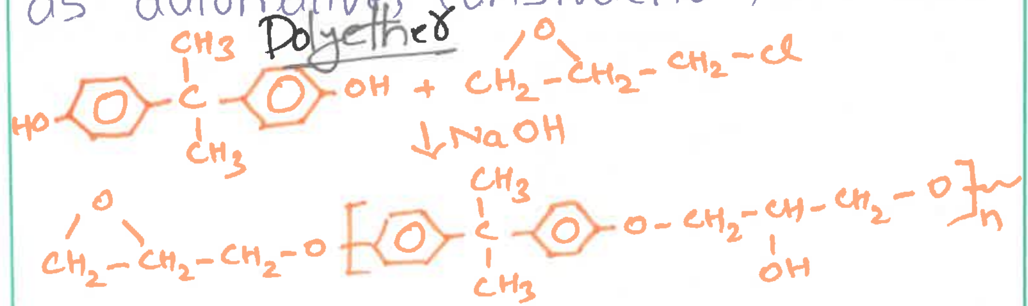
$R-N=C=O + ROH \rightarrow R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-OR$

Isocyanate alcohol urethane

(Adiprene, Elastollan, Estane, Bayflex, Bionate) (Diverse Applications)

including coatings, adhesives, foams, and elastomers in industries such as automotive, construction, furniture.

## Polyether




Loctite epoxy, Epoxy-shield, Devcon

* Adhesive and sealants in construction
* composite materials for aerospace, automotive marine, and sports equipment
* coatings and paints
* Insulation and encapsulation