

THERMODYNAMICS:

Thermodynamics — Study of heat history of a chemical reaction.

System — Part of the universe under study.

Type: Homogeneous, Heterogeneous, Open, closed & Isolated.
It predicts law for a reaction can occur.

Parameter of Thermodynamics: upto the attainment of eqm. conditions.

Enthalpy (H) ; Internal energy (E).
Entropy (S) 2. Gibbs free energy (G).

Intrinsic Property — independent of mass. Eg: Temperature, Pressure.
Extrinsic Property — dependent on mass. Eg: Force, Density.

Various Systems —
Homogeneous — uniform throughout ; (e.g. mixture of gases)

Open System — both matter & energy exchange.

Closed system — only energy exchange. Eg. Hot water contained in a closed vessel.

Isolated — neither of the two. (Eg. Two islands). \star

* Extensive properties are additive while intensive properties are not.

* → First law of Thermodynamics:

1. → Energy of the universe is always constant.
2. → Energy can neither be created nor be destroyed.
3. → Energy can be transferred from one form to another.

Eqn: Mathematical express:

$$\begin{aligned} E &= q - w \\ &\quad \text{E: Total energy.} \\ &\quad \text{-w: Work done by the system.} \\ &\quad \therefore q - (-w) \\ &\quad \therefore E = q + w \end{aligned}$$

1. Entropy of the universe is always increasing.
2. It is impossible to construct the machine with 100% efficiency in practical.

3. Heat transfer is always from hotter region to colder region.
4. Without the aid of external work, it is not possible to transfer the heat energy from cold area to hot area.

4. All the naturally occurring spontaneous processes are thermodynamically irreversible.

Third law :-

Entropy of a perfect crystalline solid is zero at absolute temperature. It helps us to calculate the absolute entropies of chemical compounds at any desired temperature.

Trauton's Rule :- *

For all the liquids having normal type of bonding, ΔS_{vap} is nearly same and the figure is approx. equal to 85 kJ/mol irrespective of the chemical nature, except for the liquids having exceptional type of bonding i.e., Hydrogen bonding in H_2O , Metallic bonding in mercury (Hg), etc.

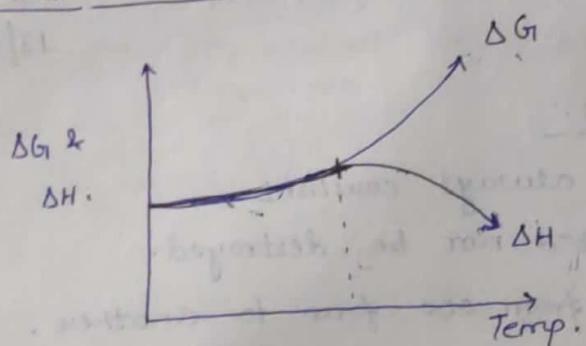
$$\frac{\Delta H_{\text{vap}}}{T_B} \approx \Delta S_{\text{vap}} \approx 85 \text{ kJ/mol.}$$

$\Delta H_{\text{vap.}}$: Heat of vapourisation.

T_B : Boiling temp.

ΔS_{vap} : Entropy of vapourisation.

* Neunst Heat Theorem:- *



Short theorem :-

The asymptotic variation of ΔG and ΔH with absolute temp.

- Applicable only to solids.

→ As the temp. decreases and approaches to absolute zero, ΔG increases and ΔH decreases, both meeting at a certain temp. and then there is levelling of both until absolute zero -

→ The Neunst heat theorem says that as absolute zero is reached, the entropy changes as for a chemical or physical transition approaches 0.

$$\lim_{T \rightarrow 0} \Delta S = 0$$

$$\Delta G_2 - \Delta E_1 = \Delta C_V (T_2 - T_1)$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

Eqm. State \rightarrow It is the condition of the system where all state variables have constant values throughout the system.

→ Chemical Potential :-

- Capacity of thermodynamic system.
- Depends on the no. of components in a system.
- cannot be calculated in a single step.

$$U_{ni} = \left(\frac{dg_i}{dn_i} \right)_{T, P, n=1, 2, 3, \dots, \infty} \text{ except } n_i$$

$n_i \rightarrow$ amount of the i th component.

→ Definition -

- chemical potential of a thermodynamics system is the sum of the individual chemical potential values of the components existing in the system. (Increase in free energy which takes place in temp. and pressure when one mole of that constituent is added to the system keeping the amt. of all other components const.)
- chemical potential of a particular component is the change in free energy of the system under eqm. when one mole of that particular component is added to the system keeping all other components const. ($P & T$ const.)

Fugacity (f): - It is a pressure substitute.

$f = \sigma \cdot p$	$f = \frac{H}{P}$	<u>Pressure Substitute:</u>
$p \rightarrow$ Pressure.	$\sigma \rightarrow$ Activity const.	$H_i = H_0 + RT \ln f_i$

Inq: * Variation of ' G_i ' with respect to 'Temp.' & 'Pressure' - *

Fugacity is defined as a substitute for pressure introduced to explain the behaviour of a real substance.

$$G_i = H_i - TS \quad (1)$$

$$H_i = E_i + PV_i \quad (2)$$

Substitute (2) in (1) +

$$G_i = E_i + PV_i - TS \quad (3)$$

$$dG_i = dE_i + PdV_i + VdP_i - TdS_i - SdT_i \quad (3)$$

$$S = q/T$$

$$q_s = ST$$

$$dq_s = TdS_i \quad (5)$$

$$E = q - N$$

$$q = E + N$$

$$dq = dE + dN$$

$$dq = dE + PdV \quad (4)$$

Equate eq. (3) & (4) $\Rightarrow dE + PdV = TdS \rightarrow (6)$.

Substitute eqn. (6) in (3) -

$$dG = dE + PdV + VdP - TdS \rightarrow PdV - SdT.$$

$dG_1 = VdP - SdT$ This exp. gives the change in free energy with change in pressure and change in temp. is a reversible process.

$$\therefore \left(\frac{dG}{dT}\right)_P = -S.$$

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

→ * Gibbs Helmholtz Equation:

$$dG = VdP - SdT.$$

$$\Delta G_i = \Delta H - T\Delta S.$$

Initial stage - $\left(\frac{dG_1}{dT}\right)_P = -S_1, ; \left(\frac{dG_2}{dT}\right)_P = -S_2.$

$$\therefore \left(\frac{dG_2}{dT}\right)_P - \left(\frac{dG_1}{dT}\right)_P = -S_2 - (-S_1) \\ = -S_2 + S_1 = -(S_2 + S_1) = -\Delta S.$$

$$\therefore d\left(\frac{\Delta G}{dT}\right)_P = -\Delta S.$$

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

15th Sept. 2018.

→ Kuichhoff's equations:- It gives the relationship b/w the variations of heat of reaction with temperature.

$$\Delta E = E_2 - E_1.$$

(E_1 and E_2 are the internal energies of the reactants and products respectively and E is the heat of the reaction)

$$d\left(\frac{\Delta E}{dT}\right) = \frac{dE_2}{dT} - \frac{dE_1}{dT}.$$

$$\therefore \left(\frac{dE}{dT}\right)_V = C_V.$$

$$\therefore d\left(\frac{\Delta E}{dT}\right)_V = C_{V_2} - C_{V_1} = \Delta C_V.$$

$$\therefore \Delta AB = \Delta C_V \cdot \Delta T$$

$$\frac{T_2}{T_1} \int d\Delta AB = \frac{T_2}{T_1} \int \Delta C_V \cdot dT$$

$$\therefore \Delta B_2 - \Delta B_1 = \Delta C_V (T_2 - T_1)$$

$$(2) \quad \Delta H = H_2 - H_1$$

$H_1 \rightarrow$ enthalpy of reactant
 $H_2 \rightarrow$ enthalpy of products

$$\therefore d\left(\frac{\Delta H}{dT}\right) = \frac{dH_2}{dT} - \frac{dH_1}{dT}$$

$$\therefore \left(\frac{dH}{dT}\right)_P = C_P \Rightarrow d\left(\frac{\Delta H}{dT}\right)_P = C_{P2} - C_{P1} = \Delta C_P$$

$$\therefore \Delta H = \Delta C_P \cdot \Delta T$$

$$H_2 \int d\Delta H = \int_{T_1}^{T_2} \Delta C_P \cdot dT$$

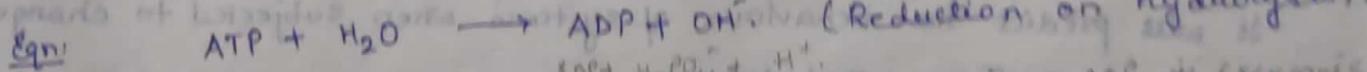
$$\therefore \Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$$

TOP Thermodynamics of Biological Systems

1 mole g of glucose ≈ 2880 kJ.

38 ATP $\rightarrow 38 \times 30 = 1140$ kJ. $(2880 - 1140) = 1740$ kJ.

ATP is the energy rich molecule which is used for various cellular processes like biosynthesis, active transport etc.



For this reaction, $\Delta H^\circ = 30$, it means the hydrolysis of ATP is exergonic and 30 kJ/mol is available for driving other reactions.

Heat of Reaction = change in the amount of heat evolved or absorbed when no. of moles of reactants undergo reaction.

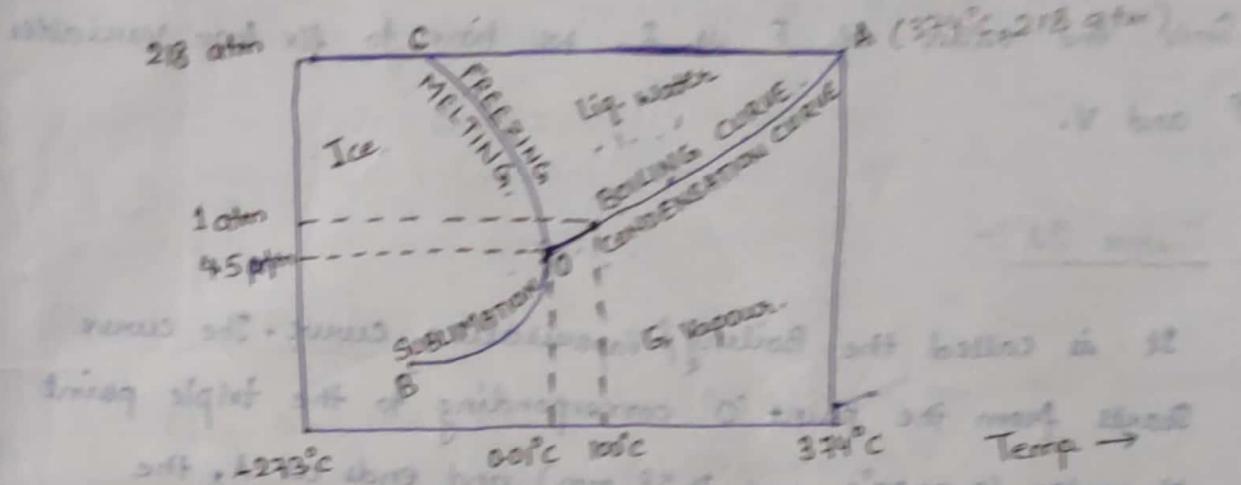
Function of ATP - Store the energy obtained during metabolism of food and supplying it later during various processes.

ATP is also used for various cellular processes like biosynthesis, active transport etc.

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(iii) It will consider under one single eqm state, not considering more than one eqm.

→ Phase Diagram of Water System :-



(1) Area AOC :- If we take area enclosed with vapour line excluding sublimation line in the system.

Area gives the liquid water phase in the system.

$$P+F = C+2$$

$$F = C - P + 2$$

$$= 1 - 1 + 2$$

$$\{ C = 1, P = 1 \}$$

Since the value of F is 2, we have to fix two variables T, P & θ so as to define the components of the system.

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(2) Area BOC :-

Area BOC gives solid ice phase in the water system.

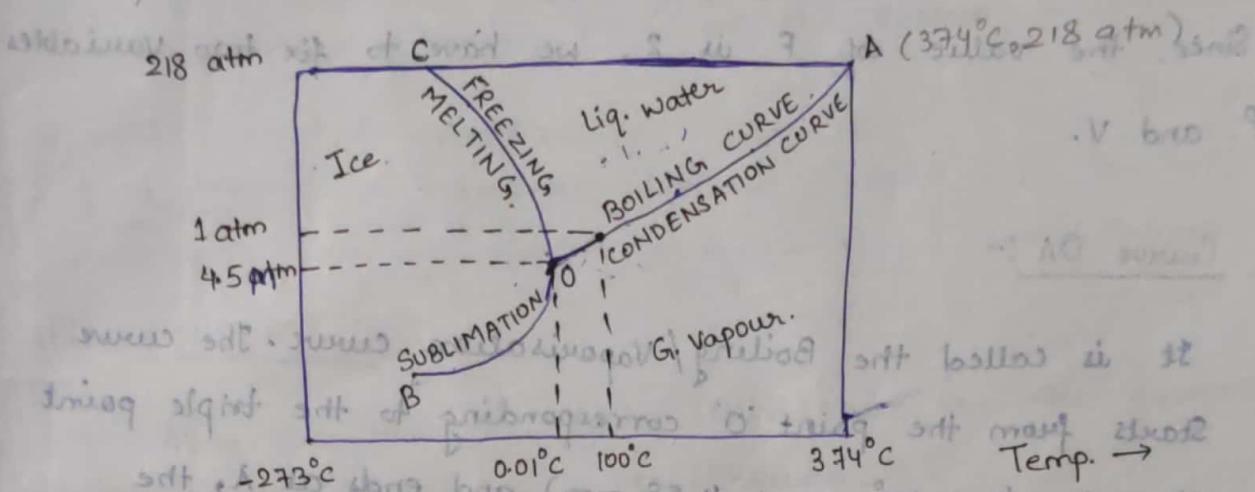
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Since, the value of F is 2, we have to fix two variables P and V .

(iii) It will consider only one single eqm. state, not considering more than one eqm.

→ Phase Diagram of Water System :-



(1) Area AOC :-

This area does not represent any physical area crossing boundaries in the system.

Area gives the liquid water phase in the system.

$$P+F = C+2$$

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 1 + 2 \end{aligned}$$

$$\{ C = 1, P = 1 \}$$

Since the value of F is 2, we have to fix two variables T , P & V so as to define the components of the system.

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$$\begin{aligned} P+F &= C+2 \\ F &= C - P + 2 \\ &= 1 - 1 + 2 \end{aligned}$$

Since, the value of $F = 2$, we have to fix two variables P and V .

(3) Area AOB:

Area ^{AOB}, gives the gaseous vapour phase in the water system.

$$P+F = C+2.$$

$$F = C - P + 2$$

$$= 1 - 1 + 2 = 2.$$

Since, the value of F is 2, we have to fix two variables P and V.

(4) Curve OA:-

It is called the Boiling / Vaporisation curve. The curve starts from the point 'O' corresponding to the triple point of water (0.0075°C and 4.58 mm), and ends at A, the critical temperature (374°C at 218 atm) beyond which the liquid phase merges into vapour phase making them no longer distinguishable from each other. At 100°C , the vapour pressure of water equals the atmospheric pressure and hence, it is called the boiling point of water.

$$C+2 = 7+9$$

$$G+9-0 = 7$$

$$S+L-L =$$

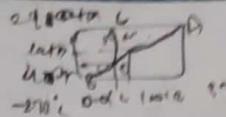
(5) CURVE OB:-

It is called the sublimation curve of ice since ice co-exists in equilibrium with water vapour along this curve. The curve OB terminates at absolute zero (-273°C) where no vapour can be present and only ice exists.

(6) CURVE OC:-

It is called the melting or freezing curve as solid, ice and liquid water coexist in eqm. along this curve. This curve indicates how the melting point of ice or freezing point of water changes with pressure. The slope of OC towards the pressure axis shows that the melting point of ice decreases with increase in pressure.

(7) BOUNDARY OA :-



Along the line OA on the liquid (water) phase and gaseous (vapour phase) coexist in equilibrium. To locate any point on this line, we need to know only temp. or pressure. Hence, $F=1$ or the system is univariant.



(8) BOUNDARY OB :-

Along the line OB, the ice (solid) phase and the gaseous (vapour phase) coexist in equilibrium.

$$\begin{aligned} F &= C-P+2 \\ &= 1-2+2 \\ &= 1. \end{aligned}$$

Hence, to locate any point on this line, we need to know only temperature or pressure. Hence, $F=1$ or the system is univariant.

(9) Boundary OC :-

Along the line OC, the ice (solid) phase and the water (liquid) phase coexist in equilibrium.

$$\begin{aligned} F &= C-P+2 \\ &= 1-2+2 \\ &= 1. \end{aligned}$$

Thus, to locate any point on this line, we need to know only temperature or pressure. Hence, $F=1$ or the system is univariant.

Triple Point :-

It is the point (at 273.16 K and 4.58 mm pressure) where all the three phases ice, water and vapour coexist.

and also $F = P + 2$ and $2 + 2 = 4$
 $= 1 - 3 + 2$
 $= 0$.

This means that all the three phases can exist at eqm. at particular temp. and pressure. The system is characterized by a fixed temp. and pressure and the system is invariant.

word of lesser or equal with no triad pns. equal at 273.16 K
in melting with $2 - 3$ pns. equal. causing no subsequent pns
• invariant

less than unity ($b < 1$) less than $2 - 3$ and with pns
• melting in fusion with (bi-pn) which

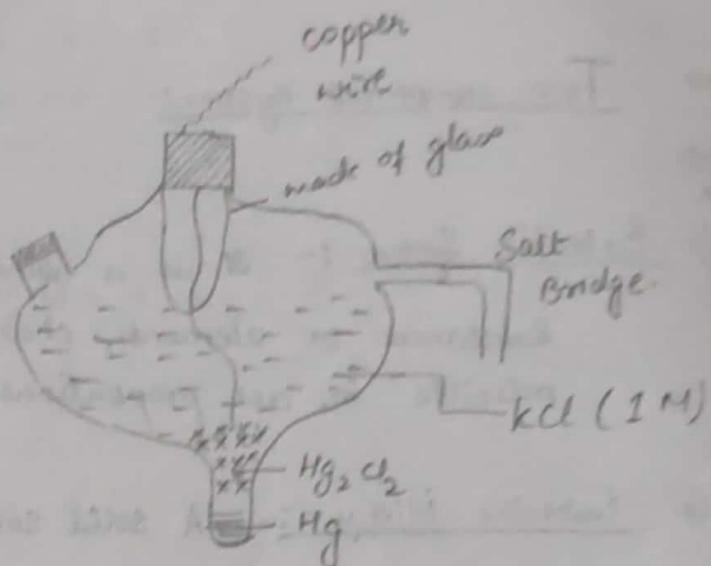
$$2 + 2 - 3 = 1$$

at lesser or equal with no triad pns. equal at 273.16 K
with $2 - 3$ pns. equal. causing no subsequent pns. equal
• invariant in melting

Rough
Page

Electro-chemistry.

Platinum added for
physical support



⇒ TYPES OF ELECTRODES:

* Solid electrode doped in its own ion. (Zn/Zn^{2+}), (Ag/Ag^{2+});
Gaseous electrodes.

G Hydrogen electrodes (NHE, SHE)

Rep: Pt, H_2 | H^+ → $2H \rightarrow H_2$ (Pt, X_2 | X^+)

→ Liquid electrodes → Amalgam electrodes

Eg:- $Zn-Hg$. (metals combined with mercury).

Rep: $Zn-(Hg)$; Zn^{2+} .

* Metal coated with sparingly soluble salt of same metal.

Rep: Ag/AgX ; X^- .

(This ion should be in metal as well as the salt)

Corrosion
Anode and Cathode.

(A + B) (B + C)
(C + D) (D + E)

HOITZUHOD

⇒ Two component system :- Min. available temp b/w the two available components
- Eutectic temp.

Imp.
*

(i) Eutectic System :- It is a binary system consisting of two substances or elements, chemically do not interact, but miscible in all proportions in the liquid phase.

(ii) Eutectic Mixture :- A solid solution of two or more substances or elements having a lowest freezing point of all the possible mixtures of the components.

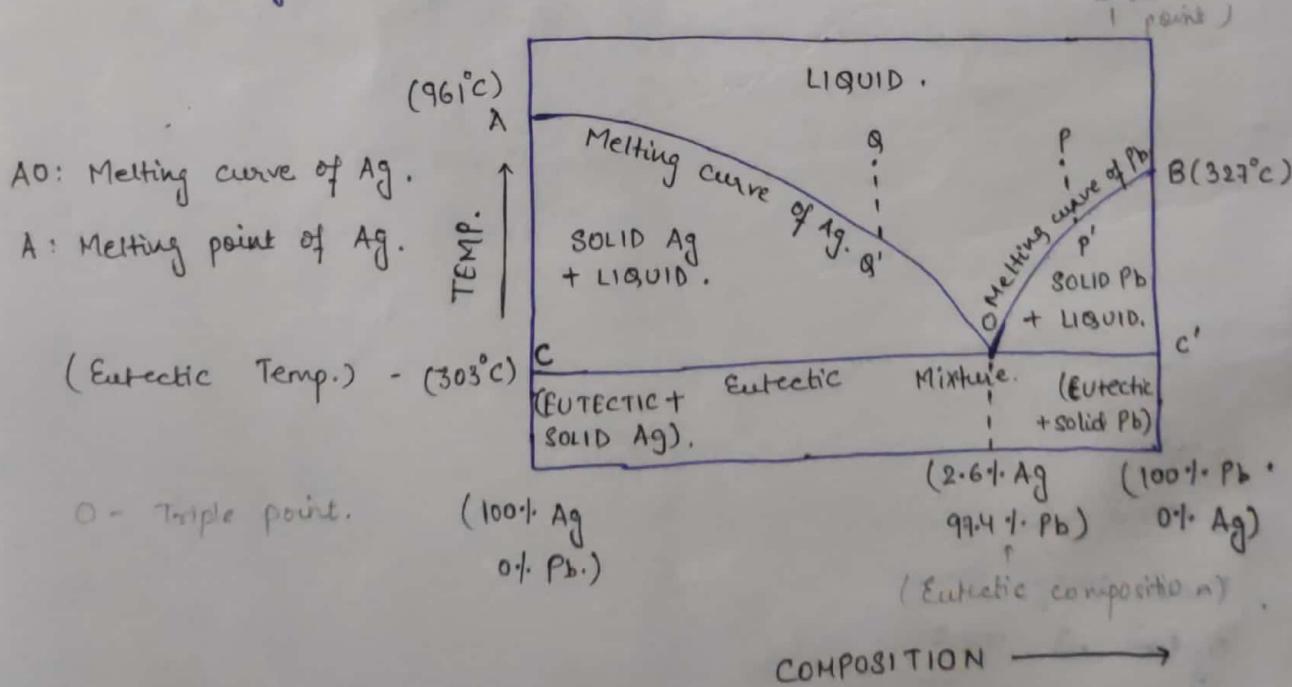
It is a solid mixture of two components and not compounds.

(iii) Eutectic Point :- In a eutectic mixture, the freezing point will be less than the individual freezing points of the components.

The lowest freezing point so obtained is known as the eutectic point.

- Phase Diagram : (Ag-Pb)

(6 points)
(3 area
2 curve
1 point)



What is phase rule with eg.

Simple eutectic \rightarrow Ag-Pb

Congruent " \rightarrow Hg-Zn.

Electrolyte Chemistry:

When iron is connected to another electrode, then it acts as electrode.
Electrolyte

Electrode: Acts as the gate for entry and exit of electrons.

Electrolysis: - Dissociation of the electrolyte by the influence of electricity.

Eq. conductivity (Λ_{eq}): - It is the conductance produced by all the ions present in one-gram eq. of the electrolyte in solution at a given dilution.

$$\Lambda_{eq} = \frac{1000 \times K}{N} \quad ; \quad \left\{ \begin{array}{l} \text{if } N = \text{Normality;} \\ V = \frac{1000}{N} \text{ cm}^3 \end{array} \right.$$

Molar conductivity (Λ_m): It is the conductance produced by all the ions present in one mole of the electrolyte in solution.

$$\Lambda_m = \frac{1000 \times K}{M}$$

* Strong electrolyte \rightarrow have high values of molar conductivity even at moderate dilutions. Eg. HCl, KCl, etc.

* Weak electrolyte \rightarrow have only low molar conductivity at ordinary dilutions and then ' Λ_m ' increases with dilution. Eg.: NH₄OH.

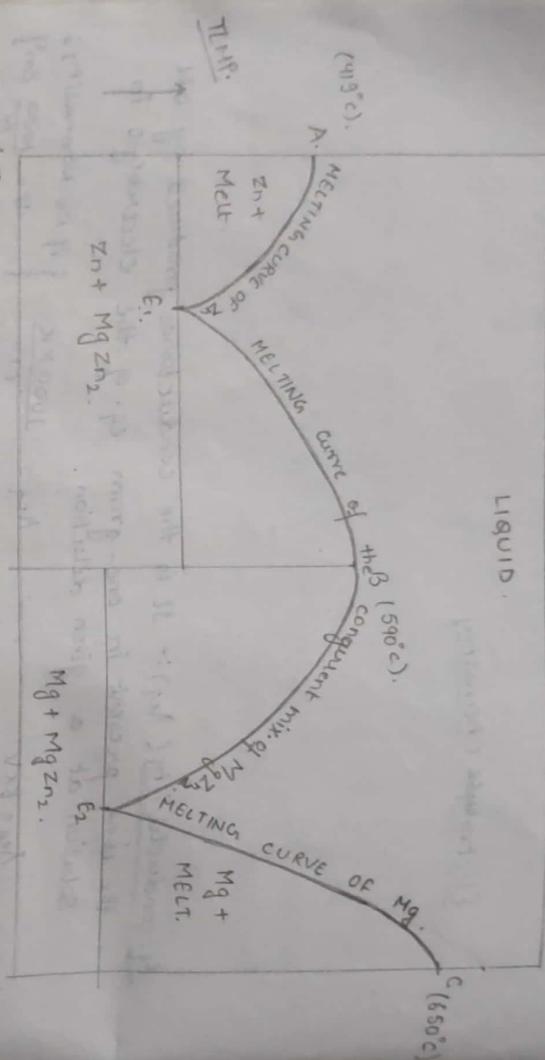
Cell constant - $K = \frac{l}{a}$

$$\text{Cell const.} = \frac{\text{conductivity}}{\text{conductance}}$$

* Eq. conductivity and Λ_m increases with dilution.

* Conductivity depends upon the no. of ions present per cm^2 of the soln. Since on dilution, no. of ions per cm^3 decreases, the conductivity of the soln. decreases on dilution.

L I Q U I D .



with 0.1 Mg₂ having solidus at 1590°C.

→ Melt in with with the minor components along a line having

E1

Two points
These curve
form area

(i) Area Above AE₁B E₂C :

$$P+F = C+1.$$

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

$$= 2.$$

$$\left[\begin{array}{l} 1 \\ 2 \end{array} \right] - \text{Invariant line}$$

Since the value of F=2, we need to fix two variables

Temp & composition.

(ii) Area Above AE₁:

$$F = C - P + 1$$

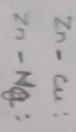
$$= 2 - 2 + 1 = 1.$$

01/10/18

ELECTRO-CHEMISTRY

- Q. What is reference electrode?
Explain any one.
Ans. - definition, SIE
(drawing, representation and reactions)

Electrode Potential :- The capacity of the electrode material, either to lose electron (oxidation) or gain electron (reduction, oxidation potential) (reduction potential)



+ Single electrode :- It does not exist. It exists only in the paired condition along with an electrolyte.
Its potential can be determined by using the reference electrode.

* Reference electrode :- It is an electrode of known potential value. ^{Q. • Standard Hydrogen electrode (SHE) [not NHE].}

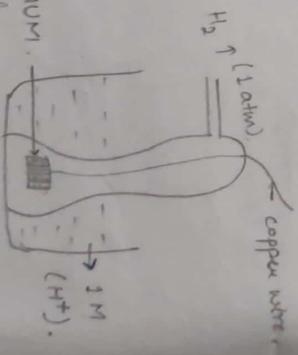
- Glass electrode.

• Saturated Calomel electrode. (SCE).

It is used to compare the potential of other electrodes.

This types Primary and Secondary Reference electrode.

↳ SHE. Calomel electrode.



Secondary ref. electrodes are those whose PLATINUM potential values being known can be compared with other electrodes to determine their unknown potential.

Role of Platinum :- It acts a conductor and through this wire conduction is possible. It provides physical connection.

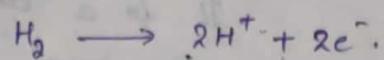
Copper wire → for connecting the two electrodes.

Gaseous electrodes → Cl2, O2, N2;

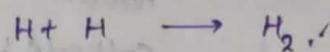
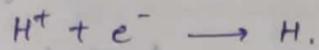
Representation of SHE: Pt, H2 (1 atm); H+ (1 M).

SHE is the electrode and H^+ is the electrolyte but as a part of SHE, not as a true electrolyte.

Reaction as Anode :-

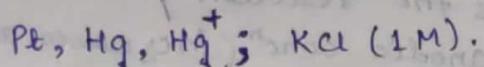


Reaction as Cathode :-

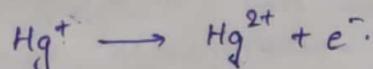


Saturated Calomel Electrode (SCE) :-

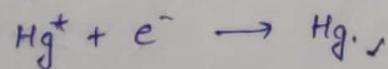
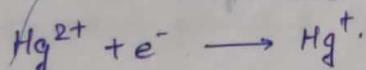
Representation :-



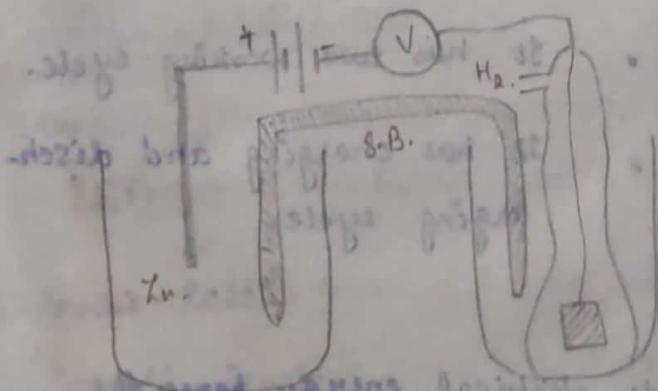
Anodic Reaction :-



Cathodic Reaction :-



Explain :- Experimental Method to find out the Single Electrode Potential :-



$$\begin{aligned} EMF &= E_R - E_L \\ &= E_{SHE} - E_{Zn} \\ &= 0 - E_{Zn} \\ \therefore E_{Zn} &= -(EMF) \end{aligned}$$

* EMF for SHE

is measured to be 0.414 V.

* EMF for SCE is 0.2045 V.

Conversion of electrical into chemical energy.

- It is a single compartment structure.
- Salt bridge is not needed.
- Anode : +ve terminal
Cathode : -ve terminal.
- Only one common electrolyte is needed for conduction.
- Electrolyte concn. will decrease as the reaction proceeds.
- Gas is evolved at the cathode.

Primary cell.

- It is of single time use.
- It has single working cycle.
It cannot be recharged.
- It has only discharging cycle. (Electrochemical).

During discharging cycle, man needs electrical energy, hence the cell is ~~an~~ electrochemical, while charging may supplier electrical energy which is converted to chemical, so the cell behaves as electrolytic cell.

Conversion of chemical energy into electrical energy.

It is a double compartment structure.

Salt bridge is needed.

Anode : +ve terminal
Cathode : -ve terminal.

Two diff. anodic and cathodic electrolytes are present.

As the reaction proceeds, anodic concn. increases and cathodic electrolyte concn. decreases.

Gas can be evolved at any one of the electrodes.

Secondary cell.

- It can be used several times.
- It has two working cycle.
It can be recharged.
- It has charging and discharging cycle.

In this method, the unknown EMF is opposed by another known EMF until the two are equal.

$$\frac{E_x}{E_s} = \frac{\text{length (AD)}}{\text{length (AB)}} \Rightarrow E_x = \frac{\text{length (AD)}}{\text{length (AB)}} \times E_s.$$

→ Fuel Cell :- → electrochemical cell (It converts chemical to electrical energy).
Fuel combustion.

* Working Principle: Fuel + Oxidant → A series of oxidation products + electricity.

Imp:

* Special features :-

- Superior Efficiency (70-75% conversion into electricity).

- Pollution-free.

- Continuous source.

- Light weight of fuel cell - used in submarines.

Used in space shuttle → (Only gaseous electrodes are used so light in weight). By-product water will substitute the water requirements.

- Electrolyte concentration will remain the same.

(Only the anodic and cathodic material will be affected).

- Common end products of all reactions.

* Drawbacks:

- It is not economic; electrolyte used is highly corrosive in nature.

(H₂-O₂) fuel cell

single, inert electrodes - used in fuel cell.

1st - H₂ (anode)

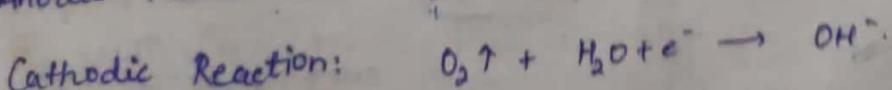
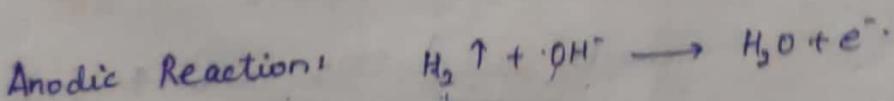
2nd - O₂ (cathode)

→ (H₂-O₂) Fuel Cell :-

Consisting of two compartments.

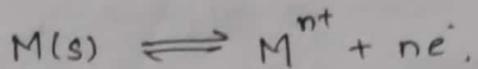
Electrolyte - 20% KOH + 1% LiOH

Electrolyte - 20% KOH and 1% LiOH.



(Drawing of
cathode
mandating)

⇒ NERNST EQUATION :-



$$\Delta G = \Delta G^\circ + RT \ln K \quad (\text{Vanoff theorem})$$

$$\Delta G = -nFE \quad (\text{from electrical energy}),$$

$$\text{from } ① \text{ & } ② \Rightarrow -nFE = -nFE^\circ - RT \ln \frac{[P]}{[R]}.$$

$$\therefore E = E^\circ + RT \ln \frac{[P]}{[R]}$$

$$\boxed{\therefore E = E^\circ - \frac{RT}{nF} \ln \frac{[R]}{[P]}}$$

$$\boxed{\therefore E = E^\circ - \frac{RT}{nF} [R].}$$

~~net whatever
ΔH_r, ΔS_r, ΔE_r~~

Solid electrode dipping

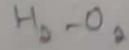
That says if two solutions containing different electrolytes are mixed then the reaction will proceed.

Inert electrolyte is the one -

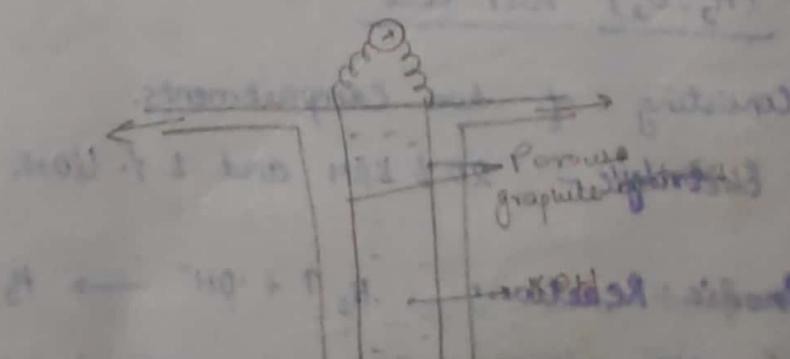
whose ions do not take part in the redox reaction and also do not react chemically with the electrolyte used in the cell.

Also the mobilities of cation and anion will be nearly the same.

Type



Fuel cell →



Types of Electrodes :-

11th Oct, 2018.

- v) Metal dipped in two diff. electrolyte of the ions of same metal.



Photo-voltaic effect :- Definition

Merits → It is renewable.

It is pollution-free.

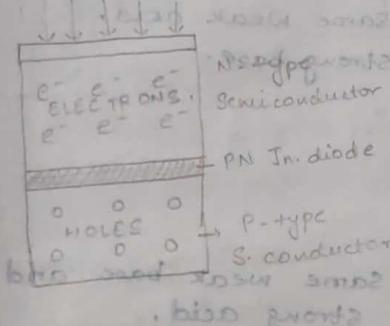
It is free of cost.

Based on structure - (a)

Active equipments - Heater, phone Battery, Cooker, Watch etc. (panelled)

Passive " - Efficiency is less due to its non-panelled structure.

SOLAR ENERGY.



Demerits :-

- Not a continuous source.
- It is not economic.
- Not much efficient.

Efficiency of H_2O to H_2 depends on -
 Buffer should be a weak electrolyte
 That's why it undergoes complete
 dissociation.
 Resulting weak acid supply net
 undegraded ions.

ACIDS AND BASES :

Arrhenius theory:

Acids - donate H^+ ion.

Bases - donates OH^- ion.

Lowry-Bronsted Theory: Bases are proton acceptors.

Bases donate lone pairs to form an ion pair.

Lewis Theory:

glass

SALT BRIDGE:- Half rectangular inverted tube filled with an inert electrolyte (Agar-agar + KNO_3) which is a connector b/w the two half cells.

Functions :- (i) It is completing the basic cell circuit.

(ii) Acting as a connector b/w the two half cells.

Acts as a passage/bridge for the transmission of ions.

mainly of KNO_3 gel. Ionic accumulation near the electrodes is avoided.

As a result, intermixing of two electrolytes can be avoided.

(iii) Maintains the electrolytic conductivity of the and neutrality of the electrodes.

$$E = E^* + \frac{RT}{4F} \log [H^{n+}] = E^* + \frac{0.0591}{Rn} \log [H^{n+}]$$

$$\begin{aligned} E_{\text{eff}} &= (\text{cathode} - \text{anode}) \cdot \Delta G = nFE \\ &= E_{\text{Nernst}} - \frac{\Delta G}{nF} = \frac{nFE}{\Delta G + RT/K} \end{aligned}$$

Reversible cell - formed in a closed loop and connected in an electric circuit.

Polarisation - When the electrolyte of the solution is consumed due to the products formed at the electrodes set up an extra opposite to that of the applied emf. This is known as the Polarisation.

Overset voltage - The extra voltage over the voltage of the cell which is necessary to reverse reaction is called overset voltage.

Liquid Junction Potential - The potential set up at the junction of the two solutions because of the difference in the speed of ion moving across the boundary is called LJP.

$$\text{Total, } E_{\text{eff}} (E) = E_1 + E_2 + E_J$$

E_1 → oxidation potential

E_2 → reduction potential.

Some points

→ Minimum resistance out of all the resistances in the circuit.

→ Inverse relationship between E_{eff} and ΔG

$\Delta G = -nFE_{\text{eff}}$

$E_{\text{eff}} = E^* + \frac{RT}{4F} \log [H^{n+}]$

$E^* = E_{\text{cathode}} - E_{\text{anode}}$

$E_{\text{cathode}} = E_{\text{cathode}}^* + \frac{\Delta G}{nF}$

$E_{\text{anode}} = E_{\text{anode}}^* - \frac{\Delta G}{nF}$

$E_{\text{cathode}}^* = E_{\text{cathode}}^* + \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{anode}}^* = E_{\text{anode}}^* - \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{cathode}}^* = E_{\text{cathode}}^* + \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{anode}}^* = E_{\text{anode}}^* - \frac{RT}{4F} \log [H^{n+}]$

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$E_{\text{cathode}}^* = E_{\text{cathode}}^* + \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{anode}}^* = E_{\text{anode}}^* - \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{cathode}}^* = E_{\text{cathode}}^* + \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{anode}}^* = E_{\text{anode}}^* - \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{cathode}}^* = E_{\text{cathode}}^* + \frac{RT}{4F} \log [H^{n+}]$

$E_{\text{anode}}^* = E_{\text{anode}}^* - \frac{RT}{4F} \log [H^{n+}]$

Electrode concentration cell :-

Electrode concentration cell :-

- * Electrode concentration is varying and electrolyte concn. is const.
 - * Solid electrode can never be used (because electrode concn. does not vary).
 - * liquid and gaseous electrodes is used.

General Representation -

Gaseous electrode: $\text{Pt}, \text{X}_1 \uparrow (\rho = \rho_1) | x \downarrow | X_2 \uparrow (\rho = \rho_2), \text{Pt}.$
 liquid electrode: $\text{Zn}(\text{Hg}) (\text{C}_1) | \text{Zn}^{2+} | \text{Zn}(\text{Hg}) (\text{C}_2).$

Electrolyte concentration cell :-

- * Drawing low values and efficiency
 - * All three physical states of electrodes can be used generally, solid electrodes are preferred.
 - * General representation:

→ EMF determination of -

R(c)

[8 - 7]

• Electrode c.c. :-

Zn(Hg) | Cu | Zn²⁺ | Zn(Hg)_(aq),
 L(A);
 Cathode : Zn²⁺ + 2e⁻

28

$$E_R = \frac{P^0 \cdot R_T}{2f} \ln \frac{a_2}{[Z_{2,2}^0]},$$

Always constant in the production.

Cell Reaction at Anode:

Reaction at Anode:

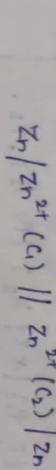
$$\therefore \text{EMF} = E_R - E_L$$

$$\Rightarrow \frac{P_T}{2F} \ln \left\{ \frac{\alpha_1}{[2m^2]} \right\} \times \left[\frac{Zm^2}{\alpha_2} \right] \quad (\Leftrightarrow) \quad \frac{P_T}{2F} \ln \left(\frac{\alpha_1}{\alpha_2} \right).$$

In case of very dil. soln. $\rightarrow a = c$.

$$\therefore \text{EMF} = \frac{RT}{2F} \ln \frac{c_1}{c_2}$$

Electrolyte C.C. :-



Cell Reaction at Cathode: $Zn^{2+}(c_2) + 2e^- \rightarrow Zn.$

$$E_R = E^\circ - \frac{RT}{2F} \ln \frac{[Zn]}{c_2}$$

Cell Reaction at Anode: $Zn \rightarrow Zn^{2+}(c_1) + 2e^-.$

$$E_L = E^\circ - \frac{RT}{2F} \ln \frac{[Zn]}{c_1}$$

$$\therefore \text{EMF} = E_R - E_L = \frac{RT}{2F} \ln \frac{c_2}{c_1}$$

29/10/18.

Polarisation :- Due to the mutual transfer, concentration variation within the electrolyte an additional EMF, other than applied EMF occurs which creates an additional EMF opposite the applied EMF. It is a negative property as the new EMF opposes the applied EMF. MnO_2 - depolariser \rightarrow used to control polarisation in a cell.

① Factors :-

- (i) Electrolyte concentration $\} \propto P.$
- (ii) Electrode conductivity. $\} \propto$ electrode potential.
- (iii) Temperature.
- (iv) Electrode nature $\} \propto V_p.$
- (v) Electrode size.

Decomposition Potential :-

Theoretical value of

Oversetage: Difference b/w the experimental voltage and theoretical voltage.

- Factors -
- presence of impurities.
 - Temperature.
 - pH of electrolyte.
 - presence of inhibitor.

POLYMERS

- macromolecules
- giant molecules
- combination of monomers.

→ Degree of Polymerisation - no. of monomers present ^{per unit} in the polymer chain. (pp - monomer units / chain).

Monomer Repeating units $\text{CH}_2 = \text{CH}_2$ $\text{and} (\text{CH}_2 - \text{CH}_2)_n$ (one bond less than monomer).
no wavy chain.
consists of wavy chain (w).

⇒ Classification of Polymers :-

(i) Based on Origin -

- Natural - Natural Rubber, protein, coconut fibre, sealer, etc.
- Synthetic - PVC, nines, fibres, polythene, etc.

(ii) Based on Structure:-

- Homo-monomer - only one type of monomer.
- Hetero-monomer - more than one type of monomer.
Eg: Buna-S, buna N, etc.

(i) co-polymer. (Based on no. of monomer units produced).

(ii) ter-polymer

- (iii) → Aliphatic - single-chain structure.
→ Aromatic - closed / ring structure.

(iv) Method of Polymerisation -

Takes place only with comp-

- Addition Polymerisation. Eg. Polythene. Ours having multiple bonds.
- Condensation polymerisation / step polymerisation. (Chain growth occurs with the elimination of small molecules like H_2O , glucose, etc.)

Eg. Nylon (Polyamide) $\rightarrow \text{R} - (\text{NH}-\text{CO}) - \text{R}'$ molecules like H_2O ,

(v) Based on the backbone structure -

- Organic polymers - main chain consists of only carbon atoms.
- Inorganic polymers - main chain consists of chain and other atoms.

Based on Nature/Properties -

(Metal - elastic in nature).

Name / Prognosis

- Rubber - non-elastic in nature.
 - Plastic - flowing tendency. (Polymer shaped into hard articles by the application of heat and pressure).
 - Fibres. - (Its length should be 100 times of its diameter).
Resin. - high molecular weight, highly viscous & liquid polymer.

- Natural Resin
- Synthetic Resin

E.g.: formaldehyde, adhesives, etc.

31/10/18

Mechanism of Polymer Preparation -

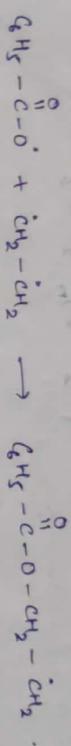
styrene after being formed
is removed quickly from
bottle, otherwise it gels

Solution Polymerization - take place in liquid presence of Initiator
Degree of Polymerization - No. of repeating units in molecule of a polymer

Free Radical Mechanism

(1) Sustitution - Mostly peroxides are used as initiating catalyst.

Initiation - Free radicals are produced by the homolytic dissociation of an initiator.



(ii) Propagation - includes the addition of large no. of mono specific species.



(iii) Termination — By disproportionation. ($Mn + Mn \rightarrow Mn_2^{+}Mn$).

$$\text{C}_6\text{H}_5 - \text{C}(\text{O})\text{CH}_2 - \text{CH}_2 \rightarrow \text{C}_6\text{H}_5 - \text{C}(\text{O})\text{CH}_2 + \text{H}_2\text{O}$$

$$\sim \text{CH}_2 + X \rightarrow \sim \text{CH}_2 * - \text{ (In case of halogen)} \\ \sim + a \rightarrow \sim \text{CH}_2 S. - \text{ (" " " solvent) }$$

$\sim \text{CH}_2$

$$\sim \text{CH}_2 + X \longrightarrow \sim \text{CH}_2 *$$

$$\sim \text{CH}_2 + S \longrightarrow \sim \text{CH}_2 S$$

- (in case of collagen)
- (" " solvent)

$$\sim \overset{\circ}{\text{CH}_2} + \overset{\bullet}{\text{CH}_2} \sim \longrightarrow \sim \text{CH}_2 - \overset{\bullet}{\text{CH}_2} \sim \quad (\text{chain doubling})$$

$\sim \text{CH}_2 + \dot{\text{CH}}_2 \sim \longrightarrow \sim \text{CH}_2 - \text{CH}_2 \sim$ - (chain doubling).
 Dead polymer - propagating radical whose growth is stopped. 03/11/18.

Ionic mechanism - It is of two types -

(i) Anionic mechanism - Also known as carbanion mechanism as

The polymer's backbone is made of carbon atoms - Aionic propagation via carbon.

$X + \text{CH}_2 = \text{CH}_2$

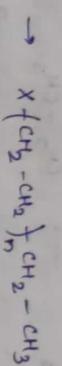
$$\bar{X} + {}^4\text{CH}_2 \xrightarrow{\downarrow} X\text{CH}_2 - \overset{\oplus}{\text{CH}}_2$$

Propagation -



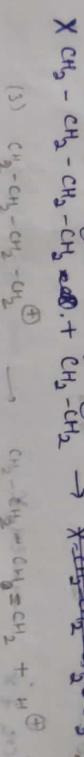
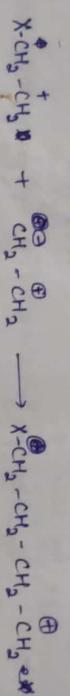
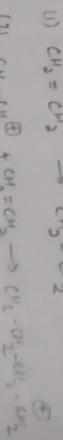
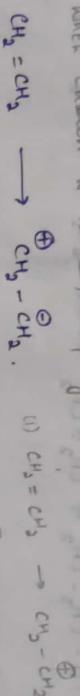
Termination -

Last product $\rightarrow X\{CH_2-CH_2\}_n CH_2-\bar{C}H_2+HX$
(inhibitor)



(ii) Cationic Mechanism :- Propagation via C^+ ion, hence called cation mechanism.

When cation is added, shifting occurs on the left side.



Zeigler Natta Catalyst Mechanism :-

complex structure is formed first

- In this mechanism, catalyst of complex structure is formed first and then this catalyst acts as the initiator.

It is also known as coordination or insertion mechanism

- because the newly formed monomers are inserted in b/w the other monomer catalyst structure.

- This mechanism forms ~~two~~ ^{regularity} specific products, having isotactic bulky groups on same side \rightarrow isotactic.

- This mechanism forms ~~two~~ ^{regularity} isotactic-regularity products. regularity \rightarrow Regularity \rightarrow

bulky groups on opposite side \rightarrow syndiotactic.

No regular structure of bulky groups \rightarrow atactic.

Properties of the catalyst -
An ~~impure~~ metal + Alkyls or

~~Salides or other derived~~

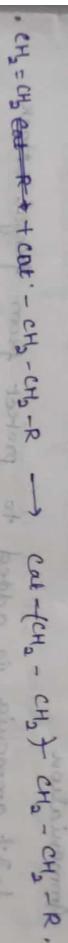
AlCl_3 , AlCl_4 .

① Halides or other derivatives of inner transition elements.

(e.g. TiCl_3 , TiCl_4) -
 e.g. $\text{Al}(\text{CH}_3)_3$, $\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}(\text{C}_6\text{H}_5)_3$.

→ Representation of catalyst complex: (CatalR)

Mechanism -



Final product \rightarrow cat - $(\text{CH}_2 - \text{CH}_2)_n$ $\text{CH}_2 - \text{CH}_2 - \text{R} + \text{H}_2\text{X}$.
(terminator)

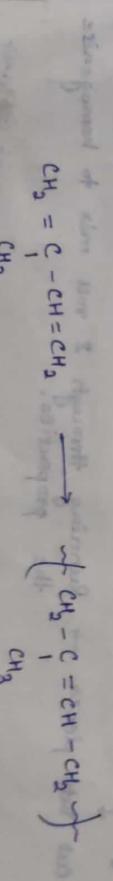
Processing of a Polymer :-

Processing - conversion of a raw polymer into the desired form.

Processing consists of two stages
① Compounding ② Moulding / shaping.

Natural Rubber → chemically polyisoprene (not completely true)

Monomer \rightarrow Isoprene



Digitized by srujanika@gmail.com

hang 1, q -
(bulka - perha)

Ergänzung - 3

Scanned with CamScanner

* Really - Natural Rubber chemically.

Laten: watery dispersion of rubber particles

65% → Water & Non-Rubbery particles
Balance → 35% → Rubber (pure).

In industries → Dry rubber is preferred.
(Reason: Large loss in energy & money).

Processing of Polymers:

① Topping.

② Ammoniation.

1-3% ammonia is added to protect from fungal attack
(can be kept safely for 7-10 days).

Function: Acting as a fungicide.

- 1-3% formic acid or acetic acid is added. The particles aggregate and forms a wet lump.
- By adjusting the nip gap, the thickness can be adjusted.

Homogenization of Dry Rubber:

Dry Rubber → Homogenization → wooden mould → wooden treatment
Cut into pieces. → Running through 2 roll mix to homogenize the properties.

- Latex based → wooden mould (for dipping slight weight is preferable)
- Dry Rubber based → cast iron mould (because we have to apply heat and pressure)

- ① Selection of latex.
- ② Ammoniation - adding 1 to 2% ammonia to prevent rubber from breaking.
causing ailments.

Dry Rubber Compounding -

Some steps -

- Ammoniation
- 1-3% formic acid or acetic acid (not lumpy).
- Coagulating
- Sheets / blocks.
- Homogenisation (to bring uniformity of properties).
- Compounding the dry Rubber -
(adding required chemicals in the homogenised block and
passing through the 2 roll mixer).
- Dry rubber moulding.

Plastic Compounding (for fibre also):

- Plastic compounding cannot be done in an open forum but in
vanduury ~~vanduury~~ mixture (huge mixture bowl) or called as
closed cavity mixing.
- Thermoplastics :- They soften when warmed and harden on cooling.
They can be heated or cooled any no. of times for moulding in
any shape. Repeating heating and cooling make no change in the
chemical str. or mol. wt. of these polymers.

Thermosets :-
They remain rigid, once set and do not soften when warmed.
The strength of these bonds is retained even on heating
and hence they cannot be softened again and removed.

8/11/8.

→ Rubber - open mixing.
Plastic - closed cavity mixing.

S. P. M.
Moulding - (4 techniques)

① Compression Moulding -

② Injection Moulding -

③ Extrusion -

④ Transfer -

① Compression Moulding :- \rightarrow moulding is done by the application of temperature and pressure.

→ applied to both thermoplastic & thermosetting resins.

Moulding Temp:

As per standard with reference to product.

Moulding Pressure:

As per standard with reference to product.

Moulding Time / Curing time: → As per standard with reference to product.

Mould should attain the stipulated pressure & temp. (Pre-heating the mould before placing it in a heated hand-pressing machine).

(Hydromatic presser (medium scale), hydraulic presser (large scale)).

② Injection Moulding -

→ upper platen is heated & lower platen is heated by separate hydromatic presser.

pt = 150°

→ Mould, Platen, Lower platen.

→ lower platen.

or or

② Injection Moulding -

Diff. stop obtained.

Mould is pressurized.

③ Extrusion M

Moving \rightarrow High P

Due to products (e.g.)

④ Transfer

Very

or or

or or

or or

or or

or or

or or

① Hydromatic Pressing -

→ upper platen is heated & lower platen is heated by separate hydromatic presser.

pt = 150°

→ Mould, Platen, Lower platen.

→ lower platen.

or or

extrusion,
bathroom bucket &
cup, etc.

mainly applicable to thermo-plastic resins.

Diff. • Piston is used to provide pressure.

- Diff. shape of products can be obtained.
 - Mould is present.
 - Extrusion Molding - long used for long uni. of area products.

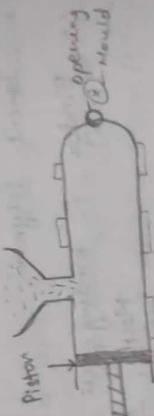


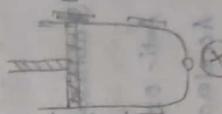
Diagram illustrating the use of a spring press for moulding:

- Moving spring.
- Moving die.
- Moving plunger.
- Mould in the form of a die kept at the mouth of barrel.
- Spring to provide pressure.
- Different types of moulds.

Due to diff. in T & P, deformation of fiber and plastic is present.
products take place.
e.g. PVC pipes, plastic ropes, cable wires.

Transfor Moulding - exclusive moulding technology for thermoset

- Vertical application of pressure, along with the gravitational pulling.
 - Very huge & very small complicated structures or objects are moulded using transfer moulding.



The benzoin-filled mice were heated to a min. temp so as to bring about a plastic cond'n. and then injected through the plunger into the

hot mould by plunger working at high pressure.

- After getting mould is taken out mechanically.

Compounding ingredients - (Plastic; Fibre; Rein- based).

1. • Parent Polymer.
 2. • Binder - binding all the other ingredients.
Machy, Resin is used.
 3. • Filler - filling the recipe.
Ex: In automobile industry, carbon black is the filler to
tyre industry hence, the tyres are black in colour.
 - Titanium filler → white in colour.
- 45% - Rubber ; 5-10% → other ingredients } for
Rest 45% is carbon black. } Tyres.
- Function of fillers →
- Filling the recipe.
 - Reducing the cost.
 - Carbon black is reinforcing filler which provides strength.
(All fillers are not reinforcing, i.e., Titanium).
- Advantages of Plastic Resins / Synthetic Resins / Oily Resins / Varnishes / Lacquers / Gesso, Shellac, Powders,
Varnishing Oil, and Impregnating Resins.
- Eg.: oil, petroleum jelly, etc.
5. Stabiliser - depends upon the site of use. improve thermal stability.
 6. Anti-oxidants. → prevent the oxidative degradation of polymer.
 7. Accelerator → used to accelerate the process.
 8. Activators + promoter for accelerator.
 9. Blowing Agent. → mostly used in automobile industry and increases the volume of rubber due to foaming formation.
- * 10. II. Fire Retardants. - reduce the chance of fire. may contain water and halogenated hydrocarbons.
- * 11. Vulcanising agents.

Vulcanisation of Rubber/Latex :-

- It is the introduction of cross links b/w the rubbery chains.
- If the cross link density (immediate cross linking) is not advised because the basic material becomes hard and rubber changes to worn rubber.

- Various properties like mechanical, electrical etc. are imparted to the rubber through vulcanisation.

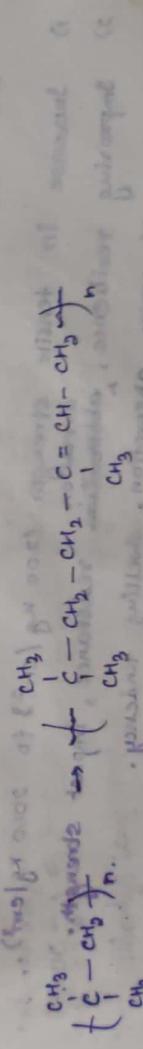
Properties -

- Abrasion → removal of the surface layer.
- > High Tensile Strength.
- > Huge Temp. Range.

ZnO → accelerator for sulphur ($S + ZnO$) → good softening agent.

Vulcanisation, discovered by Charles Goodyear. Natural raw rubber is an inferior material and it is possessing very low technological properties. On application of load, rubbery chains slip past each other and may lead to ultimate breakdown.

The introduction of occasional cross links b/w the rubbery chains into the overall performance of rubber. At the same time, the inherent rubbery nature will be retained. In order to introduce cross links a few percentage of structural unsaturation is required in the carbon backbone.



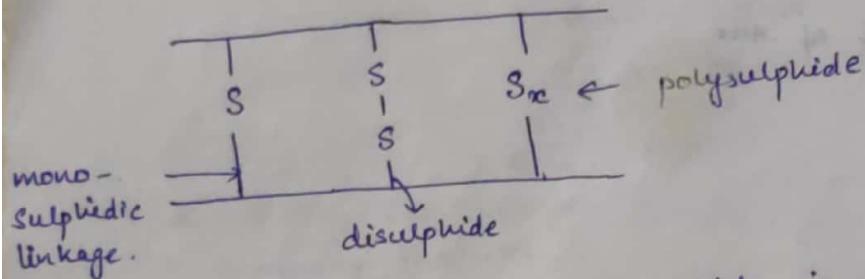
Isobutene forms polymerisation forms purely unsaturated product so it cannot perform vulcanisation. To do so, 1-5% of isoprene is added.

that monomer and forms co-polymer.

There may be two types of cross-links -

- Carbon cross links
- Sulphur cross links.

Carbon cross links is rigid over sulphur cross link. Following are the diff. types of sulphur vulcanisations -



Out of the above, poly-sulphide is more flexible.

- As per the flexibility ~~of the~~ requirement of the product, the proper sulphur system we can use.
- Depends upon the stiffness requirement of the product, the amount of sulphur is varying.
- Automobile tyre need 3-5% sulphur whereas the battery box need 30% sulphur.
- + During Vulcanisation, the compound is heated with the required amt. of sulphur at 110-140°C. The curing time is varying b/w a few minutes to 3 hours, depending upon the product.

These are the following changes on vulcanisation -

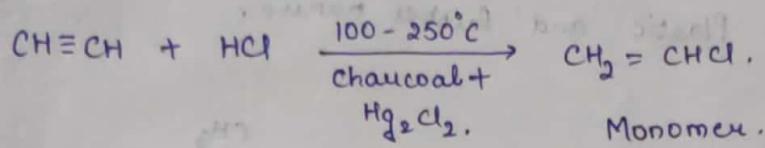
- 1) Increase in tensile strength (200 kg/cm^2) to 2000 kg/cm^2 .
- 2) Improving resilience, abrasion resistance, impact strength.
- 3) Decrease of water absorption, swelling tendency.
- 4) Improving the resistance to oxidation and temperature degradation.

- 5) Electrical properties improved.
- 6) Resistance to organic solvents increased.
- 7) Huge temperature range is improved from $(10 - 60^{\circ}\text{C})$ to $(40 - 100^{\circ}\text{C})$.

Individual Polymers :-

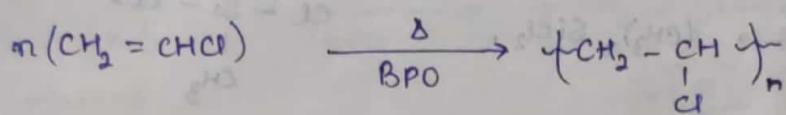
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① PVC :-



Properties of PVC :-

• Resist Water Repellancy.



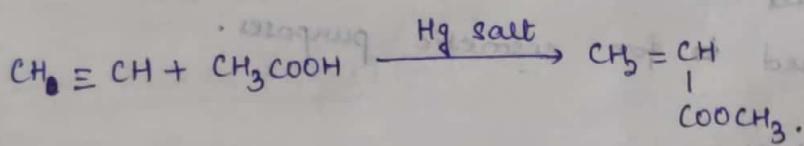
• Repellant towards oxygen.

• Resistant towards chemical.

• Rigid PVC \rightarrow insulation cables, helmets,

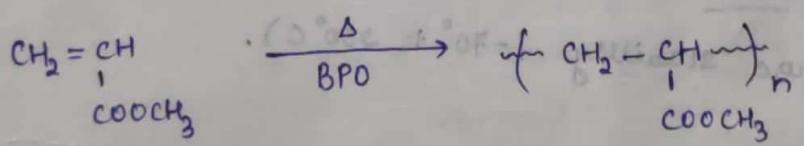
• Flexible PVC \rightarrow house furnishing, table cloth, maincoat,

② Poly-Vinyl Acetate (PVA) :-



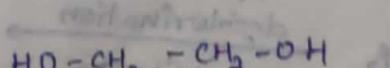
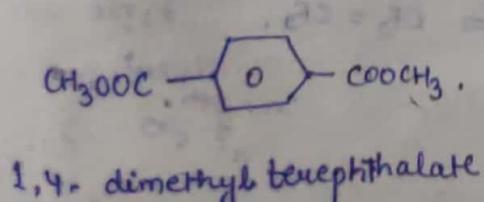
Properties :-

• Resistant to water, atm. oxygen & chemicals.

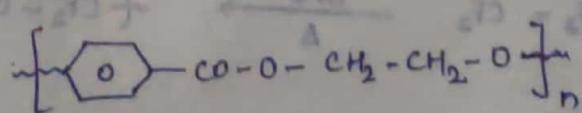


Uses :- Preparation of chewing gum and surgical resin.

③ PET :



Ethylene glycol



PET.

Proprietary:

Resistant towards good solvent and moisture.

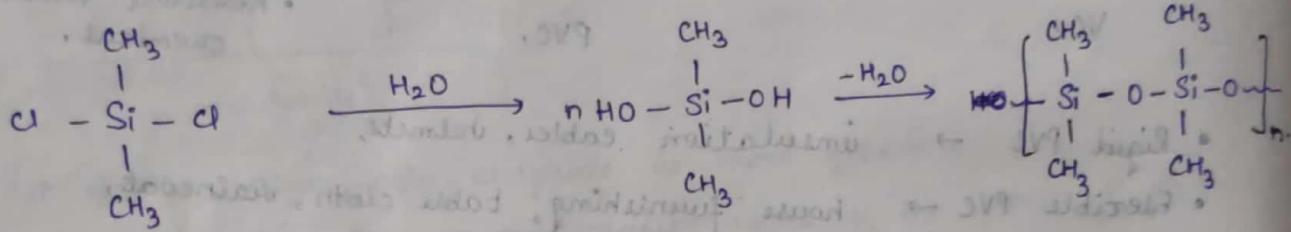
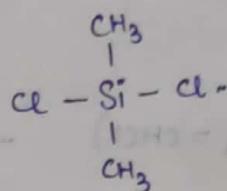
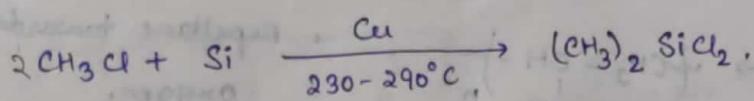
- Use:-

Used in bottle making, video film making (video, photo, etc.).

④ Silicones Polymer

Dual natured polymer - Plastic and Rubber nature.

* Silicon Plastic Polymers:



→ Use

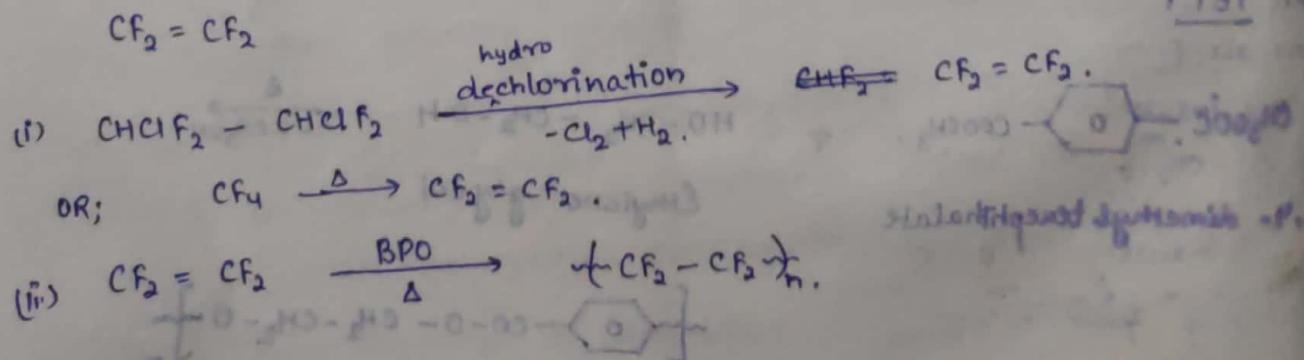
- Silicon Plastic is used to make all the common ~~articles~~
 - Silicon Rubber is used for cosmetic purposes.

→ Property of Silicone plastic

- Properties of

 - Wide range temperature stability (-70° to 250°C).
 - Weather resistant.

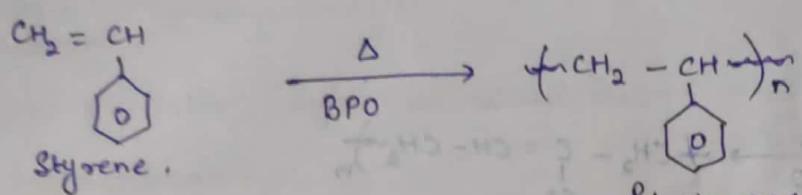
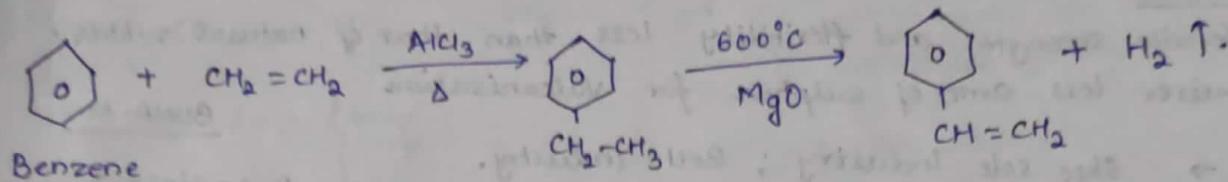
⑤ Teflon (Polytetrafluoroethylene) :-



Property → Non-sticky, high density, unaffected by water.

Use: Non-stick kitchen utensils, gaskets, glass fibres, etc.

⑥ Polystyrene -



Property:

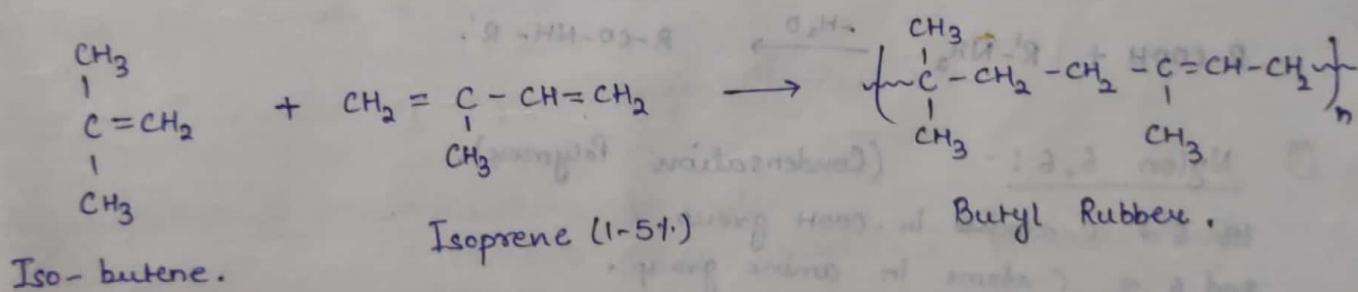
- Highest brittle plastic.
- Chemical inertness.
- Poor weathering.

• Radio and TV cabin.

Use :-

Individual Rubbers :-

① Butyl Rubber (GR-1) :-



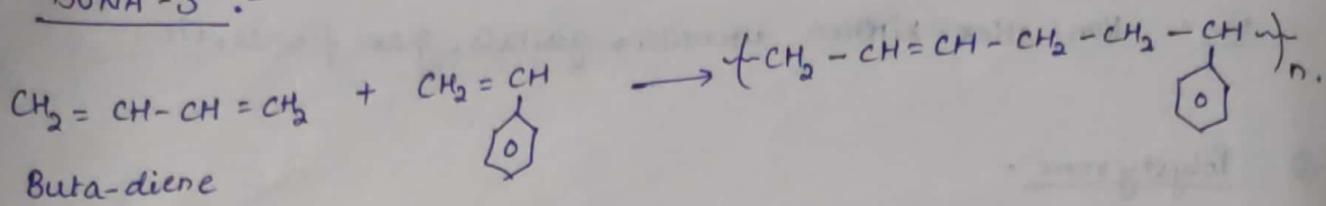
Properties:

- Low air permeability. So used in making tyre inner tube.
- Good insulation properties.

Use :

- Tyre industry and cable industry.

② BUNA - S :-

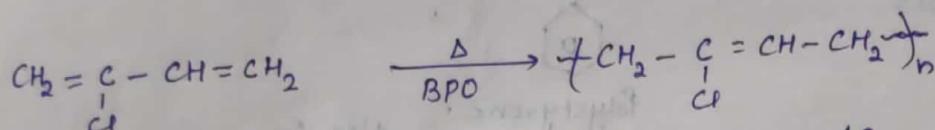


- Properties:-
 - Tensile strength and flexibility less than that of natural rubber.
 - Requires less amt. of sulphur for Vulcanisation
 - Used in shoe sole industry ; Belt industry.

BUNA-N

Butadiene +

③ Neoprene (G.R-N) :-



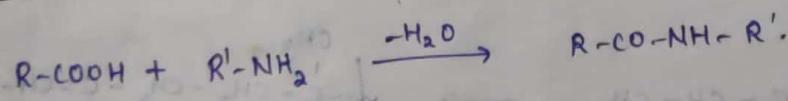
Chlorophyll

- Properties:

 - Superior oil resistance, as compared to natural rubber.

Use: oil-based industries (O-rings), conveyor belts, etc.

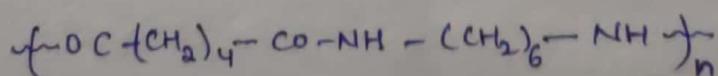
Individual fibres :-



① Nylon 6,6 :- (Condensation Polymer).

1st 6 → C-atoms in -COOH group.

2nd 6 → C-atoms in amine group

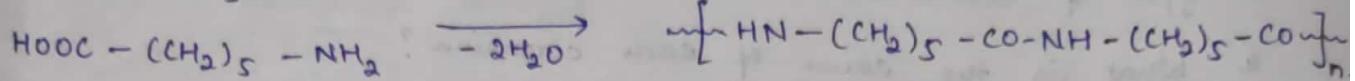
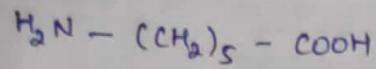


Nylon 6,6.

~~High~~ → High strength, elasticity, toughness.

Uses → Manufacture of ropes, tire cords, belts, etc.

②. Nylon 6 :- (Self poly-condensation polymer).



Caproic Acid. (Amino acid).

Nylon-6.

Use of Nylon as plastic fibre → Textile fibre, harbour industry, fishing net, climbing ropes, undergarments.

As a plastic, nylon is used as -

- metal-bearings.
- door-latches.

Nylon 6,10 ;

Nylon 11.

Property - • Mechanical strength.

- Comfortable, sweat resistant.

Properties of Poly ethene →

- High MP, density, & tensile strength.

Uses → Production of toys, detergent bottles, etc.

Poly Acrylo Nitrite →

- Resistant to water.
- Exhibits more resistance towards acids and bases.

Uses → For making mesh, manufacture of window shades, etc.

CORROSION

- Q. Compare wet corrosion and dry corrosion mechanism.
(electrochemical) (chemical)
- Q. Types of corrosion.
- Q. What is the cause of each corrosion?
- Essay Q. Factors controlling corrosion
• Nature of metal Nature of envt.
 { coating, cathodic protection,
Essay que Q. Different control methods of corrosion. → metal cladding.
- Q. Methods of coating - (brushing, dipping, spraying, electro-plating, galvanisation, tinning).
- Q. Compare galvanisation and tinning.
- Q. A common recipe of paint formation.
• thinner - makes reducing the viscosity of paint.
• pigments
• stabiliser.
• Water repellants.
- Q. Types of coating → (organic and inorganic),
oxide,
phosphate,
chromate.
- Cathodic protection → • Sacrificial anodic protection
(Types)

1st MODULETHE SOLID STATE.

Solids → close packing, definite shape and volume, rigid and has mechanical strength.

Three categories of Solids -

- Crystalline.
- Amorphous
- Poly-crystalline - more than one crystalline material in same lattice.
Eg:- Marble, granite. ; Isotropic.

Crystalline → it maintains regularity in the three-dimensional geometry. High MP.

- Anisotropic in nature. (phy. ppty are diff. along diff. diren)
Eg: ZnS, NaCl, etc.

→ It is of four types -

- i) Ionic solids - pure ionic bonding due to electrostatic force of attraction. High MP, & BP. Eg. NaCl, CuCl, etc.
- ii) Covalent solids → covalent bonding present. $sp^2 \rightarrow$ graphite
 $sp^3 \rightarrow$ diamonds
- iii) Metallic solids → metallic bonding due to electrostatic force b/w electrons and the nucleus Kernell.
- iv) Molecular solids → diff. forces like London forces, dipole-dipole interaction, etc. are present; weak Vander Waals force of attraction, etc.

Three Symmetry →

- Plane of symmetry.
- Axis of symmetry.
- Centre of symmetry.

(smallest portion of space lattice)

• Unit cell. • Space lattice. → Regular 3-D arrangement of points, which describes the "3D" particles.

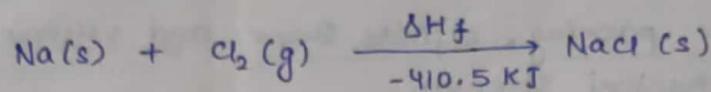
Amorphous - Random arrangement throughout the crystal.

Isotropic, don't have sharp MP.

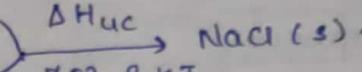
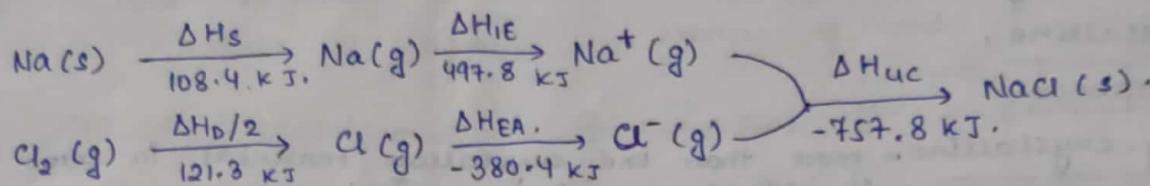
• Pseudo solids.

Insp. → Based on 1st law of thermodynamics :- It represents that in a series of reaction either single-step or multi-step, the heat of reaction remains the same. 26/11/18.

(i) Single step :-



(ii) Multi-step :-



$$\Delta H_f = \Delta H_s + \Delta H_{IE} + \frac{\Delta H_D}{2} + \Delta H_{EA} + \Delta H_{uc}.$$

$$\Rightarrow (108.4 + 497.8 + 121.3 - 380.4 - 757.8) \text{ kJ} = -410.5 \text{ kJ.}$$

Whether it is single or multi-step approach, the net heat energy involved in the crystal formation is same.

Insp. → FREE-ELECTRON THEORY :-

- Metallic crystals consists of tve. centre present in a sea of fast moving electrons.
- + The electrostatic force existing b/w the centres and electrons are responsible for ~~metal~~ stability.
- Repulsive force existing b/w electrons is negligibly small and do not affect the crystal stability.
- The tve charges are distributing throughout the crystal so these centres do not hinder the ~~electronic~~ movement of e⁻s, and do not affect crystal stability.
- The continuous collision of e⁻ will enhance the velocity of e⁻s and thus contribute to increased metallic conductivity.

CRYSTAL IMPERFECTIONS :-

(i) Atomic Imperfection or Point defects.

(ii) Electronic imperfection \rightarrow Any positional variation of e⁻s, due to change in temp. or pressure.

* POINT DEFECTS :- Irregularity in the arrangement of atoms or ions in the crystal.

STOICHIOMETRIC DEFECTS:-

\rightarrow Do not alter the stoichiometry of crystal.

\rightarrow Ratio b/w cations & anions is same.

(i) SCHOTTKY DEFECT:

• Missing defect.

• Decrease in density.

• Occurs in ionic solids of high coordination no.

• Anions and cations are of comparable size.

~~water-soluble~~

Eg:- NaCl, KCl, etc.

(ii) FRENKEL DEFECT:

• Displacement defect.

• Density is same.

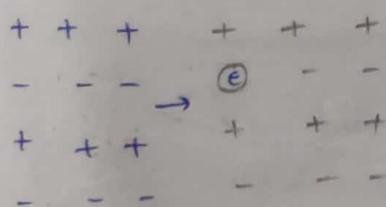
• Occurs in ionic solids of low CN.

• Anion is larger and cation is smaller.

Eg: AgCl, MgCl, etc.

NON-STOICHIOMETRIC DEFECTS:- Alters the stoichiometry of crystal.

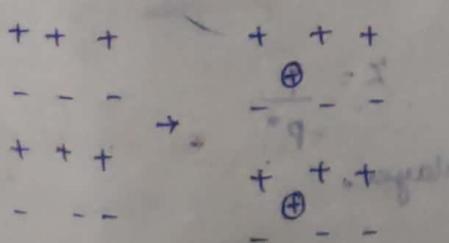
(i) Metal deficiency due to anionic Vacancies:-



- Shows paramagnetic behaviour.
- Anions are missing.
- No. of tve charge \rightarrow No. of -ve charge.
- So, as to maintain the electrical neutrality, F-electron occupies the F-centre. This e⁻ imparts colour.

Eg: NaCl, KCl, etc.

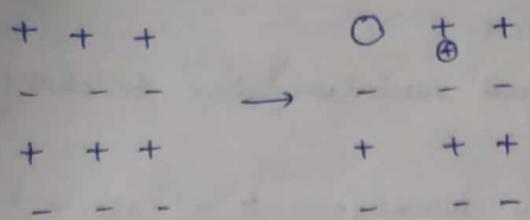
(ii) Metal deficiency due to interstitial cation (Excess defect):-



- tve $>$ -ve.
- Excess tve is countered by placing -ve electrons, so as to maintain electrical neutrality.

Eg: ZnO

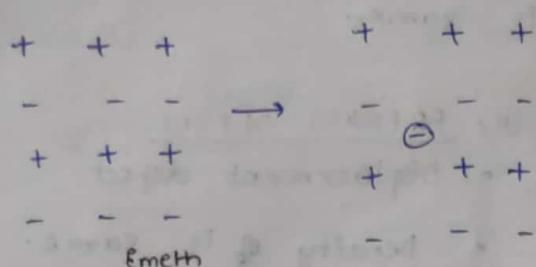
(iii) Metal deficiency due to Cationic Vacancy:-



Nearby +ve charge is doubled.

Eg: FeO_2

(iv) Metal deficiency due to interstitial Anion :-



Nearby -ve charge is doubled.

Extra -ve ion is present in the interstitial position and is neutralised by cation of higher charge present adjacent to it.

28/11/18.

Essay
Ans.

BET Isotherm :-
Brunauer, Teller

Two types of energy released -

- Energy released by the solid adsorbent.
- " " " gaseous " on liquification.

Solid adsorbent is exposed to a gaseous surface under liquification.

$$\frac{V}{V_m} = \frac{C \cdot z}{(1-z)[1-(1-c)z]}$$

c and z are constants.

$$c = e^{\frac{E_1 - E_2}{RT}}$$

P → pressure of gas at const. T

P^* → min. pressure reqd. for liquification of the gas.

$$z = \frac{P}{P^*}$$

V_m → Volume of the gas corresponding to monolayer.

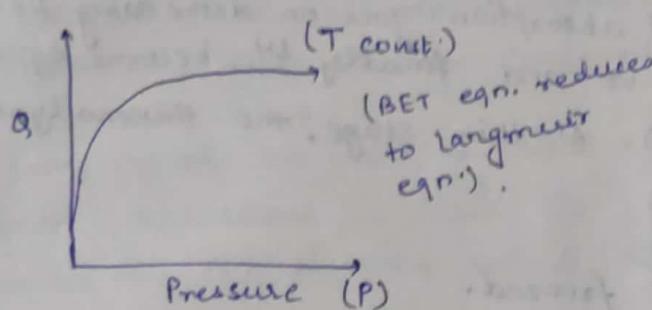
$V \rightarrow$ Volume of gas at const. temp.

$E_1 \rightarrow$ Heat of adsorption of gas in the monolayer.

$E_2 \rightarrow$ Heat energy reqd. for liquification of the gas.

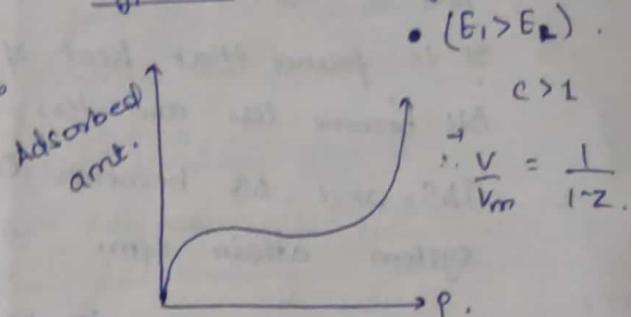
GRAPHS:

Type-I (Monolayer).



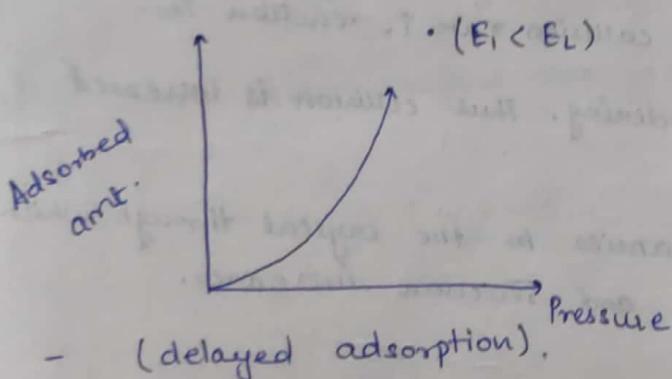
steep rise, delayed adsorption followed by levelling of region.

Type-II (Multi-layer).



gradual steep rise, delayed adsorption, levelling of region and then steep rise.

Type-III (Multi-layer).



Thermodynamics of Adsorption:-

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

ΔH is $-ve$ in adsorption process.

During adsorption, the residual forces on

- As a result of adsorption of gas liquified gas along the gas surface of solid adsorbent, the residual force and surface energy will decrease.
- Decrease of surface energy appears as heat.
- Adsorption is accompanied by decrease of enthalpy of the system i.e., ΔH is $-ve$.

- (ii) During adsorption, the adsorbate changes from a more random gaseous stage to a less random adsorbed state on the solid surface. Thereby, the entropy of system decreases i.e., ΔS° is -ve.

2nd para:

As per the Gibbs Helmholtz eqn; $\Delta G = \Delta H - T\Delta S$,

ΔG is -ve.

It is found that heat of absorption goes on decreasing i.e., ΔH become less and less -ve and finally ΔH becomes equal to $T\Delta S$, and ΔG becomes 0. At this stage, the thermodynamic system attains eqm.

The 'layer growth' will be freezed.

Insp.

Methods to Improve Reactivity of Solids:

Eg Close packing reduces the chances of collision. For collision, some space must be present.

- By enhancing temperature, K.E \uparrow , collision rate \uparrow , reaction R_{eo} .
- Increasing surface area by Powdering. Thus collision is increased and reaction R_{eo} .
- Crystal Defects: Create some vacancies in the crystal through which penetration of particle occurs and reaction increases.
- Addition of catalyst.

(V) Nucleation & Propagation (str. similarity of reactant towards the product)

Fast propagation always depends on structural similarity of reactants. If A+B have same structural similarity, product C can easily be formed.

BAND THEORY:-

Band: Range of energy possessed by the electrons. Electrons have the Fermi-level.

Band theory.

- (2)

- (10)

{ diff. singular e^- and communal e^- at.

2nd \rightarrow atomic str. upto valence

Explain the behaviour of conductor, insulator & S.C. (27) and band conduction based on energy of

Atom consists of the nucleus having protons and neutrons. Electrons keep on revolving in the \rightarrow elliptical orbits around the nucleus.

Energy associated with $\frac{1st}{2nd}$ orbital $e^- \rightarrow$ first band.
 $\frac{2nd}{3rd} \rightarrow$ second band.

Valence " " \rightarrow valence band.

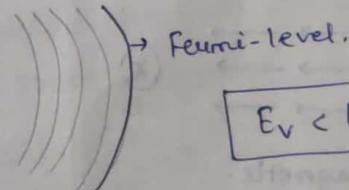
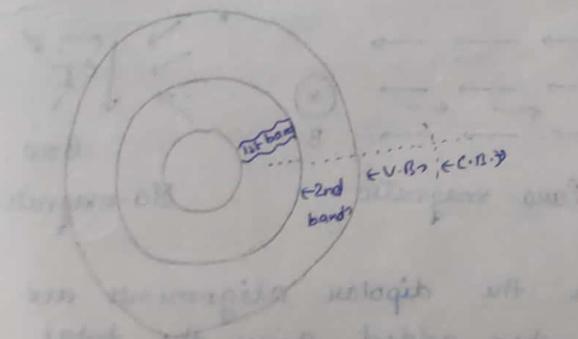
The control of nucleus of valence e^- is least due to the max. distance. These e^- 's are responsible for the conduction of elements. These e^- 's are liberated which then constitute the conduction band.

(v) Energy gap b/w V.B & C.B is called forbidden energy gap. When separation is least b/w V.B & C.B, ~~the~~ it is very easy to transfer the e^- 's from V.B to C.B, hence ~~the~~ forming a conductor.

Narrow gap b/w V.B & C.B, little force is reqd. to overlap V.B & C.B, forming a S.C.

Wide gap b/w V.B & C.B, no force is enough for the effective overlapping, forming the insulator.

(vi) Fermi level:- Highest energy level in the V.B.



$$E_V < E_F < E_C$$

(vii) Fermi-LEVEL \rightarrow It is the highest energy level an electron can occupy in the V.B at 0°K . Fermi surface is the plane of separation b/w the filled and empty stage in the ground level of the crystal. In the case of metals, the fermi-level is that energy level where the probability of occupation of e^- is half. In the case of a s.e. when 'n' no. of e^- 's occupy a band with 'n' orbitals, it is half-filled and e^- near the fermi-level are mobile.

In the case of a S.C., fermi-level is b/w E_V and E_C . ($E_V < E_F < E_C$). Normally, fermi-level will be within the forbidden gap. As the temp. increases, fermi-level rises. In the case of an N-type s.c., E_F is b/w E_D and E_A .

$$\bullet \boxed{E_D < E_F < E_C}$$

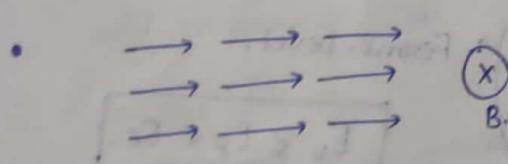
Whereas, in the case of a P-type s.c., E_F is b/w E_V and E_A .

$$\bullet \boxed{E_V < E_F < E_A}$$

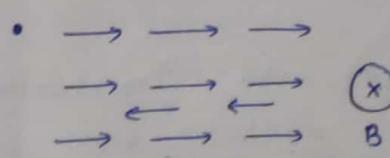
Molecular field theory of Magnetism:

Consider iron rod, which has two forms of mag. field.

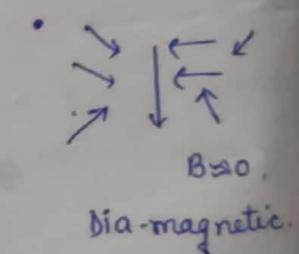
- inherent mag. field present inside the rod (inherent property).
- external mag. field which we apply.
- * Under the influence of ext. mag. field, some sort of magnetic alignment happens to the dipole inside. This dipolar alignment enhance the mag. behaviour of element.



Ferro-magnetic.



Para-magnetic.



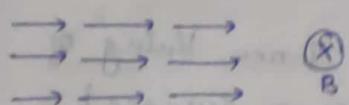
Dia-magnetic.

Mag. domains are the areas where the dipolar alignments are mostly present. All the domains when added give the total mag. strength of material.

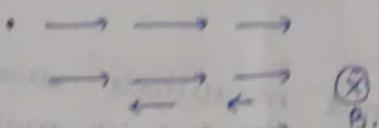
Molecular Field Theory of Magnetism:-

Ferro-magnetic substances are strongly attracted by the ext. mag. field.
e.g. Fe, Co, Ni, etc.

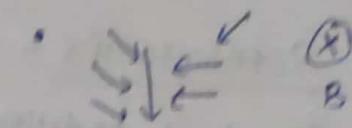
When a mag. material is taken under the influence of an ext. field, three types of behaviour are expected.



Ferro-behaviour.



Para.



Dia-magnetic

In a ferro-mag. material, there are no. of small regions called domains which are magnetised. The total magnetisation is the vector sum of the mag. moments produced due to the individual domains.

The atomic dipoles of each domain are aligned parallel to each other to produce magnetisation due to the presence of an exchange coupling b/w the adjacent dipoles. Exchange coupling is caused by a molecular field which is proportional to the magnetisation of the ferro-magnetic substance.

Weiss field (- Molecular field) $\propto M$.

$$B_w \propto M \rightarrow B_w = \frac{M}{\gamma} \quad \text{where } \gamma \text{ is Weiss field constant or molecular const.}$$

Actually, molecular field theory of ^{ferro}magnetism is based on the concept of ferromagnetic domains which are spontaneously magnetised due to the presence of an internal molecular field called the "Weiss field", or "exchange field".

Note :- (Within the magnet, circular structures called domains are present which consists of parallel alignments responsible for spontaneous magnetised material. B/w these alignments, some magnetic exchange takes place).

(Energy level splitting is also included).

The Weiss field cannot be due to magnetic dipole interactions between the neighbouring dipoles, because this may create a lower field than that clearly observed.

According to Heisenberg, the Weiss field was due to the result of quantum mechanical exchange interactions b/w the atoms.

REFRACTORIES -

The heat resistive brick materials used for lining of the furnace. Inner lining brick material of a furnace, ceramic material stable upto at very high temp. (2000°C). Depending upon the materials used in the furnace, diff refractories with different properties are used.

a. what is Refractory? Types of Refractory with example.

Phy. and chem requirement of refractory.

→ Requirements → • Low electrical conductivity.
• Resistance to temp. fluctuation.

- Chemically inert.
- Non-porous, otherwise it will lead to cracking.
- Superior thermal stability, mechanical strength, thermal conductivity.
- Dimensional stability.
(as some materials expand or contract during process).
- Oxidative stability.
- Stable towards all types of degradation.
- Quick propagation rate should be low.
Refractoriness should be high (heat withstandness).

Types → Acidic, Basic and Neutral Refractory.

Acidic Refractory : Atm - Not attacked by acidic slags.

Eg:- Aluminium,

Basic → Not attacked by basic/neutral slags.

Eg: Dolomite.

Neutral : Not attacked by slightly or acidic or neutral media.

Eg: Corundum.