



Checklist Notes Revision

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U-1

1. Gibb's Phase Rule

A. System at equilibrium must satisfy these conditions

- i) Thermal equilibrium
- ii) Mechanical equilibrium
- iii) Chemical equilibrium

$$\rightarrow \text{So, } \mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$$

$$\rightarrow \text{Degrees of freedom} = \text{Total no. of intensive variables} - \text{Total no. of connecting variables}$$

Total no. of intensive variables \Rightarrow

$$\begin{aligned} & \cdot x_1^\alpha + x_2^\alpha + x_3^\alpha + \dots + x_c^\alpha = 1 \Rightarrow c-1 \\ & x_1^\beta + x_2^\beta + x_3^\beta + \dots + x_c^\beta = 1 \Rightarrow c-1 \\ & \vdots \\ & x_1^P + x_2^P + x_3^P + \dots + x_c^P = 1 \Rightarrow c-1 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \vdots \\ \end{array} \right\} P(c-1)$$

• Along with that, T & P are 2 intensive variables
 \Rightarrow Total no. of intensive variables = $P(c-1) + 2$

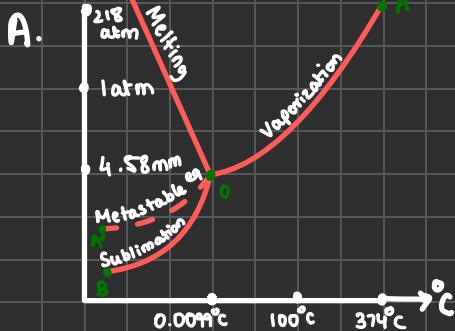
Total no. of connecting variables \Rightarrow

$$\begin{aligned} & \cdot \mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots = \mu_1^P \Rightarrow P-1 \\ & \mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \dots = \mu_2^P \Rightarrow P-1 \\ & \vdots \\ & \mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \dots = \mu_c^P \Rightarrow P-1 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \vdots \\ \end{array} \right\} c(P-1)$$

$$F = P(c-1) + 2 - c(P-1)$$

$$F = c - P + 2$$

2. Water Systemmmmm



Melting :

- ice \rightleftharpoons water
- $F = 1$
- monovariant
- Slope = -ve
- $\frac{dP}{dT} = \frac{\Delta H_{\text{fusion}}}{T \Delta V}$ $\Rightarrow \Delta V = -ve$

↓
Clausius Clapeyron

Equation

So, $\frac{dP}{dT} = -ve$

Hence, Slope = -ve

Sublimation :

- ice \rightleftharpoons water vapour
- $F = 1$
- Monovariant
- Slope = +ve
- $\frac{dP}{dT} = \frac{\Delta H_{\text{fusion}}}{T \Delta V} = +ve$

Vaporization

- water \rightleftharpoons vapour
- $F = 1$
- monovariant
- $\frac{dP}{dT} = \frac{\Delta H_{\text{fusion}}}{T \Delta V} = +ve$

Triple Point '0'

- Equilibrium b/w liq, water & ice
- All 3 Phases present together
- $F = 0$
- Invariant

Critical Point 'A'

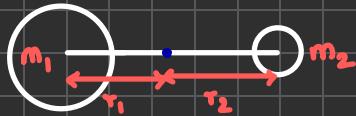
- Interface b/w water & water vapour vanishes
- Water doesn't exist as liquid above this point

Metastable Equilibrium

- Ice fails to form at triple point & continues to exist as water in liquid phase
- Vapour pressure of liquid continues along OA'. It's called supercooled water & represents metastable
- Any disturbance causes to go back to equilibrium

3. M O I Derivation

A.



By balancing moments,

$$m_1 r_1 = m_2 r_2$$

$$\text{and } r_0 = r_1 + r_2$$

$$\text{So, } I = m_1 r_1^2 + m_2 r_2^2$$

$$= m_1 r_1 r_1 + m_2 r_2 r_2$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$I = (m_1 + m_2) r_1 r_2 \longrightarrow \textcircled{1}$$

$$\text{Also, } m_1 r_1 = m_2 (r_0 - r_1)$$

$$(m_1 + m_2) r_1 = m_2 r_0$$

$$r_1 = \frac{m_2 r_0}{m_1 + m_2}$$

$$\text{Similarly, } r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad \boxed{\text{Substitute in } \textcircled{1}}$$

$$\Rightarrow I = \cancel{(m_1 + m_2)} \times \frac{m_1 r_0}{\cancel{m_1 + m_2}} \times \frac{m_2 r_0}{m_1 + m_2}$$

$$= \frac{m_1 m_2}{m_1 + m_2} \times r_0^2$$

$$\boxed{I = \mu r_0^2}$$

$$\text{where } \mu = \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$

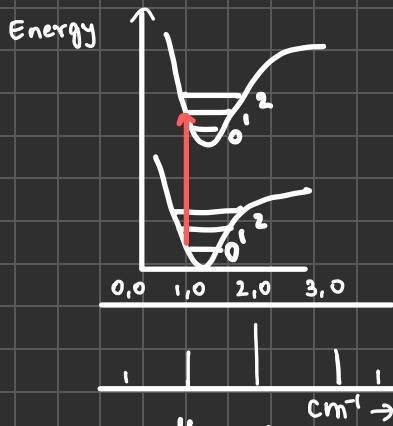
4. Franck - Condon Principle

A. The principle states that an electronic transition takes place so rapidly that vibrating molecule doesn't change internuclear distance appreciably during transition.

3 Transitions are possible :

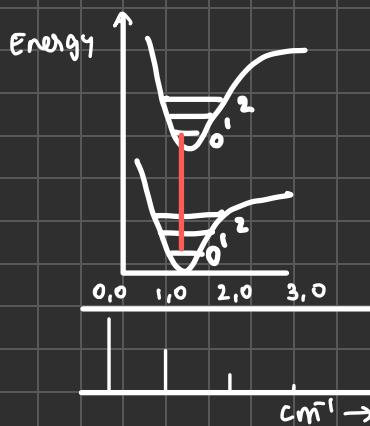
$$i) \quad \underline{r_e'' < r_e'}$$

→ Shows max intensity for $(v', 0)$ line



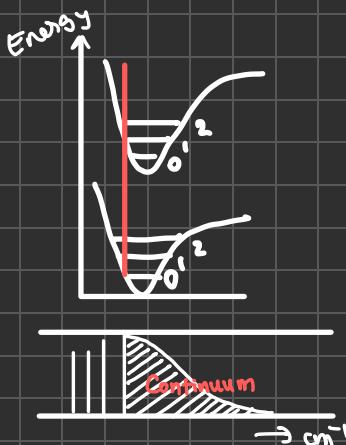
$$ii) \quad \underline{r_e'' = r_e'}$$

→ Shows max intensity for $(0, 0)$ line

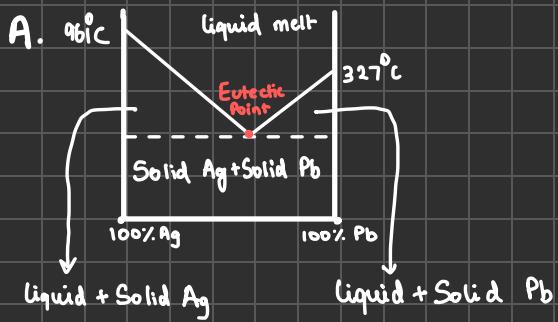


$$iii) \quad \underline{r_e'' > r_e'}$$

→ Spectrum shows continuum because transition results in molecule going beyond dissociation energy



5. Pb - Ag System & Pattinson's process



Pb 97.4% + Ag 2.6% ←

303°C

Eutectic Point

- Lowest temperature at which liquid phase is stable at given temperature
- Area above freezing point line represents liquid melt.
- Area below freezing point line but above eutectic Temperature represents mixture of liquid melt and pure solid
- Area below eutectic temperature represents mixture of 2 solid substances

Pattinson's Process

- Process of heating Argentiferous Lead containing small quantity of Silver & cooling it to get pure Lead & liquid richer in Silver

- i) Argentiferous Lead is heated above MP of pure Lead
- ii) The melt is allowed to cool
- iii) Temperature reaches freezing point of Lead & starts to separate
- iv) As it cools further, more Pb separates & liquid in equilibrium with solid Lead gets richer in Silver
- v) Lead starts to float which is removed by ladles
- vi) Further cooling solidifies mixture with Eutectic composition (2.6% Ag) subjected to recovery of Ag

6. Energy level diagram

A. We know, $E_J = BJ(J+1)$
 $E_{J+1} = B(J+1)(J+2)$

$$\Delta E_{J \rightarrow J+1} = 2B(J+1)$$

$$\Delta \bar{v}_{J \rightarrow J+1} = \Delta E_{J \rightarrow J+1} = 2B(J+1)$$

	$J = 5$	<u>J value</u>	<u>\bar{v} (cm^{-1})</u>
30B			
20B	$J = 4$	$0 \rightarrow 1$	2 B
12B	$J = 3$	$1 \rightarrow 2$	4 B
6B	$J = 2$	$2 \rightarrow 3$	6 B
2B	$J = 1$	$3 \rightarrow 4$	8 B
0	$J = 0$	$4 \rightarrow 5$	10 B

7. Numericals

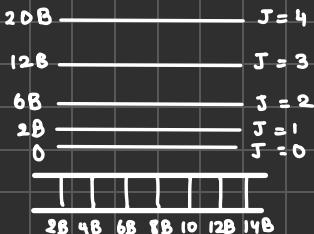
Q. Calculate energy required (cm^{-1}) for molecule to move from $J=3$ to $J=4$. $B = 10.93 \text{ cm}^{-1}$

A. $\bar{v}_{3 \rightarrow 4} = 2B(J+1)$
 $= 2 \times 10.93 \times (3+1) = 87.44 \text{ cm}^{-1}$

Q. Draw rotational energy level diagram & calculate distance b/w consecutive lines in rotational spectrum of diatomic molecule with $I = 1.34 \times 10^{-47} \text{ Js}$

A. $B = \frac{h}{8\pi^2 I C} = \frac{6.626 \times 10^{-34}}{8 \times 3.14 \times (1.34 \times 10^{-47}) \times 3 \times 10^8} = 20.87 \text{ cm}^{-1}$

$\bar{v} = 2B = 41.74 \text{ cm}^{-1}$



Q. In rotational spectrum, absorption lines are observed at constant separation of 3.84 cm^{-1} . Calculate position of line, when transition takes place from $J=2 \rightarrow 3$

A. $2B = 3.84 \text{ cm}^{-1}$
 $B = 1.92 \text{ cm}^{-1}$

$$\Rightarrow \bar{v}_{J=2 \rightarrow 3} = 2B(J+1)$$

$$= 2B \times 3$$

$$= 3(3.84) = 11.52 \text{ cm}^{-1}$$

Q. For HBr,

i) Calculate reduced mass & force constant (Nm^{-1}), when it shows harmonic oscillations & vibrational spectrum shows single intense line at 2649 cm^{-1}

ii) Calculate wave no. of fundamental absorption & first overtone when $\chi_e = 0.017$ & $\bar{v}_e = 2649 \text{ cm}^{-1}$

A. i) $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{80 \times 1}{80 + 1} \times 1.66 \times 10^{-27} \text{ kg} = 1.6395 \times 10^{-27} \text{ kg}$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \Rightarrow (2\pi c \bar{v})^2 \times \mu = k$$

$$k = (2\pi \times 3 \times 10^8 \times 264900)^2 \times 1.6395 \times 10^{-27}$$

$$= 408.89 \text{ cm}^{-1}$$

ii) Fundamental absorption = $\bar{v}_e (1 - 2\chi_e)$

$$= 2649 (1 - 2 \times 0.017)$$

$$= 2558.93 \text{ cm}^{-1}$$

$$= 2\bar{v}_e (1 - 3\chi_e)$$

$$= 2 \times 2649 (1 - 3 \times 0.017)$$

$$= 5027.8 \text{ cm}^{-1}$$

Note:
 Solve
 More:p

First Overtone

8. Phase, Component & Degree of Freedom

A. Phase

- Any homogeneous & physically distinct part of system separated from other parts of system by definite boundaries



$$P = 3$$



$$P = 2$$

↳ Considered as 1 phase

Component

- Smallest no. of independent chemical constituents by which each & every phase can be expressed
- It can be 0 and negative also

ex: Water System



Degree of Freedom

- Minimum no. of independent variables like Temperature, Pressure & Component that can be altered without disturbing equilibrium



$$F = C + P - 2$$

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

9. Rotational Spectroscopy

- Absorbs in microwave region
- Molecule should have permanent dipole moment
- Energy level expression
 $E_J = BJ(J+1)$
- Quantum Selection Rule $\Rightarrow 2B(J+1)$
- Difference b/w 2 consecutive lines is $2B$
- First line $\Rightarrow J=0 \rightarrow 1 \Rightarrow 2B$
- $B = \frac{h}{8\pi^2 Ic}$, $I = \mu r_0^2$
- Ex: HCl, CO \Rightarrow Show
 $H_2, Cl_2, CO_2 \Rightarrow$ Don't

Vibrational Spectroscopy

- Absorbs in Infrared Region
- Molecule Should have change in dipole moment
- Energy level expression
 - i) Harmonic $\Rightarrow E_v = (v + \frac{1}{2}) \bar{v}_0$
 - ii) Anharmonic $\Rightarrow E_v = (v + \frac{1}{2}) \bar{v}_e - (v + \frac{1}{2})^2 \bar{v}_e \chi_e$
- Quantum Selection Rule \Rightarrow
 - i) Harmonic $\Rightarrow \Delta E = \bar{v}_0$
 $v \rightarrow v+1$
 - ii) Anharmonic \Rightarrow Based on v & $v+1$
- Difference b/w 2 consecutive lines
 - i) Harmonic \Rightarrow Single line
 - ii) Anharmonic \Rightarrow Progressively Decrease
- First line
 - i) Harmonic $\Rightarrow \bar{v}_0$
 - ii) Anharmonic $\Rightarrow v=0 \rightarrow 1$
- $\bar{v}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$
- Ex: HCl, CO, H₂O, CO₂ \Rightarrow Show
 $H_2, Cl_2 \Rightarrow$ Don't

CO₂ doesn't possess permanent dipole moment but shows vibration spectroscopy because:

along with symmetric stretching, it shows asymmetrical stretching



10. Born- Oppenheimer Approximation

$$A. \quad E = E_T + E_V + E_e + E_R \xrightarrow{\text{Vibrational}} \text{Translational}$$

\swarrow Rotational \searrow Electronic

But E_T is almost negligible

$$\text{So, } E = E_T + E_V + E_e$$

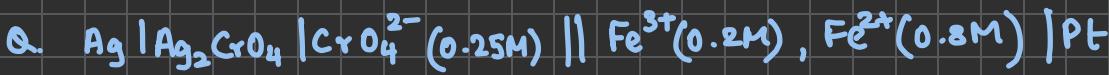
$$\Delta E_{\text{Total}} = \Delta E_{\text{rotational}} + \Delta E_{\text{vibrational}} + \Delta E_{\text{electronic}}$$

$$\Delta E_{\text{Total}} = \Delta E_{\text{rot}} + \Delta E_{\text{vib}} + \Delta E_{\text{elec}}$$

Where, All 3 are independant of each other

$$\Delta E_{\text{rot}} \times 10^6 \simeq \Delta E_{\text{vib}} \times 10^3 \simeq \Delta E_{\text{elec}}$$

U-2



i) Half cell $\text{Ag} | \text{Ag}_2\text{CrO}_4 | \text{CrO}_4^{2-}$

ii) E_{cell}° & E_{cell} at 298 K

$$\left[\begin{array}{l} E_{\text{Ag}|\text{Ag}_2\text{CrO}_4|\text{CrO}_4^{2-}}^{\circ} = 0.446\text{V} \\ E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77\text{V} \end{array} \right]$$



$$E_{\text{cell}}^{\circ} = E_{\text{rhs}} - E_{\text{up}} = 0.77 - 0.446 = 0.324\text{V}$$

$$E_{\text{cell}} = 0.324 - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2 [\text{CrO}_4^{2-}]}$$

$$= 0.324 - \frac{0.0591}{2} \log \left(\frac{0.8^2}{0.25 \times 0.2^2} \right)$$

$$= 0.2706\text{V}$$



$$\text{C}_1 = 0.2\text{g} \quad \& \quad \text{C}_2 = 0.1\text{g} \quad \text{per } 100\text{g} \text{ of Hg}$$

$$E_{\text{Zn}|\text{Zn}^{2+}}^{\circ} = -0.76\text{V} . \text{ Find EMF}$$

$$\begin{aligned} A. \quad E_{\text{cell}} &= \frac{0.0591}{n} \log \frac{\text{C}_1}{\text{C}_2} = \frac{0.0591}{2} \log \left(\frac{0.2}{0.1} \right) \\ &= 8.8954 \times 10^{-3} \text{ V} \end{aligned}$$



i) Role of Ag-AgCl?

ii) R/I_{ns} at anode & cathode

iii) E_{cell}° & E_{cell} at 298K

$$E_{\text{Fe}^{2+}, \text{Fe}^{3+}}^{\circ} = 0.77\text{V}$$

$$E_{\text{Ag} | \text{AgCl} | \text{Cl}^-}^{\circ} = 0.22\text{V}$$

A. i) Ag-AgCl is used as reference electrode



iii) $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{1} \log \left(\frac{[\text{Fe}^{2+}]}{[\text{Cl}^-][\text{Fe}^{3+}]} \right)$

$$= (0.55\text{V}) - 0.0591 \log \left(\frac{0.8 \times 10}{0.08 \times 0.1} \right)$$

$$= 0.55 - 2 \times 0.0591$$

$$= 0.4318\text{V}$$



Identify type of cell & explain why. Find E_{cell}

A. It is an electrode concentration cell because same electrodes with different activity are in contact with same electrolyte



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{P_{\text{cathode}}}{P_{\text{anode}}}$$

$$= 0 + \frac{0.0591}{2} \log \frac{P_a}{P_c} = \frac{0.0591}{2} \log \frac{8}{2} = 0.0179\text{V}$$

Q. Glass electrode coupled with Saturated calomel electrode to measure unknown pH. Cell potentials are 0.215 & 0.385V in contact with a solution of pH = 7 & solution of unknown pH.
Find unknown pH

A. $E_g^o = E_{\text{cell}} + 0.0591 \text{ pH} + E_{\text{SCE}}$ $E_{\text{SCE}} = 0.244$

$$= 0.215 + 0.0591 \times 7 + 0.244$$

$$= 0.8727$$

$$\text{pH} = \frac{E_g^o - E_{\text{cell}} - E_{\text{SCE}}}{0.0591}$$

$$= \frac{0.8727 - 0.385 - 0.244}{0.0591}$$

$$= 4.12$$

Q. A decinormal calomel electrode as cathode with SCE as anode forms a cell. Write cell representation & calculate concentration of Cl^- ion in unsaturated calomel electrode if $E_{\text{cell}} = 0.0977 \text{ V}$ at 298K

A. Cell representation : $\text{Pt} | \text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{Cl}^- (\text{x M}) || \text{Cl}^- (0.1 \text{ M}) | \text{Hg}_2\text{Cl}_2 | \text{Hg} | \text{Pt}$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{OCE}} - E_{\text{SCE}}$$

$$0.0977 = E_{\text{OCE}}^o - \frac{0.0591}{1} \log(0.1) - E_{\text{SCE}}^o + \frac{0.0591}{1} \log(x)$$

$$0.0977 = 0.0591 \log\left(\frac{x}{0.1}\right)$$

$$10^{\frac{0.0977}{0.0591}} = \frac{\log x}{\log 0.1} \Rightarrow x = 4.499 \text{ M}$$

Q. Write overall cell reaction & derive Nernst equation using thermodynamic principle

A. $\Delta G = -W_{\text{max}}$

→ Electrochemical work depends on

- i) Total no. of charges = nF
- ii) Energy per unit charge = E

So, $W_{\text{max}} = nFE = -\Delta G$

$$\Delta G = -nFE$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$-nFE = -nFE^{\circ} + RT \ln Q$$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

Q. Ion Selective Electrode \Rightarrow Glass Electrode

- Electrodes that selectively respond to a specific ion in a mixture.
- Potential developed is a function of conc. of that ion
- It has a membrane capable of exchanging specific ion with solution which it is in contact with

ex: Glass Electrode

- Consists of Glass membrane selective towards H^+ ions
- $H^+_{\text{solution}} + Na^+G_1^- \rightleftharpoons Na^+_{\text{solution}} + H^+G_2^-$

$$\text{Boundary potential } E_b = 2.303 \frac{RT}{nF} \log \frac{C_1}{C_2}$$

C_2 is constant

$$So, E_b = L + 2.303 \frac{RT}{nF} \log C_1$$

$$L = -2.303 \frac{RT}{nF} \log C_2$$

At 298 K, $n = 1$

$$So, E_b = L + 0.0591 \log [H^+]$$

$$= L - 0.0591 \text{ pH} \quad (\text{pH} = -\log[H^+])$$

$$\text{Thus, } E_{\text{Glass}} = E_b + E_{\text{ref}} + E_{\text{asymmetric}}$$

$$= L - 0.0591 \text{ pH} + E_{\text{ref}} + E_{\text{asymmetric}}$$

$$E_g = E_g^\circ - 0.0591 \text{ pH}$$

→ Glass Electrode :

- Used in chemical, industrial, agricultural & biological labs

→ Advantages :

- Easy to Construct, Simple to operate
- Potential developed is constant for long time.
- Electrode can be used even with small amount of test solution
- Electrode can be used even in presence of oxidised impurities
- Wide pH range 0-14 can be used in glass electrode

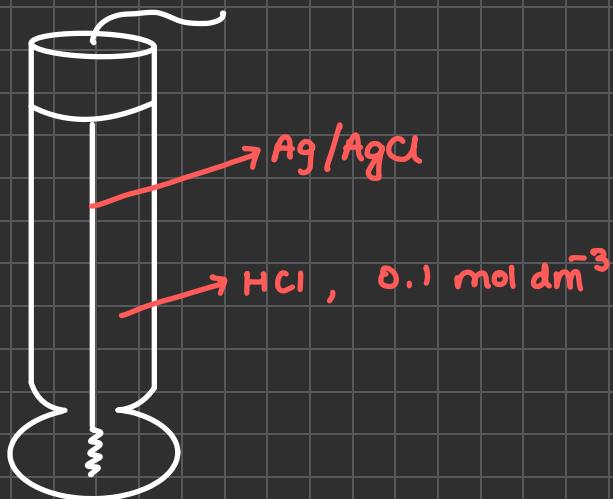
→ Disadvantages :

- Alkaline Error
 - Because of high resistance of glass, simple potentiometer can't be used.
Sensitive potentiometer must be used
 - Glass electrode is very fragile, So care must be taken
 - Alkaline error usually observed when high pH (usually above 9)

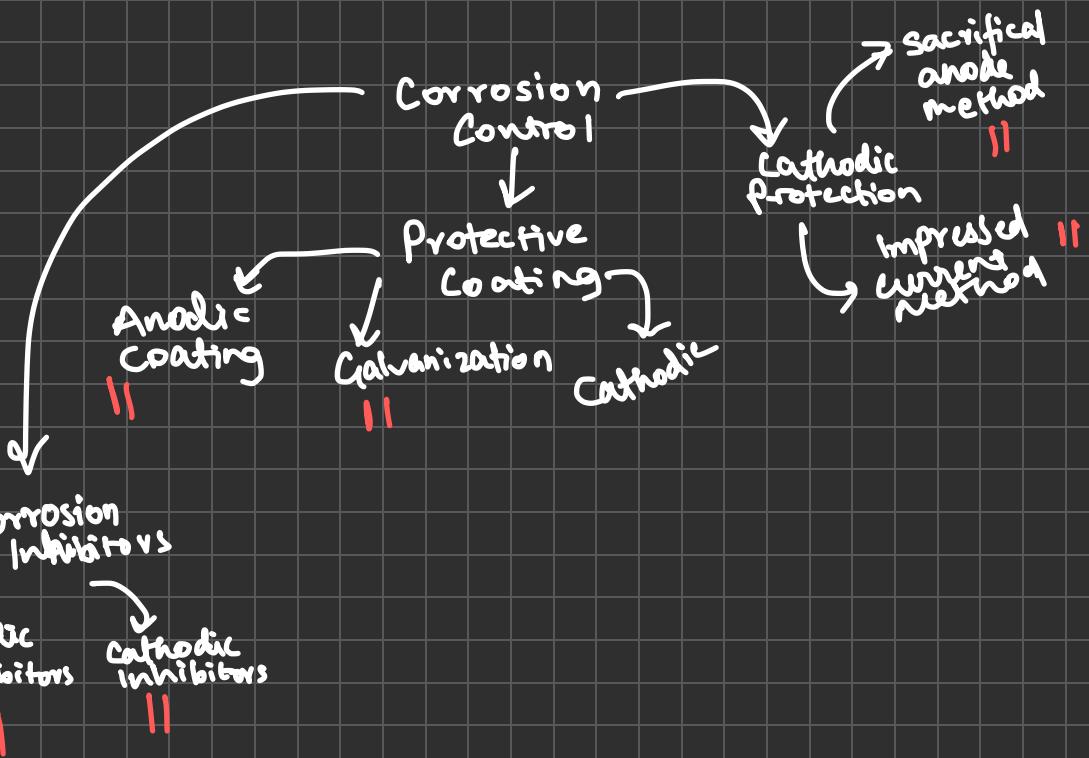


Construction of Glass Electrode

- Glass tube (End is a very thin glass membrane)
- Glass bulb made of CORNING 015 which is filled with a reference solution of known pH
- Ag-AgCl electrode is dipped inside reference solution & serves as internal reference electrode & provides external electrical contact
- Electrode immersed in solution containing H^+ , which is analyte



$$pH = \frac{E_A^{\circ} - E_{\text{calomel}} - E_{\text{cell}}}{0.0591}$$



Corrosion

- Destruction / Deterioration & consequent loss of metal through direct metal attack (or) electrochemical attack by environment

Types of Corrosion

Dry Corrosion

- Direct chemical attack due to affinity of metal to certain gases in absence of moisture/conducting medium

Wet Corrosion

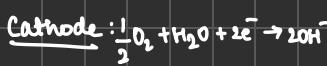
- Electrochemical attack of environment on surface of metal in presence of moisture/conducting medium leading to formation of galvanic cell

• \rightarrow Anode
• \rightarrow Cathode

Differential Metal Corrosion



More active metal undergoes oxidation, cathode is completely unaffected cuz of diff. in electrode potentials



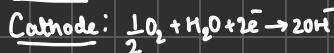
Ex:

- Fe & Cu, Cu unaffected
- Steel pipe connected to Cu
- Nuts & Bolts of diff. metal

Differential Aeration Corrosion



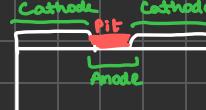
Corrosion due to formation of O₂ concentration cell due to uneven supply of air on metal



Ex:

- Nail pulled out of wall
- Paper clip on paper for long time
- Barbed wire
- Paint peeled from metal

Pitting Corrosion



Localised & accelerated corrosion forming pits/pinholes around metal which is relatively unattacked (Very Destructive)

High e⁻ demand, small anode which becomes a pit

- Ex:
i) Sn covering Fe
ii) Steel screw in Cu sheet

exception!

\hookrightarrow Zn covering Fe works in Zn Zn opposite

Stress Corrosion



Caused by effect of tensile stress & specific corrosive environment leading to cracks caused by stress

Specific environment	Metal	Environment
Mild Steel	Sn	NaOH
Brass	Fe	ammonical vapours

Ex: Bridge collapsing, Boiler explosion

Electrochemical Theory of Corrosion



• Reactions

- Anode : $M \rightarrow M^{n+} + n{e^-}$
- Cathode :
 - Liberation of H_2
 - Acidic Medium : $2H^+ + 2{e^-} \rightarrow H_2 \uparrow$
 - Alkaline Medium : $2H_2O + 2{e^-} \rightarrow H_2 \uparrow + 2OH^-$
 - Absorption of O_2
 - Acidic Medium : $O_2 + 4H^+ + 4{e^-} \rightarrow 2H_2O$
 - Alkaline Medium : $O_2 + 2H_2O + 4{e^-} \rightarrow 4OH^-$

• Iron Corrosion



Factors affecting Corrosion

- Nature of metal
 - More active \Rightarrow more corrosion
 - Noble Metals \Rightarrow less corrosion
- Difference in E° of Anode & Cathode
 - The driving force in differential metal corrosion

★ Ratio of Anodic & Cathodic Areas

- If Anodic area is small,
Cathodic area,
extent of corrosion is very high
(pitting)

★ Nature of Corrosion Product

- Passive Layer
 - Forms a passive layer on metal preventing further corrosion
ex: Al, Cr, Zn (Protective Oxide Layer)
 - They are insoluble in medium, uniform, non-porous & Stable
- Active Layer
 - Not uniform corrosion, so allows corrosion in unprotected parts
ex: Fe, Zn

Stainless Steel
 \rightarrow Cr added to Fe, forms Cr_2O_3 & doesn't corrode

★ Polarisation

- Anodic Polarisation
 - Rate of formation of metal ion faster than rate of diffusion
 - Due to ions accumulated at anode, extent of corrosion reduced
- Cathodic Protection
 - Depletion of O_2/H^+ ions in cathode reduces extent of anodic reaction
 - $\rightarrow E^\circ$ becomes less +ve

- Methods to reduce polarisation in cells:
 - Agitation \rightarrow Stir soln to move ions
 - Increase temperature
 - Add Conducting salts

★ Over voltage

- Extra voltage over theoretical voltage of electrode required to carry out particular process at electrode
- Hydrogen Overvoltage
 - metal with low hydrogen overvoltage on surface more susceptible to corrosion
 - When it is low, cathodic τ/n occurs faster making anode τ/n also faster.
 - High overvoltage, causes slower cathode, τ/n slowing down corrosion as well.

★ Temperature

- Higher Temperature \rightarrow More corrosion

Because :

rate of τ/n \uparrow

conductance \uparrow

polarisation \downarrow

Solubility of corrosion product \uparrow

Breakdown of protective film

• pH

- Low pH \Rightarrow Higher $[H^+]$
So more corrosion

U-3

Q.

1. A battery using Zn as anodic material lasts for 2 hours when a constant current of 1.25 A is drawn from it. What weight of Zn is present in the battery if the reaction at the anode is



If the electricity storage density of the battery is 180 As/g, determine the weight of the entire battery.

(Given : molar mass of Zn = 65 g, F = 96500 C/mol)

A. $I = 1.25 \text{ A}$

$$t = 2 \times 60 \times 60$$

$$C = 9000 \text{ As}$$

$$\text{ESD} = \frac{C}{\text{wt. of battery}} = 180 \text{ As/g}$$

$$\text{wt of Battery} = 50 \text{ g}$$

Q.

2. Calculate the electricity storage density of a Lithium battery which has 2.0 g of lithium as anodic material. The total weight of the battery is 65 g. Give the answer in Ah/kg.

(Given : Atomic mass of lithium is 7)

A. $\text{ESD} = \frac{C}{\text{wt. of battery}}$

$$C = \frac{WnF}{M} = \frac{2 \times 1 \times 96500}{7}$$
$$= 27571.43 \text{ AS}$$
$$= 7.658 \text{ Ah}$$

$$\text{ESD} = \frac{7.658}{65 \times 10^{-3}}$$
$$= 117.81 \text{ Ah/Kg}$$

Q.

3. Calculate the energy density and power density of 20 kg Lead acid battery which contains 5 kg lead as anode material and discharges constant current for 10 hours. The voltage of the battery is 2 V.

(Given : Atomic mass of lead is 207.2, number of electrons transferred in the redox reaction is 2, F= 96500 C/mol)

$$A. \quad C = \frac{WnF}{M} = \frac{5 \times 10^3 \times 2 \times 96500}{207.2}$$

$$= 4657335.907 \text{ As}$$

$$= 1293.7 \text{ Ah}$$

$$ED = \frac{V \times It}{W} = \frac{2 \times 1293.7}{20} = 129.37 \text{ Wh/kg}$$

$$PD = \frac{ED}{t} = \frac{129.37}{10} = 12.937 \text{ W/kg}$$

Q.

4. Calculate the efficiency of H₂-O₂ alkaline fuel cell

[Given: E^o_{Cell} = 1.20 V, ΔH_{f(H2O)} = -285.8 kJ/mole]

A.

$$\eta = \frac{\Delta G}{\Delta H} \times 100 = \frac{-nFE}{\Delta H} \times 100$$

$$= \frac{-2 \times 96500 \times 1.2}{-285.8 \times 1000} \times 100$$

$$= 81.7$$

Q.

5. If E^o_{Cell} for H₂-O₂ alkaline fuel cell is 1.23 V and efficiency is 83%, calculate the heat evolved during the reaction.

A.

$$\eta = \frac{\Delta G}{\Delta H} \times 100$$

$$83 = \frac{-nFE}{\Delta H} \times 100$$

$$= \frac{-2 \times 96500 \times 1.23}{\Delta H} \times 100 \Rightarrow \Delta H = -286 \text{ kJ}$$

