Corrosion Engineering

Hand Written Notes

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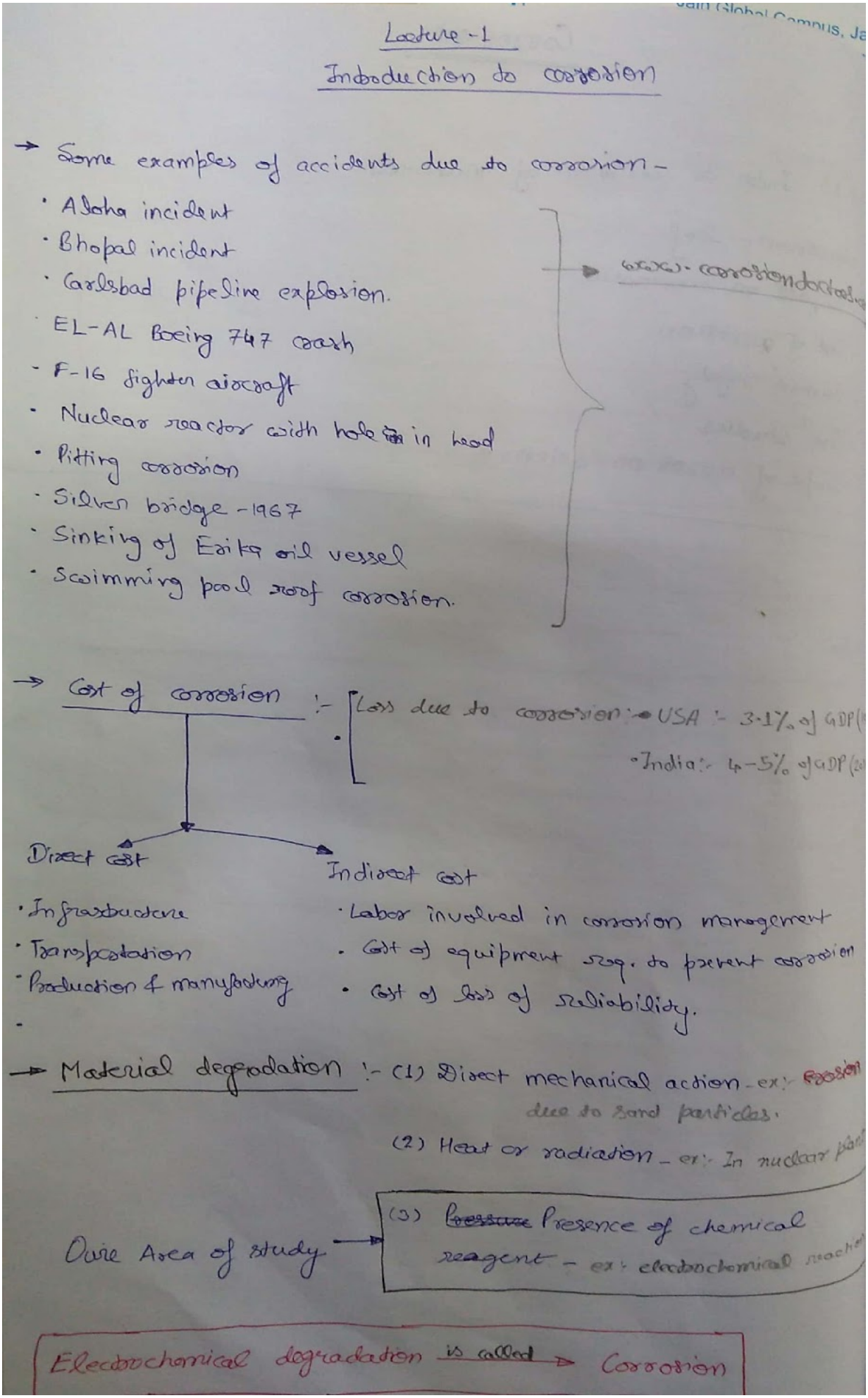
Introduction to Corrosion



Lecture - 1

Introduction to corrosion

→ Some examples of accidents due to corrosion -

- Aloha incident
- Bhopal incident
- Carlsbad pipeline explosion.
- EL-AL Boeing 747 crash
- F-16 fighter aircraft
- Nuclear reactor with hole in head
- Pitting corrosion
- Silver bridge - 1967
- Sinking of Exita oil vessel
- Swimming pool roof corrosion.

→ corrosion control

→ Cost of corrosion :- Loss due to corrosion :- USA :- 3.1% of GDP

India :- 4-5% of GDP

Direct cost

- Infrastructure
- Transportation
- Production & manufacturing

Indirect cost

- Labor involved in corrosion management
- Cost of equipment req. to prevent corrosion
- Cost of loss of reliability.

→ Material degradation :- (1) Direct mechanical action - ex:- Erosion due to sand particles.

(2) Heat or radiation - ex:- In nuclear plant

Our Area of study → (3) Presence of chemical reagent - ex:- electrochemical reaction

Electrochemical degradation is called → Corrosion

Introd

Lecture-2

Intro to corrosion-II

→ Material degradation :- Loss of performance of an engineering system.

- Loss of reflectivity in optical equipment
- " " mechanical strength due to corrosion
- " " Efficiency
- " " life time service period.

- Material degradation with environment :-

(1) Air & gas environment
- Temp.
- Humidity
- $CO_2, O_2, N_2, \ldots$ concentration

(2) Surface condition

Material, alloys, Micro-structure

(3) Aqueous condition
- Temp
- pH
- $[O_2], [Cl], \ldots$
- Flow velocity
- Conductivity.

(4) Soil
- Temp
- Acidity
- $O_2, CO_2, \ldots$ conc.
- Bateria

(5) Radiation

Energy consuming process.

iron ore → iron oxides → Refining → Reduction: $FeO + C \rightarrow Fe + CO$, $Fe_2O_3 + C \rightarrow Fe + CO_2$ → inclusion removal → Oxidation of iron: Fe, inclusion → oxidised → iron/steel

iron/steel → Oxydation of iron → iron oxides. → rust formation/Corrosion → iron oxides

Natural process (Thermodynamically stable reaction)

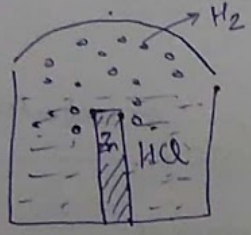
- Corrosion is natural process ⇒ Corrosion can not be prevented
  - Corrosion can be reduced

→ **Corrosion** :- • The tendency of a metal to revert to its Native state.

• **Electrochemical degradation** of metal as a result of reaction with environment

• due to corrosion - metal tries to ~~oxides~~ oxidized
• and makes a chemical compound that is similar to the mineral from which metal was extracted

• Ex:- Zn corrosion in dilute HCl :-



$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2\uparrow$$

Zn is dissolving in solution ⇒ corrosion.

$Zn - 2e^- \longrightarrow Zn^{++}$ (Anode reaction, Oxydation)

$HCl \rightleftharpoons H^+ + Cl^-$ (Cathode reaction, Reduction)

$2H^+ + 2e \longrightarrow H + H \longrightarrow H_2\uparrow$

• For corrosion to occur :- 4 components are necessary -
  • (i) Anode, (ii) Cathode → electrodes.
  (iii) Conductor → surface of Zn (from here e^- will release)
  (iv) Electrolyte → $ZnCl_2$ (from electrolyte ~~ions~~ will flow)

• Ex: Fe corrosion in aquous solution :-

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2$$

(H_2O ← from moisture)

$2[Fe - 2e^- \longrightarrow Fe^{+2}]$

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$2Fe^{+2} \longrightarrow 2Fe(OH)_2$

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Types of Corrosion

Lecture-3

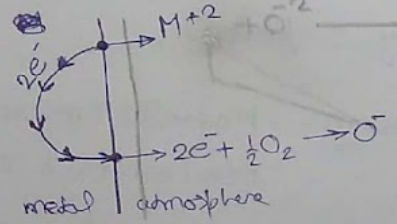
Types & forms of Corrosion

→ Corrosion
- Wet corrosion.
- Dry corrosion.

1) Dry corrosion :- • $M + \frac{1}{2}O_2 \longrightarrow MO$

• mechanism :-

Stage 1 :

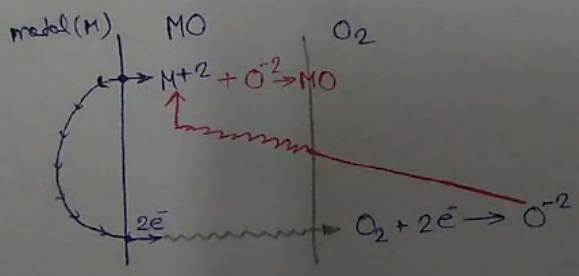


- Anode :- where M^{+2} formation takes place
- Cathode :- where O^- formation takes place
- Conductor :- Metal surface
- Electrolyte :- Atmosphere. O^{-2} moves towards M^{+2}

↓

Condition satisfied for corrosion.

Stage 2 :- When MO layer has been formed -



- M^{+2} & O^{-2} formation takes place
- Two possibility
  - M^{+2} moves & interacts with O^{-2} to form MO
  - O^{-2} moves & interacts with M^{+2} to form MO (Shown in fig)

- Anode :- where M^{+2} forms
- Cathode :- where O^{-2} forms
- Conductor :- Metal surface
- Electrolyte :- MO layer.

↓

Condition for corrosion satisfied

2) Wet corrosion :-

$Zn + HCl \longrightarrow ZnCl_2 + H_2 \uparrow$

Our focus will be on Wet corrosion

Forms of Corrosion (Based on Appearance)

→ Forms of corrosion :- (Based on appearance)

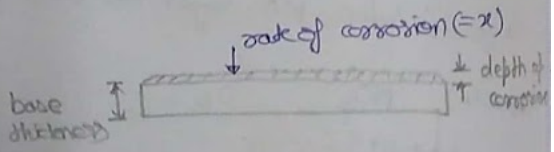
1) Uniform corrosion
2) Galvanic
3) Crevice
4) Pitting
5) Dealloying
6) Intergranular
7) Erosion — Pitting, Cavitation
8) Stress assisted — Stress corrosion, Corrosion fatigue, Hydrogen embrittl...

- These can be induced by 5 factors :-

Parameters for corrosion -
- Material (microstructure)
- Environment (O_2, H_2O, SO_2, M^{+n}, ...)
- Stress
- Design (Smooth / Rough surface)
- Time

Lecture - 4

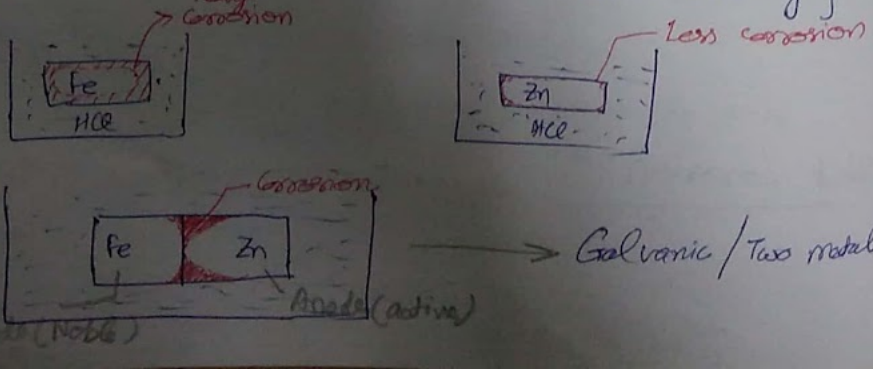
1) Uniform corrosion :-



- No localised corrosion
- No preferential location for corrosion attack
- Can be reduced by — Coating, Painting, Cathodic protection.

2) Galvanic corrosion :- - Corrosion due to connection between metals

{when Fe & Zn dipped in HCl ⇒ Fe corrodes heavily}

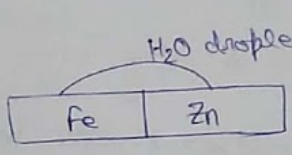


• When Fe-Zn are in contact ⇒ Zn corrodes havily but Fe is protected from corrosion

⇓

[Zinc coating is provided on iron for protection]

• How this happens:



Anode: $Zn \longrightarrow Zn^{+2} + 2e^-$

Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4\,OH^-$

$\Big]\rightarrow Zn^{+2} + 4OH^- \longrightarrow Zn(OH)_2$

(At the surface of Fe)

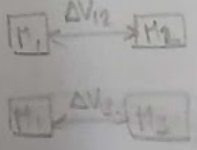
⇓

[Fe acts as cathode]

• Factors: (i) Distance: corrosion reduced away from interface.

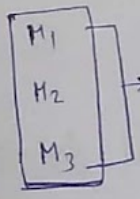
(ii) Polarity charge: Due to atm condition

(iii) Galvanic series:



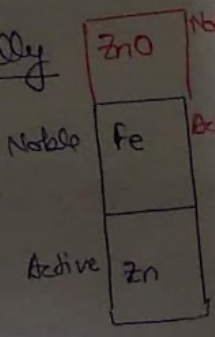
$\Rightarrow$ If $\Delta V_{13} > \Delta V_{12}$

⇓



→ Corrosion between $M_1M_3 > M_1M_2$

If temp(T) > 60°C ⇒ Initially



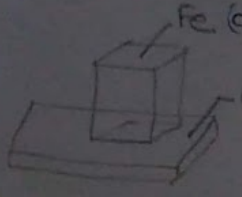
Finally

$Zn \longrightarrow ZnO$

$Fe \longrightarrow Fe^{+2}$ (Iron will corrode)

⇒ Galvanisation of Fe with Zn must be done below 60°C

(iv) Area factor:



Cu has large area	Cu has low area
⇒ many e^- are req	⇒ less e^- req.
⇒ Supply from Fe	⇒ Fe remains

⇒ Cathodic area should be small

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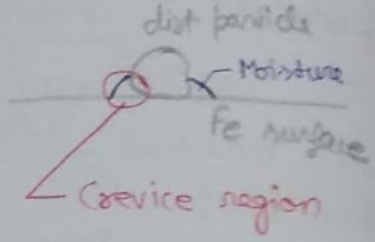
Lecture-5

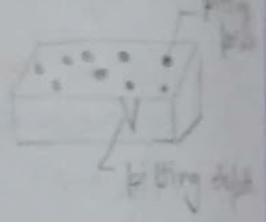
→ Crevice corrosion:



- If (i) Crevice gap is high to get water
  (ii) Water inside crevice is stagnant
  ⇓
  Corrosion is very high
- Design plays important role in crevice corrosion
- To reduce crevice attack ⇒ Clean regularly & Proper design

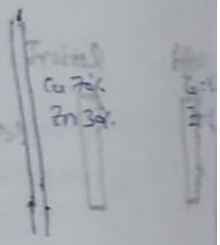
→ Pitting :

- Happens on weak/active (grain boundary, interface of alloy)
- Stagnant sol^n is req for high pitting



→ Dealloying: (Selective Bleaching)

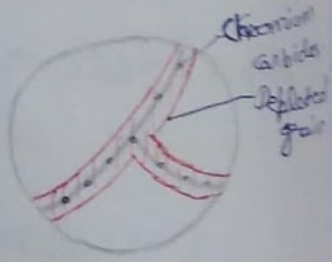
- (70%) Cu + (30%) Zn ⟶ Brass



- Ag + Zn , Zr - Pd , Zr - gold
- Good for → making porous (Nano pores) structure (very good catalyst)

→ Intergranular corrosion :-

- ex: 18:8 stainless steel (304)
  Cr Ni 0.08% C

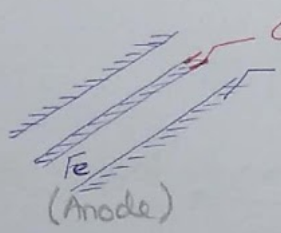


- At Temp (450°-650°C) :- $Cr_{23}C_6$ nucleus formation

$Cr_{23}C_8 \longrightarrow Cr_2O_3$ (Chromium Oxide)
due to corrosion.

- In stainless steel ⇒ Cr layer is formed at surface.
- Now at elevated temp ⇒ Near grain boundary Cr concentrates in the form of $Cr_{23}C_6$.

⇒



Cathode area is high ⇒ Fe will degrade so fast.

- How to reduce ⇒ formation of $Cr_{23}C_6$
  - Reduce C%
  - Reduce Temp. for longer time (Sensitisation)
  - Include Nb (Stabilization)

→ Erossion :-

- Hole formation at surface takes place
- Design is predominant effect.

- Erossion
  - Fretting
  - Cavitation

- Cavitation :-
  - Due to p reduction ⇒ formation of bubble
  - Due to p increase ⇒ Collapse of "
  - Shock waves are created ⇒ Metal is deformed locally.
    ⇓
    Metal become active

- Fretting :-
  - Near fish plates
  - Due to small amplitude vibration ⇒ Oxides are formed ⇒ Debris formation
  - Provide lubrication to avoid this.

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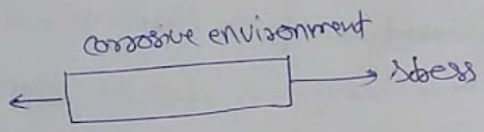
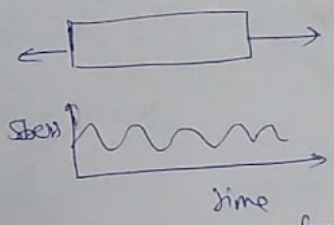
→ Stress assisted corrosion :-

(i) Stress corrosion :-



(ii) Corrosion fatigue :-



(iii) Hydrogen embrittlement :- $H + e^- \rightarrow H^+$ (very active)

(from cathode reaction)

It can react with :- $H^+ + H^+ \rightarrow H_2$

$H^+ + Ti \rightarrow$ Titanium Hydride

Hydrogen embrittlement (Blisters)

Electrochemical Nature of Corrosion

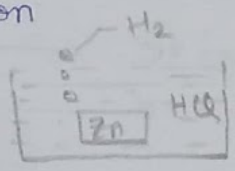
Lecture - 7

Electrochemical Nature of corrosion

→ For complete cell reaction ⇒ REDOX reaction must take place

Reduction + Oxydation

ex:- for Zn dipped in HCl solution :-



① $2H^+ + 2e \longrightarrow H_2$ (Reduction)

② $Zn - 2e \longrightarrow Zn^{+2}$ (Oxydation) ⟶ Corrosion of Zn (i.e. Oxydation of metal)

$2H^+ + Zn \longrightarrow H_2 + Zn^{+2}$

OR :- $2HCl + Zn \longrightarrow ZnCl_2 + H_2$

(1) No. of $\bar{e}$ accepted in reduction (consumption) = No. of generated $\bar{e}$ in Oxydation (Generation)

(2) Rate of reduction reaction = Rate of oxydation reaction

Consumption/time = Generation/time

⇒ Rate of reduction = Rate of Oxydation

Rate of corrosion

ex:- Zn dipped in dil HCl + $FeCl_3$ as impurity.

① $2H^+ + 2e \longrightarrow H_2$ | Reduction reaction

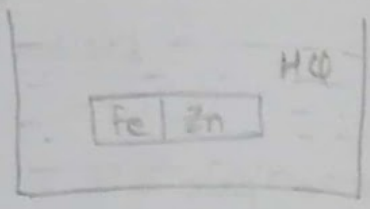
② $Fe^{+3} + e \longrightarrow Fe^{+2}$ | Reduction reaction

③ $Zn - 2e \longrightarrow Zn^{+2}$ | Oxydation reaction

Here rate of corrosion for Zn increases if —

- Include $FeCl_3$ as impurity
- Consideration of H_2 dissolvation ($O_2 + 4H^+ + 4e \longrightarrow 2H_2O$) | Reduction reaction

ex:- Fe-Zn in HCl
(Pure, No dissolved O_2)



① $2H^+ + 2e^- \longrightarrow H_2$ | Reduction

② $Fe - 2e^- \longrightarrow Fe^{+2}$
$Zn - 2e^- \longrightarrow Z^{+2}$ | Oxydation

→ Conclusion:- ① Zn dipped in HCl ⟶ 1 Red + 1 Oxydation

② Zn " " " + $FeCl_3$ inclusion ⟶ 2 Red + 1 Oxy

Highest rate of corrosion in Zn ← ③ Zn " " " + $FeCl_3$ " + dissolved O_2 ⟶ 3 Red + 1 Oxy

Lowest rate of Fe corrosion ← ④ Fe-Zn couple dipped in HCl ⟶ 1 Red + 2 Oxy

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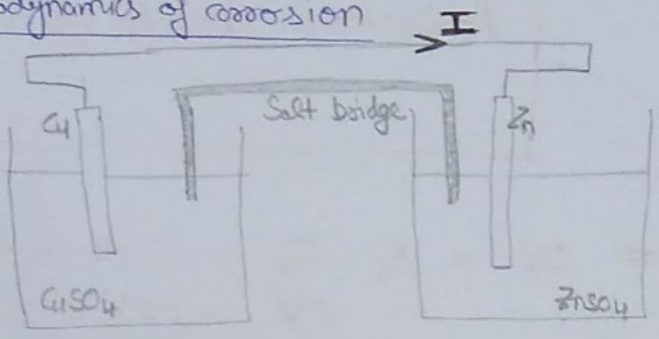
Lecture-8

Thermodynamics of corrosion

→ **Galvanic cell:-**

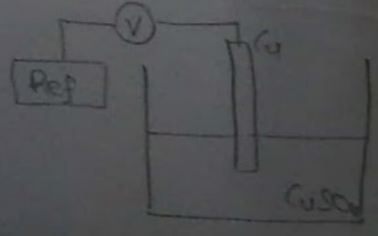
Chemical energy is used to produce electrical energy.



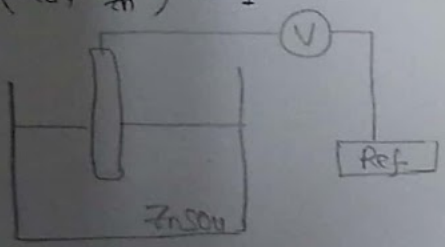
- Salt bridge – used for charge (e^-) transfer between electrolyte.
- Electrolyte – $CuSO_4$ & $ZnSO_4$
- Electrode – Cu & Zn
- If salt bridge is present ⇒ Current I will start flowing.

→ **Individual cell analysis:-**

- Reference electrode:- It is a Hydrogen electrode at 1 atm pressure & 298 K temp.
- Under such condition ⇒ Hydrogen reference electrode potential is considered Zero ($E = 4.44$ V at 45°C)
- Potential of Cu (E_1) = Voltage measured (V)
- Activity of electrolyte is assumed (a_{Cu}, a_{Zn}) = 1



- Reduction Potential
  $E_1 = 0.34$ V
- $Cu^{+2} + 2e \longrightarrow Cu$



- Reduction Potential
  $E_1 = -0.76$ V
  $Zn^{+2} + 2e \longrightarrow Zn$

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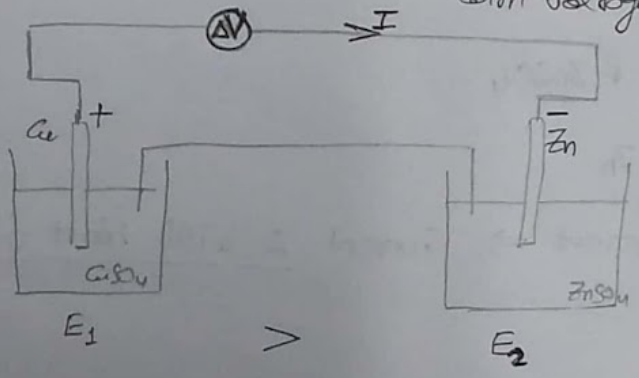
Reduction ability of Cu^{++} > Reduction ability of Zn^{+2}

$\Rightarrow \Delta V = E_1 - E_2 = 0.34 - (-0.76)$

$\Delta V = 1.1\ V$

→ Direction of current :- from Cu electrode to Zn electrode with voltage difference of ΔV



- $Cu^{+2} + 2e \rightarrow Cu$ — $Zn - 2e \rightarrow Zn^{+2}$
- Cu deposition — Zn corrosion.
  - ↓ Called cathodic protection
  - ↓ Called anodic corrosion.

→ $E_1 - E_2 = \Delta E\ (= 1.1\ V) \Rightarrow$ Can be ~~used~~ related to free energy. $(\Delta G)_{at\ 1\ atm}$

Electrical Work

Electrical energy (for moving charge) = $Q \cdot \Delta E$ (total charge, Pt diff)

• $\Rightarrow$ Electrical work = $Q \cdot \Delta E$ ——— (1)

• If 1 mole of metal ion is converted to metal –

$M^{+n} + ne \longrightarrow M$ (1 mole)

$\Rightarrow Q = nF$ ——— (2)

• Electrical work (W') = $nF\Delta E$ ——— (A)

$Q \rightarrow$ total charge for 1 mole of metal ion to metal

$n \rightarrow$ valency

$F \rightarrow$ Faraday constant

$F = 1.6 \times 10^{-19} \times 6.023 \times 10^{23}$

$\Rightarrow F = 96500$ coulombs

Gibbs free energy

• $G = H - TS$

$\Rightarrow G = U + PV - TS$

$\Rightarrow \Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - \Delta T S$ ($\Delta P = 0$, $\Delta T = 0$)

$\Rightarrow \Delta G = \Delta U + P\Delta V - T\Delta S$ ——— (1)

$U = q - W$ ($W \rightarrow$ Total work, $q \rightarrow$ Energy supplied)

$W = W' + W_{mech} (= P\Delta V)$ ($W' \rightarrow$ electrical work)

$\Rightarrow \Delta G = q - W' - P\Delta V + P\Delta V - T\Delta S$

$\Rightarrow \Delta G = q - W' - T\Delta S$

For reversible process $\Rightarrow q = T\Delta S$

$\Rightarrow \Delta G = -W'$ ——— (B)

$$\Delta G = -nFE$$

($n \rightarrow$ valency, $F (= 96500) \rightarrow$ const., $E \rightarrow$ voltage)

ΔE is replaced by E

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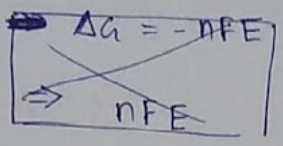
→ Other relations for E :-

(1) $\Delta G = \Delta V dp - \Delta S dT$



$$\Rightarrow \left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

Also, $\Delta G = -nFE$

$$\Rightarrow \boxed{nF\left(\frac{\partial E}{\partial T}\right)_p = \Delta S}$$

(2) $\Delta G = \Delta H - T\Delta S$

$$-nFE = \Delta H - T\, nF\left(\frac{\partial E}{\partial T}\right)_p$$

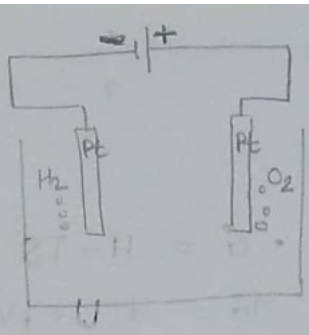
$$\Rightarrow \Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p$$

$$\Rightarrow \boxed{E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p}$$

(Now we will try to establish relation of G with reaction constant (k_p))

Water Electrolysis

Lecture-10



→ Water electrolysis :-

- Electrical energy is used to do chemical work

- $2H_2O \longrightarrow O_2 + 2H_2$
  (+ive terminal, Anode) (−ive terminal, Cathode)

- Possible reactions are -

1) $2H^+ + 2e \rightarrow H_2$
2) $2H_2O + 2e \rightarrow H_2 + 2OH^-$ → Possible if pH < 7 ⇒ Acidic
3) $O_2 + 4H^+ + 4e \rightarrow 2H_2O$ → Possible if pH > 7 ⇒ Basic (or Neutral)
4) $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

- Sign convention :-

1) Galvanic cell : Cathode (+) ← Cathodic reaction
   Anode (−)
2) Electrolysis : Cathode (−) ← Cathodic reaction
   Anode (+)

→ Chemical potential :- (μ)

- defined as - $\mu = \frac{\partial G}{\partial n_i}$

$$\mu_i = \left.\frac{\partial G}{\partial n_i}\right|_{P,T,n_j}$$

- Chemical potential of a species is → energy, that can be adsorbed or released due to change in particle no.

$$\mu_i = \left.\frac{\partial G}{\partial n_i}\right|_{p,T,n_j}$$

Derivation:- • $G = H - TS$

$$dG = d(U + pV) - d(TS)$$

$$\Rightarrow dG = dU + pdV + Vdp - TdS - SdT \quad \text{——— (1)}$$

(energy supplied)

• $dU = TdS - pdV + \sum_{i=1}^{n} \mu_i dN_i$ ——— (2)

(pdV: mechanical work; $\mu_i dN_i$: energy due to change in number particle)

(1) & (2)

$$dG = (TdS - pdV + \sum_{i=1}^{n} \mu_i dN_i) + (pdV + Vdp - TdS - SdT)$$

$$dG = Vdp - SdT + \sum_{i=1}^{n} \mu_i dN_i$$

$\Rightarrow$ {at constant p & T $\Rightarrow$ $Vdp = 0$, $SdT = 0$}

$$\Rightarrow \partial G = \mu_i \partial N_i \quad \{\text{assuming } N_j \to \text{constant}\}$$

$$\Rightarrow \boxed{\mu_i = \left.\frac{\partial G}{\partial N_i}\right|_{p,T,N_j}} \quad \text{OR}$$

$$\boxed{dG = \sum_{i=1}^{n} \mu_i dN_i} \quad (\text{at constant } p \text{ & } T)$$

At thermodynamic eqm: p & T are constant but system can exchange particle from external environment.

→ Gibbs free energy will be minimum (i.e. $dG = 0$)

$$\Rightarrow \boxed{\mu_1 dN_1 + \mu_2 dN_2 + \dots = 0} \quad (\text{for eqm})$$

We study μ because,

. if composition is fixed ⇒ Need (p, V & T) → 2 independent variables to define thermodynamic state (or eqm position)

. if composition is variable ⇒ (p, V & T) + μ is req. to define.

3 independent variables

$$G = f(p, T, n_i)$$

$$\Rightarrow dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2,\ldots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1,n_3,\ldots} dn_2 + \ldots$$

(at constant p & T)

$$\Rightarrow \boxed{dG = \sum_{n=1}^{j} \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_1,\ldots n_{i-1},n_{i+1},\ldots n_j}}$$

→ Consider eqn :- $aA + bB \longrightarrow cC + dD$

$$\Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

(c, d, a, b: mole)

$a_i = 1$ (pure component at 1 atm & 298K) [or standard chemical potential]

μ_i = chemical pot of

$$\boxed{\mu_i = \mu_i^\circ + RT \ln(a_i)}$$

a_i = Activity of component i.

$$\Rightarrow \Delta G_{p,T} = \underbrace{\left[c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ\right]}_{\Delta G^\circ} + RT\left[\ln a_C^c + \ln a_D^d - \ln a_A^a - \ln a_B^b\right]$$

$$\Delta G_{p,T} = \Delta G^\circ + RT \ln\left[\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right]$$

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$Q \rightarrow$ Reaction Quotient

$$\Rightarrow \boxed{\Delta G_{P,T} = \Delta G^\circ + RT \ln \left[\frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}\right]} \Rightarrow \boxed{\Delta G = \Delta G^\circ + RT \ln Q}$$

At eqm :- $\Delta G = 0 \Rightarrow \Delta G^\circ = -RT \ln \left[\frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}\right]$

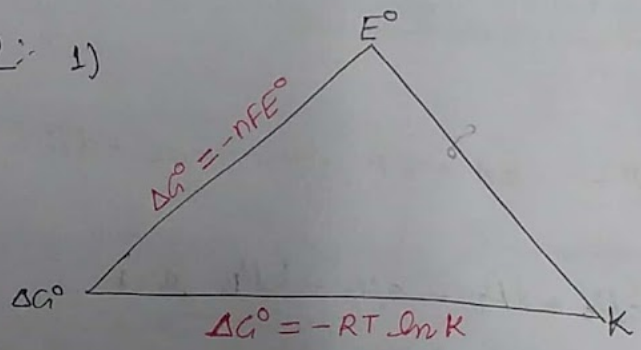
At eqm :- $Q = K$ ← Reaction eqm constant

$\Rightarrow \Delta G^\circ = -RT \ln K$

- What is standared state (or reference state) ? $\Rightarrow$ (ΔG°)

By consideration/Convention :- $\boxed{\mu^\circ_{H^+} = G^\circ_{H^+} = 0}$ at 1 atm & 298 K

→ Conclusion :- 1)



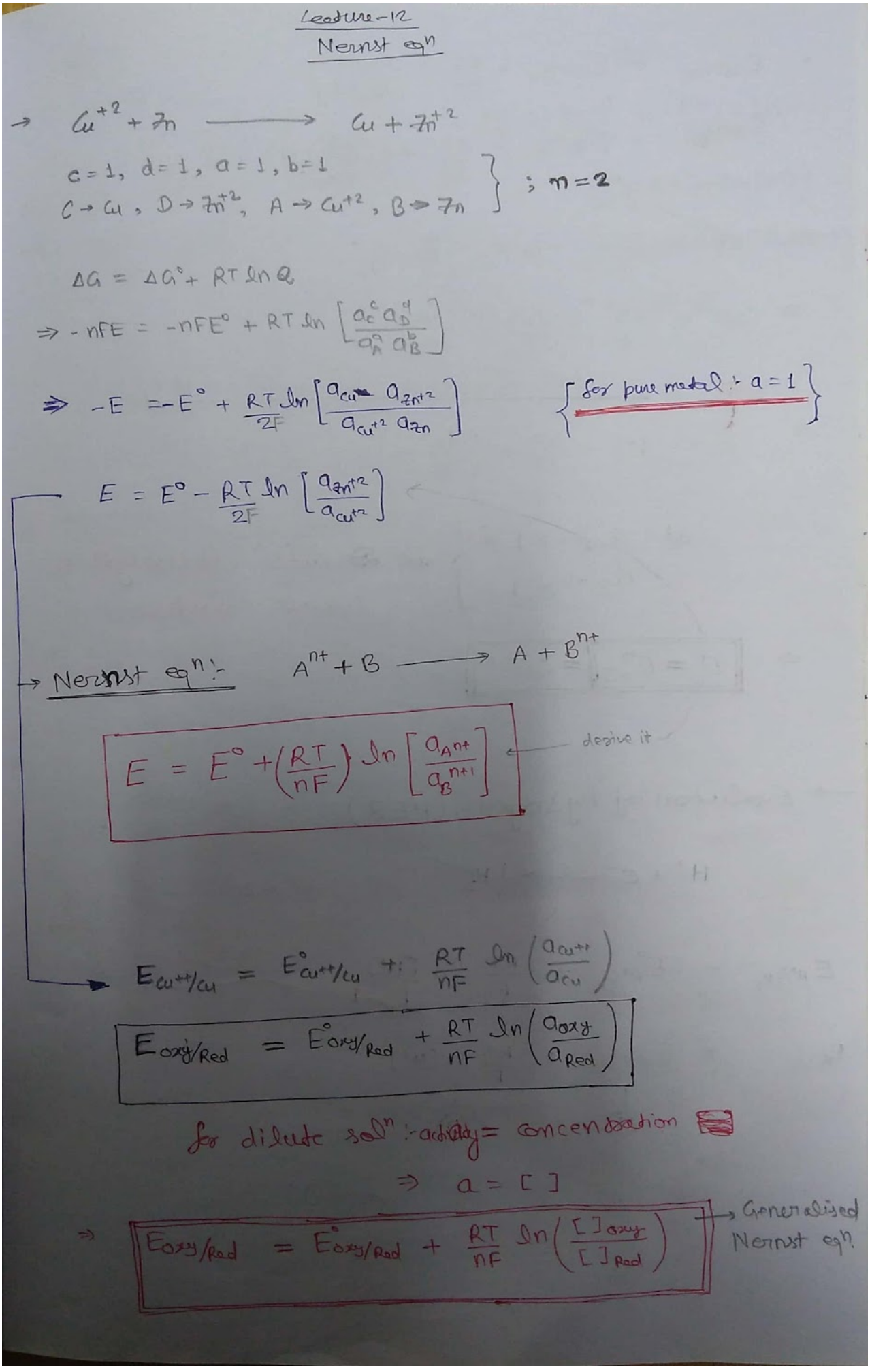
2) • These relations will be used for -

i) Where is corrosion zone
ii) " " Immune zone
iii) " " Passive zone

3)

$\Delta G = \Delta G^\circ + RT \ln Q$
$\Delta G^\circ = -RT \ln K$

Nernst Equation



- $E_{Cu^{+2}/Cu} = E^{\circ}_{Cu^{+2}/Cu} + \frac{RT}{2F} \ln\left(\frac{a_{Cu^{+2}}}{a_{Cu} \to 1}\right)$

$E_{Zn^{+2}/Zn} = E^{\circ}_{Zn^{+2}/Zn} + \frac{RT}{2F} \ln\left(\frac{a_{Zn^{+2}}}{a_{Zn} \to 1}\right)$

$\Rightarrow \quad \Delta E = E = E_{Cu^{+2}/Cu} - E_{Zn^{+2}/Zn}$

$\Rightarrow \quad \Delta E = \Delta E^{\circ}_{cell} + \frac{RT}{2F} \ln\left(\frac{a_{Cu^{+2}}}{a_{Zn^{+2}}}\right)$

$1.1\,V \; (E^{\circ}_{Cu^{+2}/Cu} = 0.34\,V \;\&\; E^{\circ}_{Zn^{+2}/Zn} = -0.76\,V)$

E_{cell}

$\Rightarrow \quad E = 1.1 + \frac{RT}{2F} \ln\left(\frac{a_{Cu^{+2}}}{a_{Zn^{+2}}}\right)$

at $a_{Cu^{+2}} = 1$ & $a_{Zn^{+2}} = 1$ } at Dilute electrolyte or Ideal solution.

$\Rightarrow \quad \boxed{E = E^{\circ}_{cell} = \Delta G^{\circ}}$

→ Evolution of Hydrogen :- (HER) :- (To find E_{cell}) :-

$H^+ + e^- \longrightarrow \frac{1}{2} H_2 \quad (\text{or} \quad 2H^+ + 2e^- \longrightarrow H_2)$

$E_{H^+/\frac{1}{2}H_2} = E^{\circ}_{H^+/\frac{1}{2}H_2} + \frac{RT}{F} \ln \frac{[H^+]}{p_{H_2} \to 1}$

$E_{H^+/\frac{1}{2}H_2} = E^{\circ}_{H^+/\frac{1}{2}H_2} + \frac{RT}{F} \ln [H^+]$

① ②

(1) ⇒

$\Delta G^\circ = \frac{1}{2}\mu^\circ_{H_2} - \mu^\circ_{H^+}$

$\mu^\circ_{H_2} = 0$, $\mu^\circ_{H^+} = 0$ (at 1 atm & 298K)

$\Delta G^\circ = 0$

but, $\Delta G^\circ = -nFE^\circ$

$\Rightarrow E^\circ = 0$

(2)

$\frac{RT}{F}\ln[H^+] = -\frac{RT}{F}(-\ln[H^+])$

$= -\frac{RT}{F} \times 2.303 (-\log[H^+])$

$= -\frac{8.314}{96500} \times 2.303 \times 298 (-\log[H^+])$

$= -0.0591\ pH$

$\Rightarrow E_{H^+/\frac{1}{2}H_2} = E^\circ_{H^+/\frac{1}{2}H_2} + \frac{RT}{F}\ln[H^+]$

$= 0 - 0.0591\ pH$

$\Rightarrow \boxed{E_{H^+/\frac{1}{2}H_2} = -0.0591\ pH}$

Leecture-13

Standared reduction pot of pure metal

→ $Ox + ne^- \longrightarrow Red$

- $\boxed{E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{nF}\ln\left(\frac{a_{ox}}{a_{Red}}\right)}$

- $\boxed{a = \gamma\ Conc}$

Activity — Activity coefficient → for dilute solution: $\gamma = 1$

$\Rightarrow \boxed{a = conc.}$

- Standard Reduction potential = $E^\circ_{ox/Red}$ (At 25°C, 1 atm & $a_{ox} = a_{Red} = 1$)

$E_{ox/Red} = E^\circ_{ox/Red}$

Reduction Potential of Pure Metal

→ Reduction potential of pure metals:

$M^{n+} + ne^- \longrightarrow M$ (↑ pure metal)

⟶ (Ex: $Ni^{+2} + 2e \longrightarrow Ni$)

- $\Delta G^\circ = \mu^\circ_{Ni} - \mu^\circ_{Ni^{+2}} = +48250 = -2FE^\circ_{Ni^{+2}/Ni}$ (given)

μ°_{Ni} (25°C, 1 atm, solid) = 0 ↑ Since Ni at these T&P is stable ⇒ $\mu^\circ = 0$ even for O_2 → if stable

$\Rightarrow E^\circ_{Ni^{+2}/Ni} = -0.25$ volt.

⟶ (Ex: $Al^{+3} + 3e \longrightarrow Al$)

- $\mu^\circ_{Al} = 0$; $\mu^\circ_{Al^{+3}} = -481200$ J/mole
- $\Delta G^\circ = 481200 = -3FE^\circ_{Al^{+3}/Al}$

$\Rightarrow E^\circ_{Al^{+3}/Al} = -1.662$ V

⟶ (Ex: $Zn^{+2} + 2e \longrightarrow Zn$; $\mu^\circ_{Zn^{+2}} = 147030$)

$E^\circ = -0.76$ V

⟶ (Ex: $Ag^+ + e \longrightarrow Ag$; $\mu^\circ_{Ag^+} = 77120$)

$E^\circ = 0.799$ V

→ Standard reduction potential series:

(Assumption: $a_{M^{n+}} = 1$, M → pure, 25°C & 1 atm)

0.799 $E^\circ_{Ag^+/Ag}$ ↑ Noble/Deposition [Cathodic] ← Accept e^-

0 $E^\circ_{H^+/\frac{1}{2}H_2}$

−0.25 $E^\circ_{Ni^{+2}/Ni}$

↓ Corrosion/Active [Anodic] ← loose e^-

−0.76 $E^\circ_{Zn^{+2}/Zn}$

Lecture-14

Basic medium :

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

$\mu^\circ_{O_2}$ (Stable)

$$\Delta G^\circ = 4\mu^\circ_{OH^-} - \mu^\circ_{O_2} + 2\mu^\circ_{H_2O} = 4(-157147.1) - 2(-236964.2)$$

$$= -154660$$

$$\Delta G^\circ = -nE^\circ F \Rightarrow E^\circ_{O_2/OH^-} = 0.401$$

$$E_{O_2/OH^-} = E^\circ_{O_2/OH^-} + \frac{RT}{nF} \ln\left(\frac{P_{O_2}^{1} \cdot a_{H_2O}^{2}}{a_{OH^-}^{4}}\right)^{1}$$

$$= 0.401 + \frac{0.0591}{4} \log\left(\frac{1}{[OH]^4}\right)$$

$$= 0.401 + 0.0591\, pOH$$

$$= 0.401 + 0.0591\,(14 - pH) \Rightarrow \boxed{E_{O_2/OH^-} = 1.228 - 0.0591\, pH}$$

Acidic Medium :-

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O$$

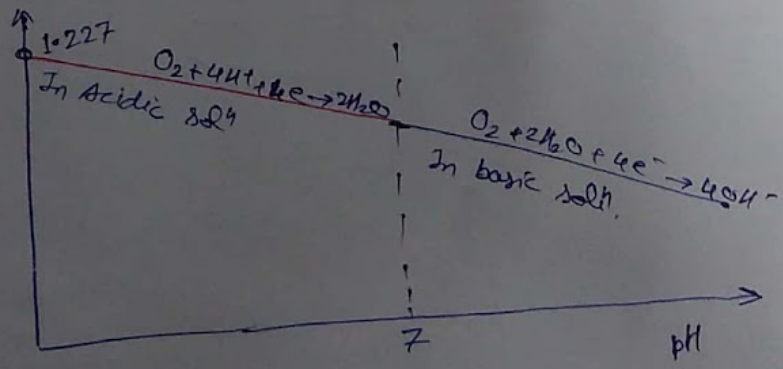
$$\boxed{E_{O_2/H_2O} = 1.227 - 0.0591\, pH}$$

-236964.2 $\quad 0$ (ref.) $\quad 4$

$$\Delta G^\circ = 2\mu^\circ_{H_2O} - \mu^\circ_{O_2} - 4\mu^\circ_{H^+} = nFE^\circ$$

$$\Rightarrow E^\circ_{O_2/H_2O} = 1.227\,V$$

$$\Rightarrow E_{O_2/H_2O} = E^\circ_{O_2/H_2O} + \frac{RT}{nF} \ln\left(\frac{a_{H_2O}^{2}}{P_{O_2}^{1} \cdot a_{H^+}^{4}}\right)^{1} \Rightarrow E_{O_2/H_2O} = 1.227 - 0.0591\, pH$$



→ In basic medium :- Other possibility is

$$2H_2O + 2e \longrightarrow H_2 + 2OH^-$$

$$\begin{cases} \mu^\circ_{H_2} = 0 \\ \mu^\circ_{OH} = -157147.1 \\ \mu^\circ_{H_2O} = 237968.2 \end{cases}$$

$$E^\circ_{2H_2O/OH^-} = -0.827\ V$$

$$E_{2H_2O/2OH^-} = -0.0591\ pH$$

→ Conclusion :-

Acidic → ① $O_2 + 4H^+ + 4e \longrightarrow 2H_2O$ $\quad E_{O_2/H_2O} = 1.23 - 0.0591\ pH$

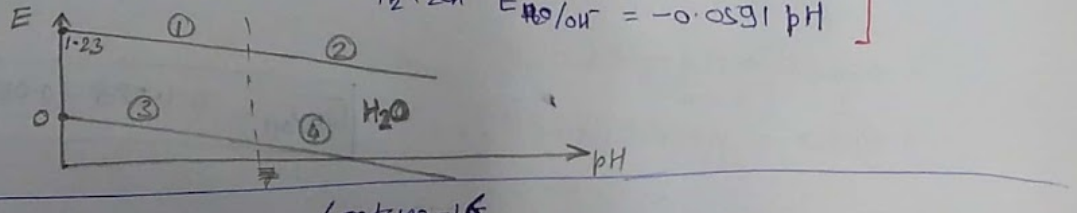
Basic → ② $O_2 + 2H_2O + 4e \longrightarrow 4OH^-$ $\quad E_{O_2/OH^-} = 1.23 - 0.0591\ pH$

} Aqueous medium, & dissolved O_2 is avail.

Acidic → ③ $2H^+ + 2e \longrightarrow H_2$ $\quad E_{2H^+/H_2} = -0.0591\ pH$

Basic → ④ $2H_2O + 2e \longrightarrow H_2 + 2OH^-$ $\quad E_{H_2O/OH^-} = -0.0591\ pH$

} Acidic/Basic medium



Lecture-16

→ • Standard reduction potential Series is → Suitable for pure Metal ($a = 1$)

• Galvanic Series is → Suitable for alloy ($a < 1$)

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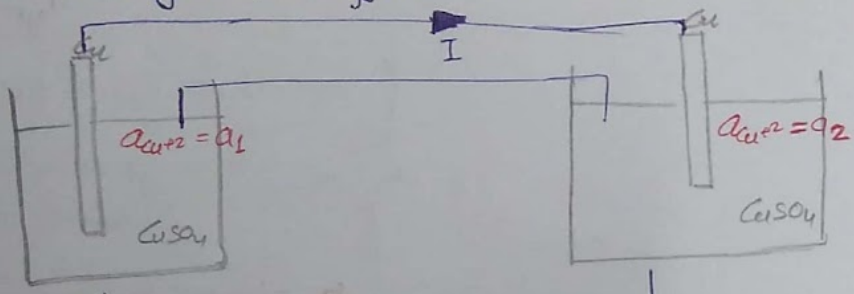
Lecture-17
Concentration cell

→ **Concentration cell :-**

- Ex:- $Cu^{+2} + 2e \longrightarrow Cu$ → $a = 1$ [explain it]

- Due to difference in conc. of Cu^{++} ⇒ activity an charge ⇒ Different $\bar{E}$ ⇒ Galvanic couple ⇒ Concentration cell



- $E^{(a_1)}_{Cu^{+2}/Cu} = E^{\circ}_{Cu^{++}/Cu} + \frac{RT}{2F} \ln a_1$ & $E^{(a_2)}_{Cu^{++}/Cu} = E^{\circ}_{Cu^{++}/Cu} + \frac{RT}{2F} \ln a_2$

Same

- (let $a_1 > a_2$) ⇒ $E^{(a_1)}_{Cu^{+2}/Cu} > E^{(a_2)}_{Cu^{+2}/Cu}$

⇒ Due to $E^{(a_1)}_{Cu^{++}/Cu} > E^{(a_2)}_{Cu^{++}/Cu}$ ⇒ Galvanic potential is generated.

⇒ Concentration cell is formed ∴ Cu deposition in cell ①.

Conclusion ⇒ Due to conc. change → Concentration cell is formed

Corrosion can occur

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Corrosion of Fe in Moisture

→ Corrosion of Fe in moisture (atmosphere) :-

- Atmosphere can be assumed to neutral in nature.

$$\Rightarrow O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

$$E_{O_2/4OH^-} = E_1 = E^\circ_{O_2/4OH^-} + \frac{RT}{4F} \ln\left(\frac{P_{O_2} \cdot a^2_{H_2O}}{a^4_{OH^-}}\right)$$

$a_{H_2O} = 1$ ← H_2O is pure.

a_{OH^-} → const (a depends on solubility only at T & P fixed)

P_{O_2} → partial P of O_2 in soln.

$$\Rightarrow E_{O_2/4OH^-} = E_1 = E^\circ_{O_2/4OH^-} + \frac{RT}{4F} \ln(P_{O_2})$$ ← since $a^{-4}_{OH^-}$

- $2Fe + O_2 + 2H_2O \longrightarrow 2Fe(OH)_2 \downarrow$

$2Fe(OH)_2 + 2OH^- \longrightarrow 2Fe(OH)_3 \downarrow$ (precipitate) ← stable

$2Fe + O_2 + 2H_2O + 2OH^- \longrightarrow 2Fe(OH)_3$

or

$2Fe - 2e \longrightarrow 2Fe^{+2}$

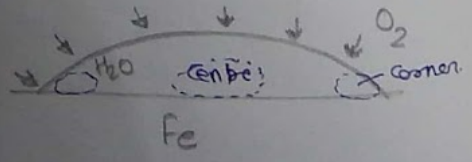
$2Fe^{+2} - 2e \longrightarrow 2Fe^{+3}$

$2Fe - 4e^- \longrightarrow 2Fe^{+3}$

$$E_{Fe/Fe^{+3}} = E_2 = E^\circ_{Fe/Fe^{+3}} + \frac{RT}{4F} \ln\left(\frac{a^2_{Fe}}{a^2_{Fe^{+3}}}\right)$$

Note, $E_1^{(P_1)} = E^\circ_{O_2/OH^-} + \frac{RT}{4F} \ln\left(P^1_{O_2}\right)$

$E_1^{(P_2)} = E^\circ_{O_2/OH^-} + \frac{RT}{4F} \ln\left(P^2_{O_2}\right)$



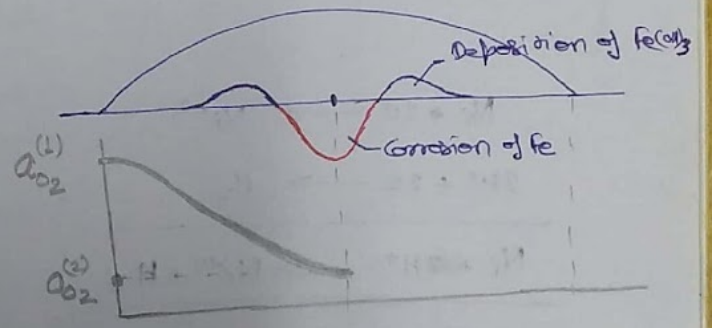
Initially:- O_2 dissolved in H_2O will contribute in reaction. As the time passes ⇒ dissolved O_2 in H_2O diminishes

At corner points O_2 from atm get dissolved in H_2O & maintains $p_{O_2}^{(1)}$.

At centre there is no availability of O_2 & $p_{O_2}^{(2)}$ decrease

⇒ After some time ⇒ $p_{O_2}^{(1)} > p_{O_2}^{(2)}$

~~Redox reaction at~~



Since, activity at corner is large now ⇒ Reaction $Fe \rightarrow Fe^{+3}$ will preferencially take place & Deposition (of $Fe(OH)_3$) will take place.

where as in central & part corrosion of Fe will take place.

It is called rain water corrosion

Lecture - 18

→ If $\Delta G < 0 \Rightarrow$ Reaction is possible (Corrosion may take place)

$\Delta G > 0 \Rightarrow$ Reaction is not feasible

Que:- Ni in deaerated water. pH = 8. Assume corrosion products are H_2 & $Ni(OH)_2$.

$K_{sp}(Ni(OH)_2) = 1.6 \times 10^{-16}$	T = 298 K
$E^{\circ}_{Ni^{+2}/Ni} = -0.25\ V$	P = 1 atm

Ans:- Suppose:- $Ni \rightarrow Ni^{+2} + 2e$ is taking place.

[Now calculate ΔG for system, If $\Delta G < 0 \Rightarrow$ Spontaneous reaction
Corrosion will take place]

$$Ni \rightarrow Ni^{+2} + 2e$$

$$2H^{+} + 2e \rightarrow H_2$$

$$Ni + 2H^{+} \rightarrow Ni^{+2} + H_2$$

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$+ Ni(OH)_2$.

pH = 8. Assume corrosion product as

$K_{sp}(Ni(OH)_2) = 1.6 \times 10^{-16}$	$T = 298K$
$E^\circ_{Ni^{+2}/Ni} = -0.25\ V$	$P = 1\ atm$

Ans:- Suppose:- $Ni \xrightarrow{-2e} Ni^{+2}$ is taking place.

Now calculate ΔG for system, If $\Delta G < 0 \Rightarrow$ Spontaneous reaction

Corrosion will take place

$$Ni \xrightarrow{-2e} Ni^{+2}$$
$$2H^+ + 2e \longrightarrow H_2$$
$$Ni + 2H^+ \longrightarrow Ni^{+2} + H_2$$

→ In Standard condition:- $\Delta G^\circ = -RT \ln K$

Case I st :-

$\Delta G^\circ < 0$
$\Rightarrow K > 1$
$E^\circ_{Ox/Red} > 0$

} forward reaction ⇒ corrosion ($Ni - ne \longrightarrow Ni^{+2}$)

Case II nd :-

$\Delta G^\circ > 0$
$K < 1$
$E^\circ_{Ox/Red} < 0$

} Less probability of forward reaction ⇒ deposition

$Ni - ne \longleftarrow Ni^{+2}$

Case III rd :-

$\Delta G^\circ = 0$
$K = 1$
$E^\circ_{Ox/Red} = 0$

} eqm ⇒ No corrosion.

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~~Lecture - 18~~ Lecture - 19

In Non Standard solution:

$\Delta G = \Delta G^\circ + RT \ln \left[\frac{a_{m^{n+}}}{a_M}\right]^{243 \leq [R2}$

$\Delta G > 0 \Rightarrow$ forward RXL is not possible

$\Delta G < 0 \Rightarrow$ Corrosion will take place.

Que:- Calculate tendency of Ni to corrode in water (pH = 8)

$T = 298^\circ K$, $P = 1$ atm. $K_{sp}(Ni(OH)_2) = 1.6 \times 10^{-16}$, $E^\circ_{Ni^{+2}/Ni} = -0.25\ V$

Ans:- If Ni corrosion is taking place :- i.e. $Ni - 2e \longrightarrow Ni^{+2}$ (E_1)

- $\left\{ \begin{array}{l} 2H^+ + 2e \longrightarrow H_2 \quad (E_2) \\ Ni + 2H^+ \longrightarrow Ni^{+2} + H_2 \end{array} \right\}$

  Ni^{+2} → it will react with OH^- to form $Ni(OH)_2$ ⟸ K_{sp} (solubility product for $Ni(OH)_2$ is low ⇒ stable compound.)

- $[H^+][OH^-] = 10^{-14} \Rightarrow [OH^-] = 10^{-6}$ ($H^+ = 10^{-8}$)

- $Ni(OH)_2 \rightleftharpoons Ni^{+2} + 2[OH^-]$

  $K_{sp} = \frac{[Ni^{+2}][OH^-]^2}{[Ni(OH)_2]} \to 1$ (precipitate) ($OH^- = 10^{-6}$)

  $\Rightarrow [Ni^{+2}] = \frac{K_{sp}}{(10^{-6})^2} = 1.6 \times 10^{-4}$

- $E_2 = E_{Ni^{+2}/Ni} = E^\circ_{Ni^{+2}/Ni} + \frac{RT}{2F} \ln \frac{[Ni^{+2}]}{[Ni] \to 1}$ ($E^\circ = -0.25$)

$E_1 = E_{Ni^{+2}/Ni} = -0.25 + \frac{0.0591}{2} \log [Ni^{+2}] = -0.25 + \frac{0.0591}{2} \log(1.6 \times 10^{-4})$

$E_1 = -0.362\ V$

$E_2 = E_{H^+/H_2} = E^\circ_{H^+/H_2} + \frac{RT}{2F} \ln \frac{[H^+]}{[H_2]} \to 1$ ($E^\circ = 0$ (Ref))

$\Rightarrow E_2 = -0.0591\ pH$

$\Rightarrow E_2 = -0.473\ V$

$\Delta E = E_2 - E_1 = -0.473 + 0.362 = -0.111\ V$

$\Delta G = -nFE = +ive \Rightarrow \Delta G = +ive \Rightarrow$ Non spontaneous reaction

$\Rightarrow$ Ni will not corrode.

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Lecture - 20

→ Pourbaix diagram :- Plot between pH Vs potential of the metal exposed to aqueous medium ($O_2, H_2O, H^+, OH^-, M^{+n}, M, H_2$)

- It is stability diagram

- For formation of Pourbaix diagram, we will consider -

1) Presence of only → $O_2, H_2O, H^+, OH^-, M, M^{+n}, M(OH)_n, M_2O_n$

(No consideration of other compounds)

- $CO_2 + H_2O \longrightarrow H_2CO_3$ ← can not be considered in pourbaix diagram

↳ No metal ⇒ Type 1 reaction

- $M^{+n} + ne^- \longrightarrow M$ ← No H^+ ⇒ Type 2 reaction

- $M + 2H_2O \longrightarrow M(OH)_2 + 2H^+ + 2e$ ← Effect of pH ⇒ Type 3 reaction

- $M^{+2} + 2H_2O \longrightarrow M(OH)_2 + 2H^+$ ← No e^- involved ⇒ Type 4 reaction

↳ E can not be defined

$$K = \frac{a^1_{M(OH)_2} \cdot a^2_{H^+}}{a_{M^{+2}} \cdot a^2_{H_2O}}$$

$$\Rightarrow \log K = -2pH - \log [M^{+2}]$$

→ These type of reaction can only be presented in Pourbaix diagram.

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2) Presence of H^+, OH^-, O_2, H_2O, H_2

$2H^+ + 2e \rightarrow H_2$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$] pH < 7

$O_2 + 2H_2O + 4e \rightarrow 4OH^-$

$H_2O + 2e \rightarrow H_2 + 2OH^-$] pH ≥ 7

- Possibility of reactions are -

(i) potential dependent + pH independent

(ii) potential dependent + pH dependent

(iii) potential independent + pH dependent

3) Thermal stability diagram → requires H.

Lecture-21

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→ Forms of corrosion :-

A) Galvanic cell corrosion :- · When two dissimilar metals are connected electrically.

· Galvanic series :- · $M \longrightarrow M^{n+} + ne^-$ $(E_{M/M+n})$

$N \longrightarrow N^{m+} + me^-$ $(E_{N/N^{+m}})$

if M corrodes :- M looses e^- & N accepts electron

↑ ↑

Anode Cathode

↑ ↑

Corrosion Deposition.

· Galvanic series is a list of corrosion potential (electrode potential)

1.498	$Au^{+3} + 3e^- \rightarrow Au$
0.799	$Ag^+ + e^- \rightarrow Ag$
0.771	$Fe^{+3} + e^- \rightarrow Fe^{+2}$
0.401	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
+.342	$Cu^{+2} + 2e^- \rightarrow Cu$
0	$2H^+ + 2e^- \rightarrow H_2$
−0.447	$Fe^{+2} + 2e \rightarrow Fe$
−0.744	$Cr^{+3} + 3e \rightarrow Cr$
−0.762	$Zn^{+2} + 2e \rightarrow Zn$
−1.662	$Al^{+3} + 3e \rightarrow Al$
−2.372	$Mg^+ + e \rightarrow Mg$
−2.71	$Na^+ + e \rightarrow Na$
−2.931	$K^+ + e \rightarrow K$

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Effects on galvanic corrosion :-

i) Area effect : large ratio of cathode to Anode is to be avoided.

ii) Effect of exchange current density :-

$\underbrace{Au-Zn}_{\Delta E_1}$ & $\underbrace{Pt-Zn}_{\Delta E_2}$ $\Rightarrow \Delta E_2 > \Delta E_1$ $\Rightarrow$ due to polarisation in the presence of Zn Pt will corrode fast.

iii) Measurement :- By — Polarization in Galvanic couples.

— Zero resistance Ammeters.

— Galvanic current by polarisation resistance

iv) Determining rate of galvanic corrosion :- Using galvanic current dia

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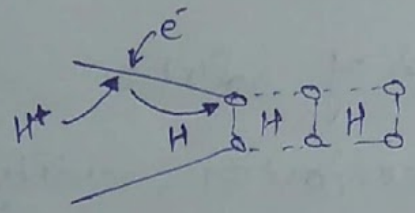
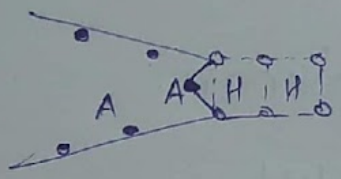
→ Mechanism of Stress assisted corrosion for Hydrogen embrittlement :-

(i) 

dissolved H atom dilate lattice & weakens atomic bonds.

(ii) 

adsorption of A further weakens crack tip bond

(iii)

Atoms migrate out of crack tip.

(iv)

Crack growth by anodic dissolution at crack tip & film rupture takes place.

(v)

Brittle crack propagates.

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Unit 1:- Intro to corrosion of materials.

- Corrosion - Def.
- Impact on economics.
- Cost of corrosion.
- Human safety
- Case studies.
- Scope of corrosion science

deo

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