Set - 1

Part-A :-

1. (c) = 0

2. $\Delta G = H - TS$ (enthalpy, Temperature (K), entropy)
   [H → 19.07 Kcal; S → 90 cal = 0.09 Kcal]
   $\therefore G = 19.07 - (293) \times (0.09)$
   $\Rightarrow G = -7.3$ kcal ∴ Option (d)

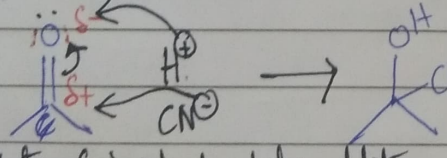
3. $PBR = \frac{V_{oxide}}{V_{metal}}$ ∴ Option (a)
   For Protective layer :- $1 \leq PBR \leq 2$
   For Non- " " :- $PBR < 1$ (or) $PBR > 2$
   ∴ PBR ranges from 1 to 2 for it to be protective

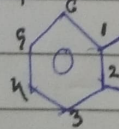
4. Electrode potential depends on :-
   1) Nature of Electrode
   2) Concentration of Ion
   3) Temperature
   4) Pressure
   5) pH of sol^n
   ∴ Option (d) Size of electrode

5. Option (d) For an endothermic process, ΔH is negative

6. Option (d) Hydrogen

7. Option (a) $Zn | ZnSO_4 || CuSO_4 | Cu$, E = 1.09 volt

8. 
   [Nucleophile → lone pairs in O, N & π-bond; Electrophile → +ve charge / δ+]
   Option (a) Nucleophilic addition

9. 
   We can have Br at Ortho, Meta, Para
   (1,2) (1,3) (1,4)
   ∴ Option (b)

10. Option (a) [Vertical → away; Horizontal → towards observer]

Part-B

11. (a) (i) Derive Helmholtz free energy:-

It is part of internal energy that is isothermally available

$$A = E - TS$$

(E: internal energy; S: entropy)

It is the energy available in system for doing useful work at constant temperature (in reversible system

$$\Rightarrow \Delta A = \Delta E - T\Delta S$$

But Change in Entropy $\Delta S = \frac{q_{rev}}{T}$ (By 2nd law)

$$\therefore \Delta A = \Delta E - q_{rev}$$

But Change in Internal Energy $\Delta E = q_{rev} - W$ (By 1st law)

(W: work done by system)

$$\therefore \Delta E = q_{rev} - W$$

$$\therefore \Delta A = q_{rev} - W - q_{rev}$$

$$\Rightarrow \Delta A = -W_{max}$$

$$\Rightarrow -\Delta A = W_{max}$$

When $\Delta A \rightarrow$ -ve Max Work done by system

When $\Delta A \rightarrow$ +ve Min Work done By system

The physical significance of Helmholtz free energy is that when free energy of system decreases, the reaction can proceed and work can be done

(*)

(ii) For Daniel cell :- $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

$(64.4\ kJ/mol)$ $(-154\ kJ/mol)$

We know, $\Delta G^\circ = G_{Zn^{2+}} - G_{Cu^{2+}}$ (Right − Left)

[ΔG° for cathode/Zn^{2+} → −ve; for anode/Cu^{2+} → +ve]

$= (-154) - (64.4)$

$\Rightarrow \Delta G^\circ = -218.4\ kJ/mol$

To find E°_{cell} :-

$\because \Delta G^\circ = -nFE^\circ_{cell}$

$\Rightarrow E^\circ_{cell} = \dfrac{\Delta G^\circ}{-nF}$ [$n = 2$, $F = 96500\ C$]

$= \dfrac{-218.4 \times 10^3\ J/mol}{2 \times 96500}$

$\Rightarrow E^\circ_{cell} = 1.13V$

(*)

11(b) (i) Potentiometric Redox titration is a technique that uses two electrodes to measure the electric potential across a solution and for determine concentration of ions in it.

It is based on the principle of redox reaction where both oxidation and reduction takes place.

This potential is measured by Nernst Equation :-

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

(oxidised form → Anode; reduced form → Cathode)

This eq^n is used for :-

1) Calculating EMF of acid-base reaction

For acidic medium :-

Standard reduction potential (E_R) = 0.242V [For Fe^{2+}]

& $-\log[H^+] = pH$ → measure of acidity of solution

$$\therefore E_{cell} = E_R - E_L$$
$$= 0.242 - \frac{0.0591}{n} \log[H^+]$$
$$\Rightarrow E_{cell} = 0.242 + \frac{0.0591}{n} pH$$

2) Predict Spontanity / Feasibility of reaction

Spontaneity of reaction can be predicted from EMF of cell reaction

For a cell :-

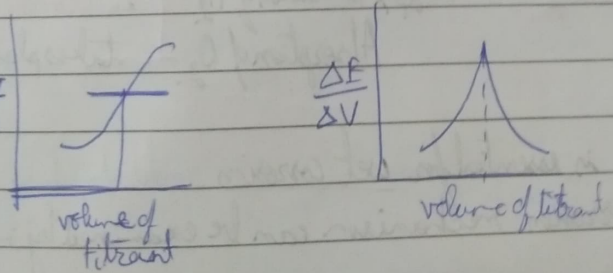
- If Emf → +ve, $\Delta G < 0$ → Reaction feasible
- If Emf → -ve, $\Delta G > 0$ → Reaction not feasible

E_1 → potential of oxidising agent
E_2 → potential of reducing agent

Then :- $\boxed{E_{cell} = \frac{E_1 + E_2}{2}}$ → For redox reaction

This formula is applicable at equivalence point (during redox titration)

Graph :-



Emf v/s Volume of titrant $\frac{\Delta E}{\Delta V}$ v/s Volume of titrant

(ii) Corrosion is any destruction / disintegration of solid metal by unwanted electromical attack by its environment starting from its surface

This leads to :-

1) Reduction of metal thickness
2) Property of metal such as ~~due~~ malibility, ductibility & conductivity is lost

Two types of Corrosion → Dry (Chemical corrosion)
→ Wet (Electrochemical corrosion)

Dry Corrosion	v/s	Wet Corrosion
• Corrosion that occurs in absence of moisture		• Corrosion that occurs in presence of electrolyte
• This is due to direct reaction of metal surface with gases (O_2, CO_2, S_2)		• This is due to electrochemical reaction that occurs between cathode & anode side
• Rate of corrosion → slower		• Rate of corrosion → faster
• Oxidation of metal with O_2 takes place		• Ox Evolution of H_2 / Absorption of O_2] in cathode side takes place

12(a) Pourbaix Diagram is essential for wet corrosion understanding. It shows us how corrosion mechanism can be examined by :-

- Temperature
- pH
- Concentration of reacting species

These diagrams can be constructed based on Nernst Equation and Solubility data for metal

By Nernst eqⁿ :-

$$\Delta E = \Delta E^\circ - \frac{0.059}{n_e} \log Q$$

For pH :- $E_{pH} = E^\circ_{H^+} + \frac{0.059}{n_e} pH \quad \left(\because pH = -\log[H^+]\right)$

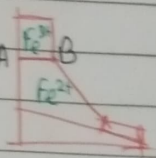
- Proton reduction :- $2H^+ + 2e^- \rightleftharpoons H_2$
- Oxygen reduction :- $2H_2O + O_2 + 4e^- \rightleftharpoons 4OH^-$

pH dependence of above 2 reactions can be expressed by Pourbaix diagram.

* In Pourbaix graph, E/V vs pH
Horizontal line → pH independent
Non-linear/slope → pH dependent

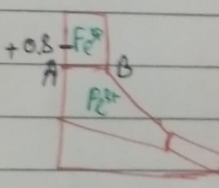
∴ For Iron (Fe) :-

1) Reduction of $Fe^{3+} \rightarrow Fe^{2+}$:-



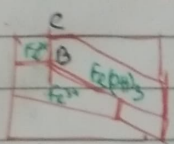
$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \quad \therefore E^\circ = +0.77V$$

This reaction does not involve H^+ ions, ∴ Its not pH dependent
∴ We have horizontal/linear line AB in the graph



This line AB → indicates pH independent
→ boundary line between Fe^{2+} & Fe^{3+}

2) Acid-base reaction between Fe^{3+} & H_2O :-



~~Hydrolysis~~ $Fe^{3+} \rightarrow Fe(OH)_3$ (Hydrolysis)

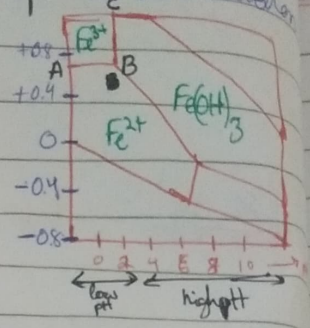
$$Fe^{3+}(aq) + 3H_2O(l) \longrightarrow Fe(OH)_3(s) + 3H^+(aq)$$

$Fe^{3+} \rightarrow +3$; $H \rightarrow 1$; $Fe \rightarrow +3$; $H \rightarrow 1$

In this reaction, there is no change in oxidation no of any element
∴ Its not Potential dependent

∴ We have vertical line CB in the graph

However, this boundary BC depends on pH as this reaction involves H^+ ions



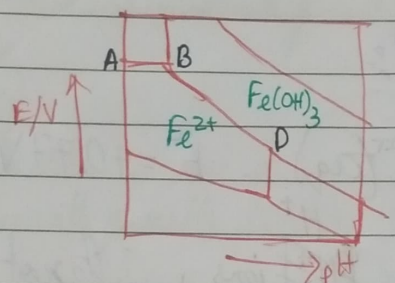
Here, Fe^{3+} → favoured by low pH
$Fe(OH)_3$ → favoured by high pH

3) Reduction of $Fe(OH)_3 \rightarrow Fe^{2+}(aq)$:-

$$Fe(OH)_3(s) + 3H^+ + e^- \rightarrow Fe^{2+}(aq) + 3H_2O(l)$$

This reaction is a combination of Redox & Acid-base reactions
This reaction involves H^+ ions, it is pH dependent

As pH increases, potential continues to drop
The sloppy line BD is the boundary line bet^n Fe^{2+} & $Fe(OH)_3$



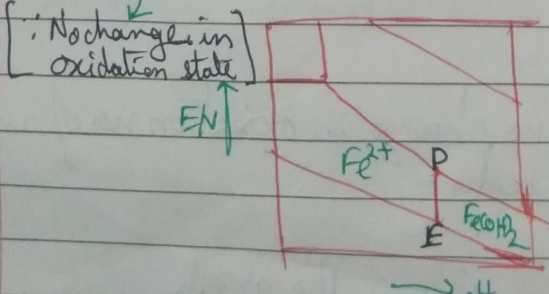
Fe^{2+} → pH independent (during $Fe^{3+} \rightarrow Fe^{2+}$)
pH dependent (during $Fe(OH)_3 \rightarrow Fe^{2+}$)

4) Hydrolysis of $Fe^{2+}(aq) \rightarrow Fe(OH)_2$:-

$$\underset{Fe\rightarrow+2}{Fe^{2+}(aq)} + 2H_2O(l) \rightarrow \underset{Fe\rightarrow+2}{Fe(OH)_2(s)} + \underset{H\rightarrow+1}{2H^+(aq)}$$

This reaction involves H^+ ions, it is pH dependent
Hydrolysis is not redox reaction It is acid-base reaction

The vertical line DE is the boundary line bet^n Fe^{2+} & $Fe(OH)_2$

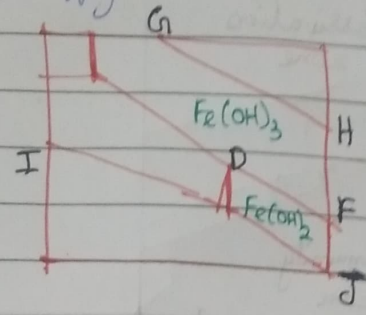


5) Reduction of $Fe(OH)_3 \rightarrow Fe(OH)_2$:

$$Fe(OH)_3(s) + H^+(aq) + e^- \rightarrow Fe(OH)_2(s) + H_2O$$

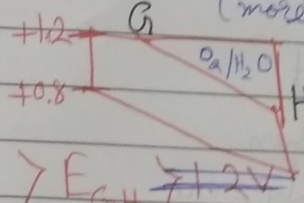
This reaction is a combination of Redox & Acid base reaction
This reaction involves H^+ ions, it is pH dependent

As pH increases, potential continues to drop
The 3rd sloppy line DF is the boundary line bet^n $Fe(OH)_3$ & $Fe(OH)_2$



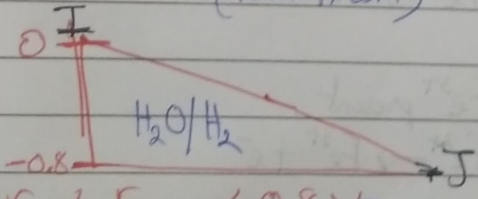
Upper GH & lower IJ
[Represents stability field of water]

Case 1 :- E value is more +ve than upper line GH
(more than)



$\therefore E > E_{GH}$ ~~+1.2V~~
Then H_2O is oxidised to O_2

Case 2 :- E value is more -ve than lower line IJ
(less than)

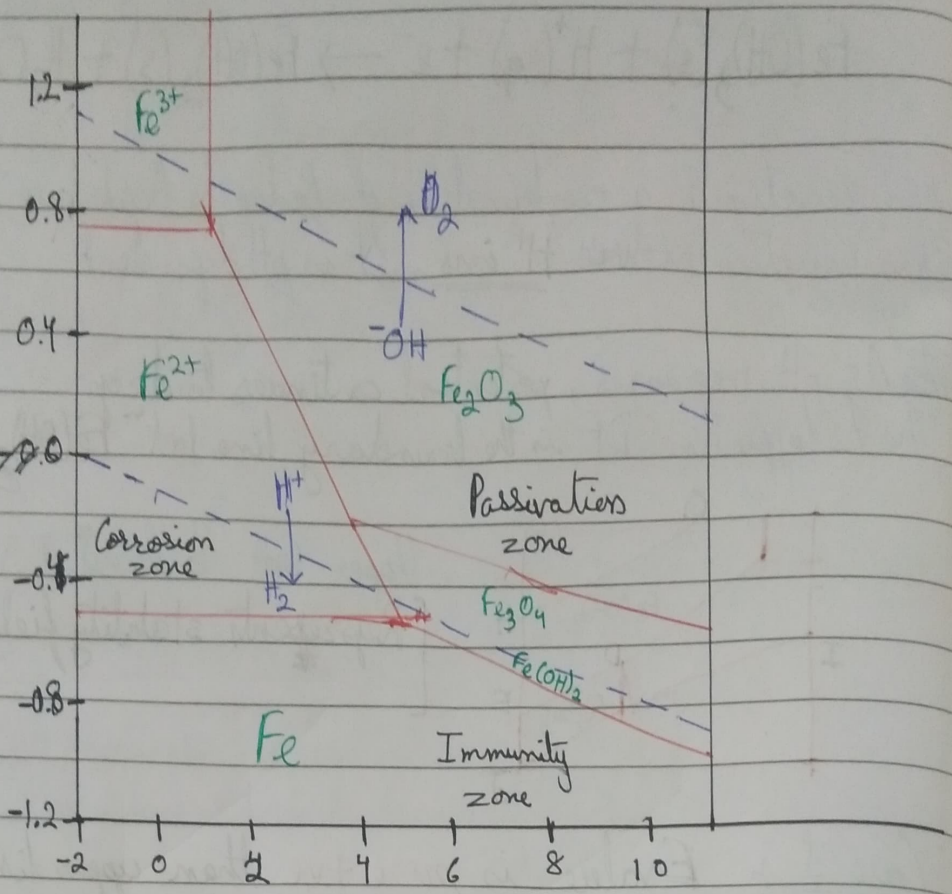


$\therefore E < E_{IJ}$ ~~-0.8V~~
Then H_2O is reduced to H_2

Hence :- All redox reactions in water fall within Stability field of H_2O

In this field, no species can oxidise/reduce H_2O

Overall graph :-



- **Fe zone :-**
  - Fe present
  - No corrosion
  - Immunity zone
- **Fe^{2+} zone :-**
  - Fe^{2+} present
  - Corrosion zone
  - $Fe \longrightarrow Fe^{2+} + 2e^-$
- **Fe^{3+} zone :-**
  - Fe^{3+} present
  - $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
- **$Fe(OH)_2$ zone :-**
  - Passivation zone
  - Green rust is unstable
  - Corrosion ppt produced at oxygen environment.

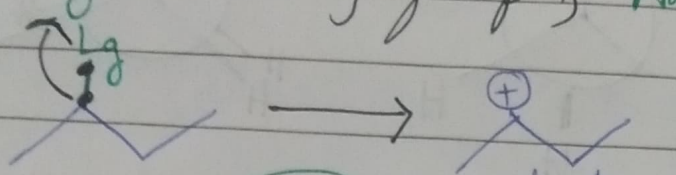
12) (i) S_N1 mechanism :-

S_N1 → Unimolecular Nucleophilic substitution

↓ 1 molecule at a time ↓ proton loving

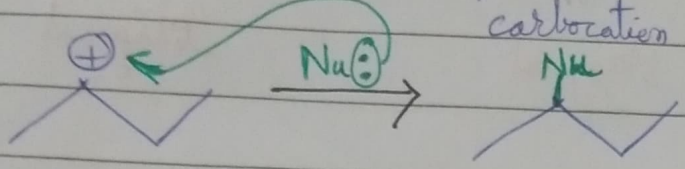
Let Lg → leaving group, Nu: → nuchophile

Mechanism :- ①



→ Rate determining step

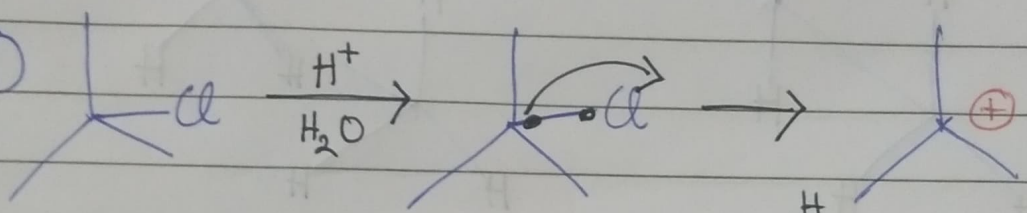
②



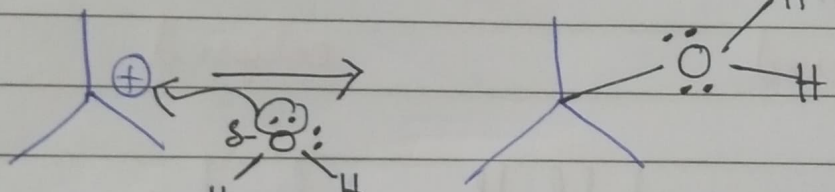
∴ Lg → good leaving group

Nu: → weak nuchophile

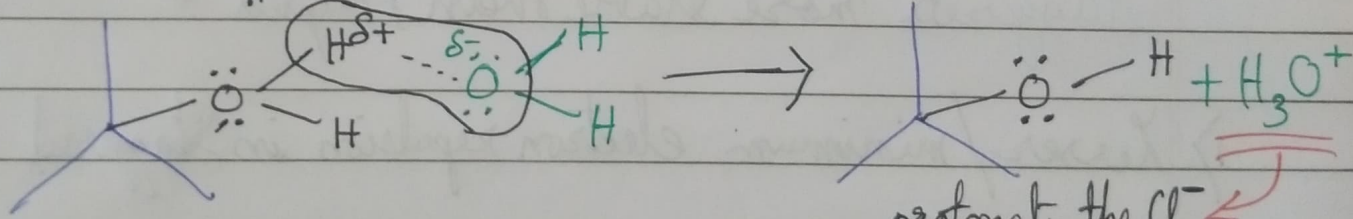
Eg :- ①



②



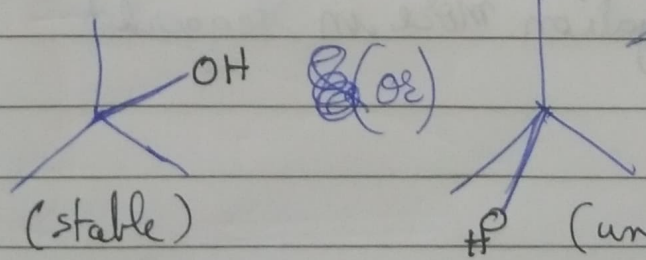
③



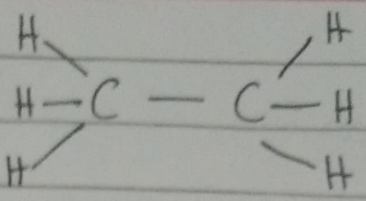
protonates the Cl^-

~~H_3O^+~~

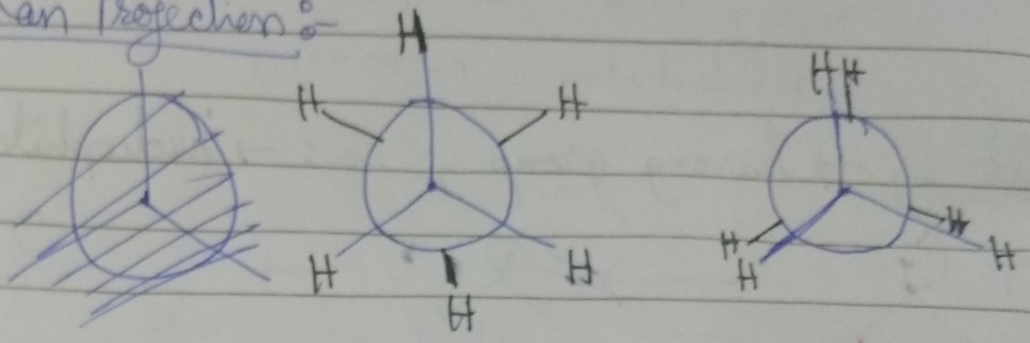
Product :-



(ii) Ethane : C_2H_6 ⇒

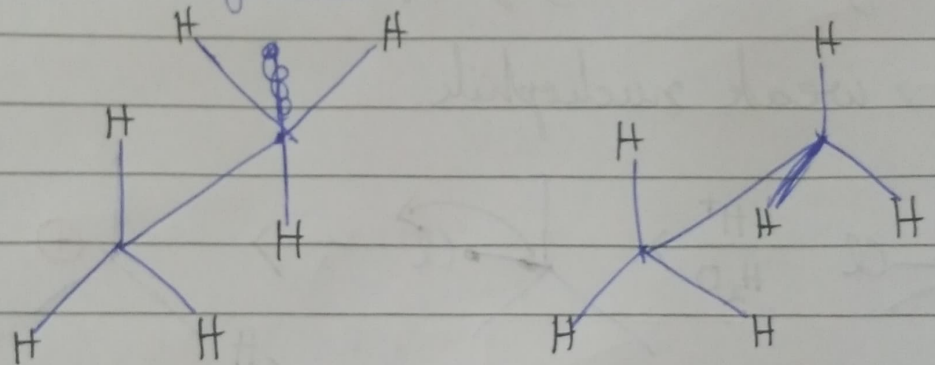


Newman Projection :-



staggered eclipsed

Sawhorse Projection :-



staggered eclipsed

Staggered more stable than Eclipsed :-

1) Lesser / minimum electron repulsion in Staggered

2) Hyperconjugation more in Staggered