

1A. Consider the redox equilibrium between ferrocenium ( $\text{Fc}^+$ ) and ferrocene ( $\text{Fc}$ ) for a one-electron reduction process. Using the Nernst equation, explain how the electrode potential depends on the ratio  $[\text{Fc}^+]/[\text{Fc}]$ . What conditions lead to the formal potential  $E^\circ$ ? (4+1=5 Marks)



Nernst Equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]}$$

$$= E^\circ - \frac{RT}{nF} \ln \frac{[\text{Fc}]}{[\text{Fc}^{\oplus}]}$$

→ If  $[\text{Fc}^+] > [\text{Fc}] \Rightarrow \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]} > 1 \Rightarrow \ln \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]} \rightarrow \text{increase}$

⇒ making  $E_{\text{cell}}$  more positive

→ On the other hand, if  $[\text{Fc}] > [\text{Fc}^{\oplus}] \Rightarrow \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]} < 1$

⇒  $\ln \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]}$  decreases ⇒ making  $E_{\text{cell}}$  less positive

# When,  $[\text{Fc}] = [\text{Fc}^{\oplus}]$  i.e., at equilibrium,

$$\ln \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]} = \ln 1 = 0$$

$$\therefore E = E^\circ_{\text{Fc}^+/\text{Fc}} \text{ (Formal potential)}$$

1B. Consider the  $\text{Fc}^+/\text{Fc}$  redox couple with a formal potential,  $E^\circ = 0.400 \text{ V vs. Ag/AgCl}$ . Using the Nernst equation, calculate the electrode potential when:  $[\text{Fc}^+] = 5.0 \times 10^{-4} \text{ M}$ ,  $[\text{Fc}] = 1.0 \times 10^{-3} \text{ M}$  (5 Marks)

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]}$$

$$= E^\circ + 2.3026 \frac{RT}{nF} \log_{10} \frac{[\text{Fc}^{\oplus}]}{[\text{Fc}]}$$

Now,  $E^\circ = 0.4 \text{ V vs Ag/AgCl}$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T = 298 \text{ K}$$

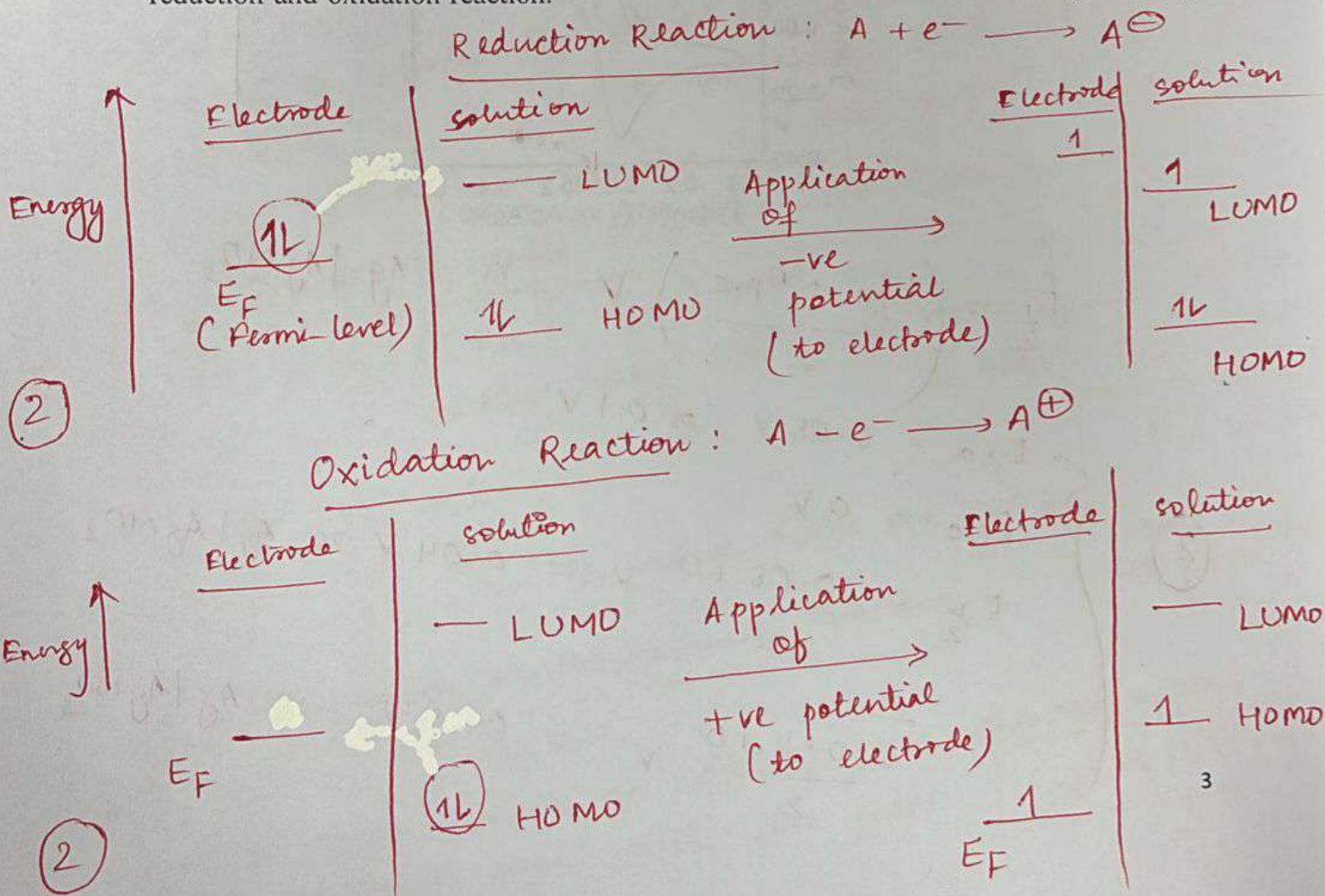
$$n = 1$$

$$F = 96485.33 \text{ C/mol}$$



$$\begin{aligned}
 \therefore E &= 0.4 \text{ (V)} + 0.0591 \text{ (V)} \log \left( \frac{5 \times 10^{-4} \text{ M}}{1 \times 10^{-3} \text{ M}} \right) \\
 &= 0.4 \text{ (V)} + 0.0591 \text{ (V)} \log (5 \times 10^{-1}) \\
 &= 0.4 \text{ (V)} + 0.0591 \text{ (V)} (-0.301) \\
 &= 0.4 \text{ (V)} + (-0.0178 \text{ V}) \\
 &= 0.3822 \text{ V vs Ag/AgCl} \\
 &\approx 0.4 \text{ V vs Ag/AgCl}
 \end{aligned}$$

2A. Draw and explain the energy profile of a working electrode for an electrochemical reduction and oxidation reaction. (6 Marks)



∴ If Fermi level ( $E_f$ ) is above redox state  
⇒ reduction occurs.

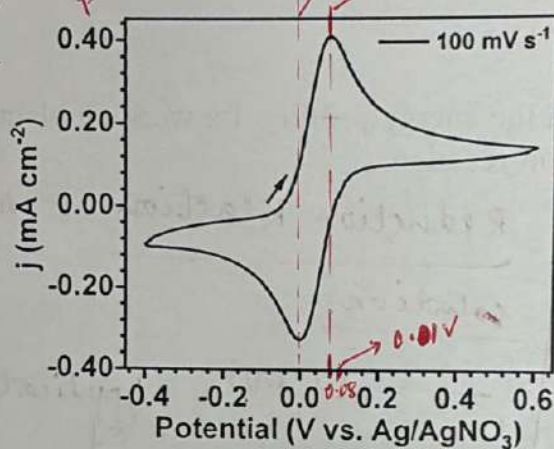
If  $E_f$  is below the redox state  
⇒ oxidation occurs.

② {  
⇒ If potential is made more -ve ⇒ raises  $E_f$   
⇒ promotes reduction.  
⇒ If potential is made more +ve ⇒ lowers  $E_f$   
⇒ promotes oxidation.



2B. The following is a cyclic voltammogram of ferrocene recorded in acetonitrile solution using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Glassy carbon (GC), Ag/AgNO<sub>3</sub>, and Pt wire were used as working, reference, and counter electrodes, respectively. Show the oxidation, reduction peaks associated with the redox processes, and half-wave redox values ( $E_{1/2}$ ) with units. One can use a ruler to find the peak position.

( $E_{p,c}$ : reduction potential)  $\leftarrow$  0.0 V  $\leftarrow$  0.08 V ( $E_{p,a}$ : oxidation potential) (4 Marks)



$$E_{1/2} = \left( \frac{E_{p,a} + E_{p,c}}{2} \right) \text{ V } \quad \text{vs } \text{Ag} | \text{AgNO}_3$$

$$E_{p,a} = 0.08 \text{ V } \quad \underline{\underline{0.1 \text{ V}}}$$

$$E_{p,c} = 0 \text{ V}$$

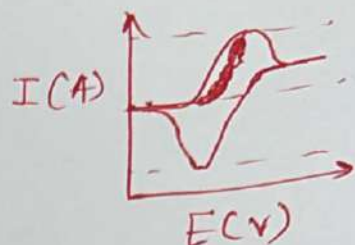
$$E_{1/2} = \frac{0.08 + 0}{2} \text{ V} = 0.04 \text{ V } \quad \text{vs } \text{Ag} | \text{AgNO}_3$$

$$\text{or} \quad E_{1/2} = \frac{0.1 + 0}{2} \text{ V} = 0.05 \text{ V } \quad \text{vs } \text{Ag} | \text{AgNO}_3$$

3A. Write three conditions for each of an electrochemical reaction: (i) reversible, (ii) quasi-reversible, and (iii) irreversible processes. (6 Marks)

(i) Reversible Electrochemical Reaction

a)  $\Delta E_p = (E_{p,a} - E_{p,c}) = 59 \text{ mV}/z$   
(at 298K) (peak-to-peak separation)



(2) b)  $\frac{I_{p,a}}{I_{p,c}} \approx 1$  for all scan rates

c) ~~Area~~ Area under the curve for  $I_{p,a} \approx I_{p,c}$

d) Peak position should not change with scan rates.

e)  $I_{p,a} \propto \sqrt{v} \Rightarrow I_{p,a} = \text{const.} \times \sqrt{v}$

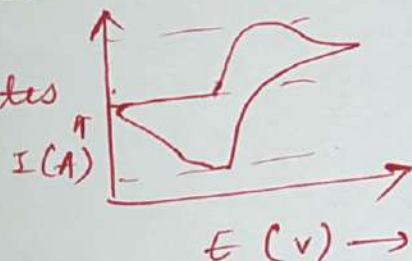
(ii) Quasi-Reversible Electrochemical Reaction

a)  $\Delta E_p = (E_{p,a} - E_{p,c}) > 59 \text{ mV}$

(2) b) Peak position vary with scan rates

c)  $\frac{I_{p,a}}{I_{p,c}} \neq 1$

d) area under the curve peaks are not equal



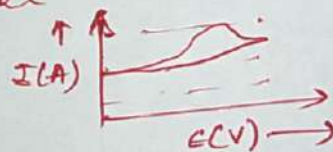
(iii) Irreversible Electrochemical Reaction

a)  $\Delta E_p \gg 59 \text{ mV}$

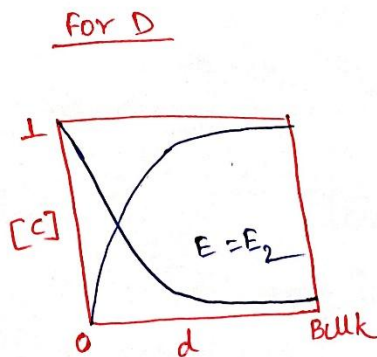
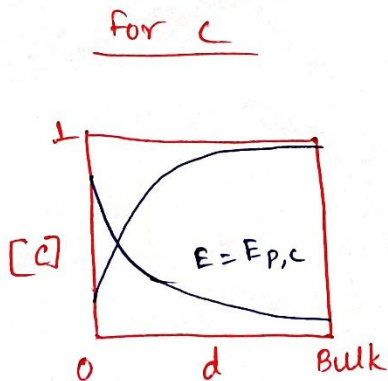
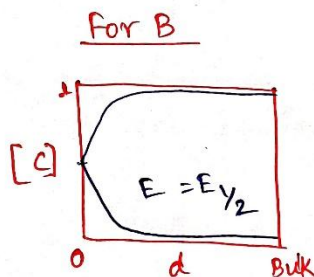
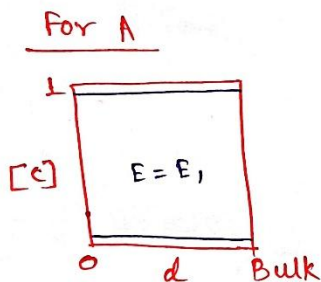
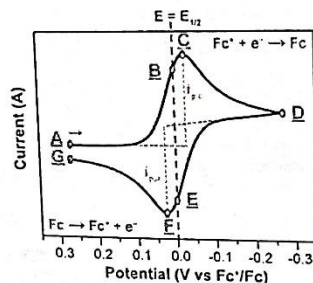
b) Either anodic or cathodic peak

c) signal varies with scan rates.

does not appear  
 $I_{p,a} \propto \sqrt{v}$



3B. Sketch the concentration profiles with proper labelling for the electrochemical reduction of  $\text{Fc}^+$  to  $\text{Fc}$  as a function of the distance from the working electrode surface to the bulk at points A to D during the voltammogram. (4 Marks)



(For each labelled diagram 1 marks will be given)



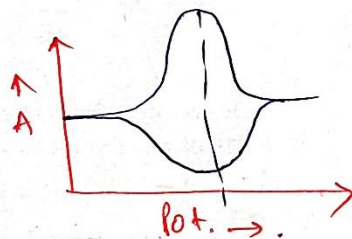
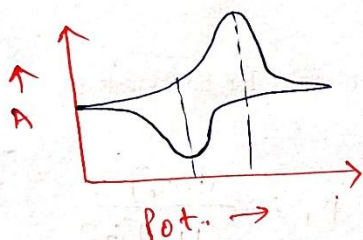
4A. How do you distinguish freely diffusing redox species vs. redox species adsorbed on the electrode surface from the cyclic voltammograms? Write some features for both. (4 Marks)

1) i)  $i \propto \omega^{1/2}$ , for freely diffusing redox species

ii)  $\Delta E_p = 59.1 \text{ mV} (n=1)$

2) i)  $i \propto \omega$ , adsorbed one

ii)  $\Delta E_p \approx 0 \text{ V}$



(For each features 1 marks)

4B. Explain why  $\text{Ni}[(\text{en})_2]^{2+}$  (en = ethylenediamine) complex is more stable than  $\text{Ni}[(\text{NH}_3)_6]^{2+}$  complexes. (6 Marks)

For (en), chelation, driven by entropy

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

So, for  $[\text{Ni}(\text{en})_3]^{2+}$ ,  $\Delta S$  will be more

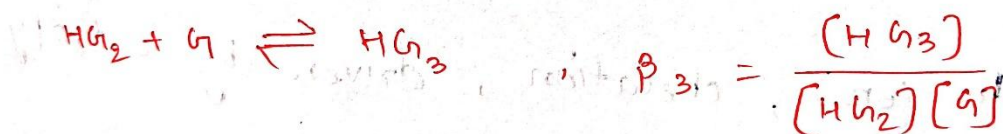
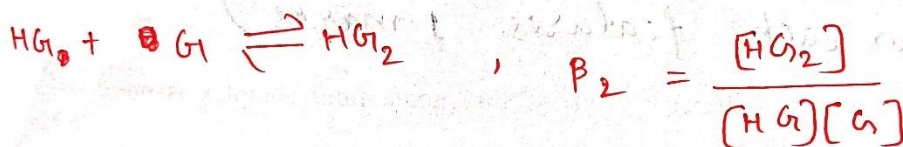
So,  ~~$\Delta S$  more~~ ve'  ~~$\Delta G$~~

$\Delta S \uparrow$ ,  $\Delta G = \text{more negative}$

Spontaneous reaction, more stable

5A. Derive stepwise and overall binding constants for host-guest (up to 3 guests) interactions and show their relationship. (6 Marks)

Stepwise :-



Overall :-



Hence by equating the above equation

$$\boxed{\beta = \beta_1 \times \beta_2 \times \beta_3}$$

2 marks { This is the relationship of overall and stepwise binding constant for host-guest.



5B. Explain the relation between Gibbs free energy and binding constant with a few examples. (4 mark)

3  
marks

$\Delta G = -RT \ln K$ , This is the relation between binding constant and Gibbs free energy.

Here,

$\Delta G$  = Gibbs free energy

$R$  = Ideal gas constant,  $8.314 \text{ J/(mol}\cdot\text{K)}$

$T$  = Temperature (K)

$K$  = Binding constant.

1  
marks

for example :-

if  $K = 10^3$ ,  $\Delta G = -RT \ln(10^3)$

$K = 10^5$ ,  $\Delta G = -RT \ln(10^5)$