M.Sc (Chemistry)

ELECTRODE KINETICS – ELECTRODICS-II

LECTURE NOTES

MULTI STEP MULTI-ELECTRON REACTION (Complex)

The Multi Step Multi-Electron Reaction is termed complex in the sense the rate determining step (RDS) itself can be a multi-step reaction occurring in υ number of times, known as stoichiometric number.

This reaction scheme differs only in the RDS step

Consider a multi electron reaction, **A + ne → Z** occurring as follows:

$$A + e \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \quad \text{Step-}\mathbf{1}$$

$$B + e \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C \quad \text{Step-2}$$

$$\mathbf{P + e \rightleftharpoons R \quad Step\text{-}\vec{\gamma}}$$

Number of steps **BEFORE** rds = $\vec{\gamma}$

$$\upsilon(R + re \underset{k_S}{\overset{k_R}{\rightleftharpoons}} S)$$ **RDS** repeated **υ** (stoichiometric number) times with **r** electron(s) each time

NB- ***r*** *Electrons in the rds step will be added in* ***r*** *ways totaling to* ***rυ*** *steps with* ***rυ electrons***

$$\mathbf{S + e^- \rightleftharpoons T \quad Step: \overleftarrow{\gamma} = (n - \vec{\gamma} - r\upsilon)}$$

$$Y + e \overset{K_n}{\rightleftharpoons} Z \quad \text{Step: } \mathbf{n}$$

Number of steps **AFTER** rds = $\overleftarrow{\gamma}$

Note: *Even in a multi-step reaction, a step will occur with the addition only one electron in each step.*

$\overrightarrow{\gamma}e + rve + \overleftarrow{\gamma}e = ne$; so that $\overrightarrow{\gamma} + rv + \overleftarrow{\gamma} = n$

Applying law of mass of action to the equilibrium steps

$\overrightarrow{i} = \overleftarrow{i} = i_o$ (for all equilibrium steps) = nF υ = nF{k.conc}

NB: $k = (k_bT/h)\exp(-\Delta G^*/RT)$

$\Delta G^* = \Delta G^*_c + \Delta G^*_{ec}$

Where, $\Delta G^*_{ec} = (1-\beta)F\Delta\phi$ **or** $(-\beta)F\Delta\phi$

So that the term with ΔG^*_c is taken as the chemical reaction rate constants ($k_1, k_{-1}, k_2, k_{-2}, \ldots$.)

i.e., $nF\overrightarrow{\upsilon} = nF\overleftarrow{\upsilon}$ (for all equilibrium steps)

Let (1-β) and β be the symmetry factors of the anodic and cathodic steps respectively

$Fk_1C_Ae^{-\beta F\Delta\phi / RT} = Fk_{-1}C_Be^{(1-\beta)F\Delta\phi / RT}$ for the first equilibrium step

$C_B = K_1C_A\, e^{-F\Delta\phi / RT}$

$C_C = K_2C_Be^{-F\Delta\phi / RT} = K_1K_2C_Ae^{-2F\Delta\phi / RT}$ **(2nd step of the reaction)**

III[ly]

$C_D = K_1K_2K_3C_Ae^{-3F\Delta\phi / RT}$ (3rd step of the reaction)

Hence, coming to the step before rds

$$C^{\upsilon}_R = \prod_{i=1}^{\overrightarrow{\gamma}} K_i\, C_A\, e^{-\overrightarrow{\gamma} F\Delta\phi / RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

***NB**-R Builds up **υ** number of times and appears **υ** number of times for rds to occur*

$$\text{Hence, } C_R = \left\{\prod_{i=1}^{\overrightarrow{\gamma}} K_iC_A\right\}^{1/\upsilon} e^{-(\overrightarrow{\gamma}/\upsilon)F\Delta\phi / RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 2$$

The forward electrochemical rate of rds is given by its forward current, $\overrightarrow{i}_R$

$$\overrightarrow{i}_R = F\overrightarrow{k}_R\, C_R\, e^{-r\beta F\Delta\phi / RT}$$

{Note the appearance of r in the RDS current as no of electrons in the rds.The exponential term is free energy which is extensive depending on the number of electrons, r}

Substituting for C_R as from eq-2

$$\overrightarrow{i}_R = Fk_R \left[\prod_{i=1}^{\overrightarrow{\gamma}} K_i C_A \right]^{1/\upsilon} e^{-(\overrightarrow{\gamma}/\upsilon) F\Delta\phi/RT} \; e^{-r\beta F\Delta\phi/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3}$$

Replacing $\Delta\phi$ by $(\Delta\phi_e + \eta)$ we get

$$\overrightarrow{i}_R = i_0 \exp\{-(\overrightarrow{\gamma}/\upsilon + r\beta)F\eta/RT\} \qquad \text{“For the forward step of rds”} \ldots\ldots\ldots\ldots\ldots \mathbf{4}$$

The same reasoning can be applied to all the backward reactions of the equilibrium steps from the last (n^{th}) step back to the reverse step of **RDS** **viz.,** S → R + re which occurs υ times(Z to S).

So that

$$C_S = \left[\prod_{i=n}^{\overleftarrow{\gamma} = (n - \overrightarrow{\gamma} - r\upsilon)} K_i \quad C_Z \right]^{1/\upsilon} e^{(\overleftarrow{\gamma}/\upsilon)F\Delta\phi/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{5} \quad \text{(Similar to eq-2 above)}$$

*N.B-“**S** has to appear **υ number** of times for rds as mentioned above”*

The reverse electrochemical rate of rds is given by, $\overleftarrow{i}_S$

$$\overleftarrow{i}_S = F k_s C_S e^{r(1-\beta)F\Delta\phi/RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{6}$$

(For the anodic process, symmetric factor is (1-β) ,the free energy term is taken as positive and gets multiplied by r as it is an extensive quantity)

Substituting for C_s as above

$$\overleftarrow{i}_S = Fk_s \left[\prod_{i=n}^{\overleftarrow{\gamma} = n - \overrightarrow{\gamma} - r\upsilon} K_i \; C_Z \right]^{1/\upsilon} e^{(\overleftarrow{\gamma}/\upsilon) F\Delta\phi/RT} \quad e^{r(1-\beta)F\Delta\phi/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{7}$$

Replacing $\Delta\phi$ by $(\Delta\phi_e + \eta)$ we get

$\overleftarrow{i}_s = i_o \exp\{[(\overleftarrow{\gamma}/\upsilon)+ r\text{-}r\beta]\, F\eta/RT\}$ ***"For the reverse step of* RDS"** **……………………….8**

The net reaction rate= Rate of rds = The net current at rds , i_{rds}

$$i = i_{rds} = \overleftarrow{i}_S - \overrightarrow{i}_R$$

$$= i_o\{\exp\{[(\overleftarrow{\gamma}/\upsilon)+ r\text{-}r\beta)]F\eta/RT\} - \exp\{-[\overrightarrow{\gamma}/\upsilon + r\beta]F\eta/RT\}$$

$$\mathbf{i = i_o[e^{\overleftarrow{\alpha}F\,\eta/RT} - e^{-\overrightarrow{\alpha}\,F\,\eta/RT}]} \qquad \text{………………………..9}$$

Where $\overleftarrow{\alpha} = (\overleftarrow{\gamma}/\upsilon) + r\text{-}\,r\beta = [(n\text{-}\overrightarrow{\gamma}\text{-}r\upsilon)/\upsilon] + r\text{-}r\beta = [(n\text{-}\overrightarrow{\gamma})/\upsilon]\text{-}r\beta$

$\overrightarrow{\alpha} = (\overrightarrow{\gamma}/\upsilon) + r\beta$

So that $\overleftarrow{\alpha} + \overrightarrow{\alpha} = \mathbf{n/\upsilon}$ ………………………..10

The parameters in eq-9 $\overleftarrow{\alpha}$ & $\overrightarrow{\alpha}$ are the coefficients of "$F\eta/RT$" in the Butler Volmer equation and are called ***transfer coefficients***. The transfer coefficients, similar to symmetry factor, are the slopes of log i vs η (Tafel slope) – useful in the determination on mechanism of reaction.

$$\mathbf{i = i_o[e^{\overleftarrow{\alpha}F\,\eta/RT} - e^{-\overrightarrow{\alpha}\,F\,\eta/RT}]}$$

NB:- ***For an elementary multistep reaction,***

$$i = i_o\{\exp\{[(\overleftarrow{\gamma} + 1\text{-}\beta]F\eta/RT\} - \exp\{-[(\overrightarrow{\gamma} + \beta]F\eta/RT\}$$

For an complex multistep reaction,

$$i = i_o\{\exp\{[(\overleftarrow{\gamma}/v)+ r\text{-}r\beta]F\eta/RT\} - \exp\{-[(\overrightarrow{\gamma}/v) + r\beta]F\eta/RT\}$$

- *i.e.,in the case of complex multistep reaction, the γ terms get divided by v and the symmetry terms get multiplied by r.*

HFA

$\ln i = \ln i_o + \overleftarrow{\alpha}F\eta/RT$ "at high + ve η" **Anodic** behavior ***Tafel equation***

$\ln i = \ln i_o - \overrightarrow{\alpha}F\eta/RT$ "at high – ve η" **Cathodic** behavior ***Tafel equation***

Hence, plot of "ln i vs η" should give $\overleftarrow{\alpha}$ and $\overrightarrow{\alpha}$ from slope and i_o from the intercept.

The above **General Butler Volmer** equation for a multi-electron process (both category) get reduced to simple **Butler Volmer** for a one electron single step process as

$$\mathbf{i = i_o(e^{(1-\beta) F\eta/RT} - e^{-\beta F\eta/RT})}$$

For n = 1(one electron reaction); Number electrons in rds , r = 1; υ = 1 rds occurs once with one electron . No steps before and after rds i.e., $\overrightarrow{\gamma} = 0$, $\overleftarrow{\gamma} = 0$.

Where $\overleftarrow{\alpha} = [(n-\overrightarrow{\gamma}) / \upsilon] - r\beta = (1-\beta)$

$\overrightarrow{\alpha} = (\overrightarrow{\gamma} / \upsilon) + r\beta = \beta$

The sum of the transfer coefficients, $\overleftarrow{\alpha} + \overrightarrow{\alpha}$, will be greater than or equal to one (The number of times rds that occurs will be less than the total number of electrons added in the reaction i.e., $\upsilon < n$)

$\mathbf{\overleftarrow{\alpha} + \overrightarrow{\alpha} = n/\upsilon > 1}$

But, the sum of the ***symmetry factor*** will always be equal to one: $(1-\beta) + \beta = 1$