

M.Sc (Chemistry)

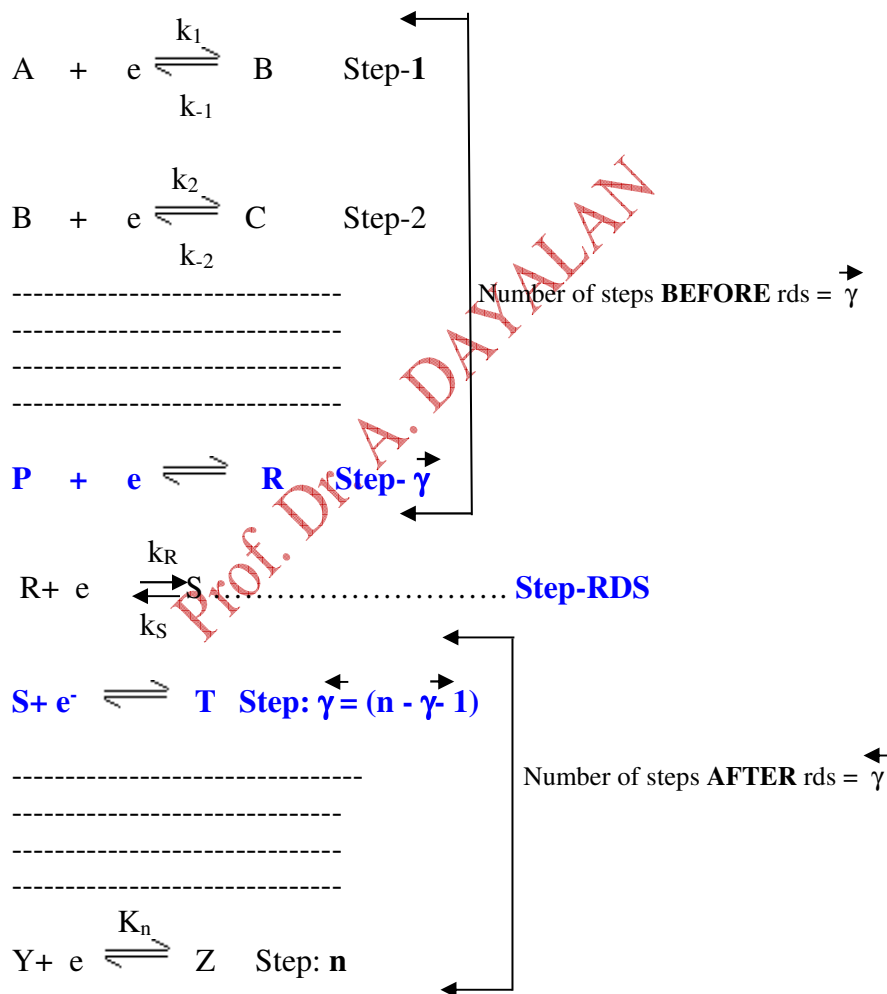
ELECTRODE KINETICS – ELECTRODICS-II

LECTURE NOTES

MULTI STEP MULTI-ELECTRON REACTION (Simple)

The Multi Step Multi-Electron Reaction occurs in more number of steps such that each one is an elementary step (Electrochemical; Non-Electrochemical) including the rate determining step (RDS) occurring as an elementary step like any other step of the reaction.

Consider a multi electron reaction, $A + ne \rightarrow Z$ occurring as follows:



Note:

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

$$\vec{\gamma} + 1 + \overleftarrow{\gamma} = n$$

- There may be non-electrochemical steps
- The RDS may electrochemical or non-electrochemical steps

Applying law of mass of action

$$\vec{i} = \overleftarrow{i} = i_0 \text{ (for all equilibrium steps)} = nF v = nF \{k \cdot \text{conc}\}$$

$$\text{NB: } k = (k_b T/h) \exp(-\Delta G^*/RT)$$

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

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

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

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

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

$$Fk_1 C_A e^{-\beta F\Delta\phi / RT} = Fk_{-1} C_B e^{(1-\beta)F\Delta\phi / RT} \quad \text{(1st step of the reaction)}$$

$$C_B = K_1 C_A e^{-F\Delta\phi / RT}$$

$$C_C = K_2 C_B e^{-F\Delta\phi / RT} = K_1 K_2 C_A e^{-2F\Delta\phi / RT} \quad \text{(2nd step of the reaction)}$$

III^{ly}

$$C_D = K_1 K_2 K_3 C_A e^{-3F\Delta\phi / RT} \quad \text{(3rd step of the reaction)}$$

Hence, coming to the step before rds

$$C_R = \prod_{i=1}^{\gamma} K_i C_A e^{-\gamma F\Delta\phi / RT} \quad \text{(Step- } \gamma \text{ of the reaction) } \dots(1)$$

The forward electrochemical rate of rds is given by its forward current, i_R

$$\vec{i}_R = F k_R C_R e^{-\beta F\Delta\phi / RT}$$

Substituting for C_R as from eq-1

$$i_R = Fk_R \prod_{i=1}^{\gamma} K_i C_A e^{-\gamma F\Delta\phi/RT} e^{-\beta F\Delta\phi/RT} \dots\dots\dots 2$$

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

$$i_R = i_0 \exp\{-(\gamma + \beta)F\eta/RT\} \text{ "For the forward step of rds"} \dots\dots\dots 3$$

The same reasoning can be applied to all the backward reactions of the equilibrium steps from the last (n^{th}) up to the step before **rds** viz., $S \rightarrow R + e$.

So that

$$C_S = \prod_{i=n}^{\gamma = (n - \gamma - 1)} K_i C_Z e^{\gamma F\Delta\phi/RT} \dots\dots\dots 4 \text{ (Similar to eq-1 above)}$$

The reverse electrochemical rate of rds is given by, i_S

$$i_S = Fk_S C_S e^{(1-\beta)F\Delta\phi/RT} \dots\dots\dots 6$$

(For the anodic process, symmetric factor is $(1-\beta)$ and the free energy term is taken as positive)

Substituting for C_S as above

$$i_S = Fk_S \prod_{i=n}^{\gamma = n - \gamma - 1} K_i C_Z e^{\gamma F\Delta\phi/RT} e^{(1-\beta)F\Delta\phi/RT} \dots\dots\dots 7$$

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

$$i_s^{\leftarrow} = i_o \exp\{[(\gamma + 1 - \beta)F\eta/RT]\} \text{ “For the reverse step of rds”} \dots\dots\dots 8$$

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

$$\begin{aligned} i = i_{rds} &= i_s^{\leftarrow} - i_R^{\rightarrow} \\ &= i_o \{ \exp\{[(\gamma + 1 - \beta)F\eta/RT]\} - \exp\{-[(\gamma + \beta)F\eta/RT]\} \} \\ &= i_o \{ \exp\{[(n - \gamma - \beta)F\eta/RT]\} - \exp\{-[(\gamma + \beta)F\eta/RT]\} \} \dots\dots\dots 9.a \end{aligned}$$

$$i = i_o [e^{\alpha^{\leftarrow} F \eta / RT} - e^{-\alpha^{\rightarrow} F \eta / RT}] \dots\dots\dots 9.b$$

Where $\alpha^{\leftarrow} = \gamma + 1 - \beta = n - \gamma - \beta$ Since, $\gamma = n - \gamma - 1$
 $\alpha^{\rightarrow} = \gamma + \beta$

The parameters in eq-9 α^{\leftarrow} & α^{\rightarrow} 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.

$$i = i_o [e^{\alpha^{\leftarrow} F \eta / RT} - e^{-\alpha^{\rightarrow} F \eta / RT}]$$

Equation-9.a is reduced to 9.c, if the RDS is non-electrochemical

$$i = i_o \{ \exp\{(n - \gamma)F\eta/RT\} - \exp\{-\gamma F\eta/RT\} \} \dots\dots\dots 9.c$$

HFA

$$\ln i = \ln i_o + \alpha^{\leftarrow} F\eta/RT \quad \text{“at high + ve } \eta \text{” Anodic behavior *Tafel equation*}$$

$$\ln i = \ln i_o - \alpha^{\rightarrow} F\eta/RT \quad \text{“at high - ve } \eta \text{” Cathodic behavior *Tafel equation*}$$

Hence, plot of “ $\ln i$ vs η ” should give α^{\leftarrow} and α^{\rightarrow} from slope and i_o from the intercept.

The above **General Butler Volmer** equation for a multi-electron process reduces to simple **Butler Volmer** for a one electron single step process as

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

For $n = 1$ (one electron reaction), no steps before and after rds i.e., $\gamma^{\rightarrow} = 0$, $\gamma^{\leftarrow} = 0$.

PROBLEM

The Tafel anodic and cathodic slopes $\frac{\partial \Delta \phi}{\partial \log i}$ for a 2e process were found to be 0.04 & 0.12, respectively. Determine the transfer coefficients and stoichiometric number for the reaction.

Solution: FOR ANODIC PROCESS

For large +ve η

$$i \cong i_0 e^{\frac{\leftarrow \eta F}{RT}} ;$$

$$\log i^{\leftarrow} = \log i_0 + \frac{\leftarrow \eta F}{2.303RT}$$

$$\left(\frac{\partial \log i^{\leftarrow}}{\partial \eta} \right) = \frac{\leftarrow F}{2.303RT} = \frac{1}{0.04}$$

$$\leftarrow \alpha = \frac{2.303RT}{F} \times \frac{1}{0.04} = 1.48 \Rightarrow \frac{3}{2}$$

SIMILARLY, FOR CATHODIC PROCESS:

$$\frac{\partial \log i^{\rightarrow}}{\partial \eta} = \frac{\partial \log i^{\rightarrow}}{\partial \Delta \phi} = \frac{\rightarrow F}{2.303RT} = \frac{1}{0.12}$$

$$\rightarrow \alpha = \frac{2.303RT}{F} \times \frac{1}{0.12} = 0.49 \Rightarrow \frac{1}{2}$$

\therefore Stoichiometric number = n/ sum of transfer coefficients = 2/2 = 1

NOTE: The proper slope is $\frac{\partial \log i}{\partial \Delta \phi}$ and not $\frac{\partial \Delta \phi}{\partial \log i}$