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 \( \nu \) number of times, known as stoichiometric number.

This reaction scheme differs only in the RDS step.

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

\[
\begin{align*}
A + e & \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} B \quad \text{Step-1} \\
B + e & \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} C \quad \text{Step-2} \\
P + e & \underset{k_R}{\overset{k_S}{\rightleftharpoons}} R \quad \text{Step-} \gamma \\
\end{align*}
\]

Number of steps BEFORE rds = \( \gamma \)

\( \nu( \text{R+ re} \underset{k_S}{\overset{k_R}{\rightleftharpoons}} S) \) RDS repeated \( \nu \) (stoichiometric number) times with \( r \) electron(s) each time.

NB- \( r \) Electrons in the rds step will be added in \( r \) ways totaling to \( rv \) steps with \( rv \) electrons.

\[
\begin{align*}
S + e^- & \underset{K_n}{\overset{K_n}{\rightleftharpoons}} T \quad \text{Step: } \gamma = (n - r \cdot \nu) \\
\end{align*}
\]

Number of steps AFTER rds = \( \gamma \)

\[
\begin{align*}
Y + e & \underset{K_n}{\overset{K_n}{\rightleftharpoons}} Z \quad \text{Step: } n
\end{align*}
\]
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06-Butler-Volmer Equation for Multi Step Multi-Electron Rexn (Complex)

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

\[ \gamma e + r v e + \gamma e = n e; \text{ so that } \gamma + r v + \gamma = n \]

Applying law of mass of action to the equilibrium steps

\[ i = i_o \text{ (for all equilibrium steps) } = n F v = n F \{k.\text{conc}\} \]

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

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

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

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

i.e., \( n F v = n F \upsilon \) (for all equilibrium steps)

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

\[ F k_1 C_A e^{\beta F \Delta \phi / RT} = F k_1 C_A (1-\beta) F \Delta \phi / RT \text{ for the first equilibrium step} \]

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

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

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

Hence, coming to the step before rds

\[ \gamma \]

\[ C^n_R = \prod_{i=1}^{\gamma} K_i C_A e^{-\gamma F \Delta \phi / RT} \]

**NB-R** Builds up \( \upsilon \) number of times and appears \( \upsilon \) number of times for rds to occur

Hence, \( C_R = \left\{ \prod_{i=1}^{\gamma} K_i C_A \right\}^{1/\upsilon} e^{-\gamma F \Delta \phi / RT} \)

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

\[ i_R = F k_R C_R e^{-\beta F \Delta \phi / RT} \]
{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

\[
i_R = F k_R \left[ \gamma \prod_{i=1}^{\gamma} K_i C_A \right]^{1/\upsilon} e^{-\left(\gamma / \upsilon\right) F \Delta \phi / RT} e^{-r \beta F \Delta \phi / RT} \]

Replacing \( \Delta \phi \) by \((\Delta \phi_c + \eta)\) we get

\[
i_R = i_0 \exp\{-(\gamma/\upsilon + r \beta F \eta / RT)\} \quad \text{"For the forward step of rds"} \]

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

So that

\[
C_S = \left[ \gamma = (n - \gamma \upsilon) \prod_{i=n}^{\gamma} K_i C_Z \right]^{1/\upsilon} e^{\left(\gamma / \upsilon\right) F \Delta \phi / RT} \]

(N.B-“\( S \) has to appear \( \upsilon \) number of times for rds as mentioned above”)

The reverse electrochemical rate of rds is given by, \( i_S \)

\[
i_S = F k_S C_S e^{r(1-\beta) F \Delta \phi / RT} \]

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

Substituting for \( C_S \) as above

\[
i_S = F k_S \left[ \gamma = (n - \gamma \upsilon) \prod_{i=n}^{\gamma} K_i C_Z \right]^{1/\upsilon} e^{\left(\gamma / \upsilon\right) F \Delta \phi / RT} e^{r(1-\beta) F \Delta \phi / RT} \]
Replacing $\Delta \phi$ by $(\Delta \phi_e + \eta)$ we get

$$i_s = i_o \exp\{[(\gamma / \nu) + r - r \beta]F\eta/RT}\} \quad \text{"For the reverse step of RDS"} \quad \cdots \cdots \cdots 8$$

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

$$i = i_{\text{rds}} = i_s \downarrow - i_r$$

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

$$i = i_o[\alpha \exp\{\eta F\eta/RT\} - \exp\{-\alpha F\eta/RT\}] \quad \cdots \cdots \cdots 9$$

Where $\alpha = (\gamma / \nu) + r - r \beta = [((n - \gamma) / \nu) + r - r \beta]$$

$$\uparrow \alpha = (\gamma / \nu) + r \beta$$

So that $\alpha + \alpha = n / \nu \quad \cdots \cdots \cdots \cdots 10$

The parameters in eq-9 $\alpha$ & $\alpha$ 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 $\eta$ (Tafel slope) – useful in the determination on mechanism of reaction.

$$i = i_o[\alpha \exp\{\eta F\eta/RT\} - \exp\{-\alpha F\eta/RT\}]$$

NB: For an elementary multistep reaction,

$$i = i_o\{\exp\{[(\gamma + 1 - \beta)F\eta/RT\} - \exp\{-[(\gamma + \beta)F\eta/RT\} \}$$

For an complex multistep reaction,

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

\(\therefore\) In the case of complex multistep reaction, the $\gamma$ terms get divided by $\nu$ and the symmetry terms get multiplied by $r$.

**HFA**

$$\ln i = \ln i_o + \alpha F\eta/RT$$ \quad \text{“at high + ve $\eta$”} \quad \text{Anodic behavior \hspace{1cm} Tafel equation}

$$\ln i = \ln i_o - \alpha F\eta/RT$$ \quad \text{“at high – ve $\eta$”} \quad \text{Cathodic behavior \hspace{1cm} Tafel equation}

Hence, plot of “$\ln i$ vs $\eta$” should give $\alpha$ and $\alpha$ 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

\[ i = i_0 (e^{(1-\beta) \frac{F\eta}{RT}} - e^{-\beta \frac{F\eta}{RT}}) \]

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

Where \( \alpha = [(n-\gamma) / \nu] - r\beta = (1 - \beta) \)

\[ \alpha = (\gamma / \nu) + r\beta = \beta \]

The sum of the transfer coefficients, \( \alpha + \alpha \), 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., \( \nu < n \))

\[ \alpha + \alpha = n/\nu > 1 \]

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