5.2: REDUCTION OF I_3^-

$$I^-_3 + 2e \longrightarrow 3I^-$$

Reaction mechanism:

$$I_3^- \overset{K_1}{\rightleftarrows} I_2 + I^- \qquad \text{..........(1)}$$

$$I_2 \overset{K_2}{\rightleftarrows} 2I \qquad \text{..........(2)}$$

$$2\,(I + e \overset{K_3}{\rightleftarrows} I^-) \text{ ...... } rds \qquad \text{..........(3)}$$

Step-1: Fast chemical equilibrium

Law mass action & Equilibrium constant

Step-2: Fast chemical equilibrium

Law mass action & Equilibrium constant

Step-3: Slow(RDS) electrochemical equilibrium

Anidic & cathodic currents are not equal

Consider Step-3 as RDS: Slow electrochemical equilibrium.

$\overleftarrow{\gamma} = 0$; $\overrightarrow{\gamma} = 0$ (There are no electrochemical steps before or after rds) $\nu = 2$; $r = 1$

Therefore, $\overleftarrow{\alpha} = (\overleftarrow{\gamma}/\upsilon) + r - r\beta = 0 + 1 - 1\,(½) = ½$

$\overrightarrow{\alpha} = (\overrightarrow{\gamma}/\upsilon) + r\beta = 0 + 1\,(½) = ½$

The overall rate of the reaction is equal to the rate of RDS, which is equal to the net current of RDS. The net current of the above RDS (step-3, slow (RDS) electrochemical equilibrium) is given as.

$$i = nF(\overleftarrow{\upsilon} - \overrightarrow{\upsilon}) = 1.F\{\, k_{-3}[I^-]\, e^{(1-\beta)\Delta\varphi F/RT} - k_3\,[I]\,e^{-\beta\Delta\varphi F/RT} \}$$

The species, I is an intermediate in the reaction and must be eliminated in terms of I^- or I_3^- or both.

Hence , from steps-1 & 2 (Fast chemical equilibria)

$$[I] = \{K_2\,[I_2]\}^{½} = K_2\{K_1\,[I_3^-]\,/[I^-]\}^{½}$$

Substituting for [I]in the Butler-Volmer equation we get

$$i = F\,(k_{-3}\,[I^-]\,e^{(1-\beta)\Delta\varphi F/RT} - k_3 K_2 K_1^{½}\,[I_3^-]^{½}[I^-]^{-½}\,e^{-\beta\Delta\varphi F/RT})$$

Hence, ***The anodic orders*** w.r.t $I^- = 1$ & $I_3^- = 0$

The cathodic orders w.r.t $I^- = -½$ & $I_3^- = ½$

The above equation after replacing $\Delta\varphi$ by $\Delta\varphi_e+\eta$ becomes $\mathbf{i = i_o[e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]}$

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

Hence, the sum of the coefficients of $\eta F/RT$ is found to be one $\overleftarrow{\alpha} = 1/2$ & $\overrightarrow{\alpha} = ½$

The transfer coefficients appear in terms of β. However, the equation appears to be identical to elementary reaction.

$\overleftarrow{\alpha} + \overrightarrow{\alpha} > 1$ confirms multistep reaction process.But, this being equal to one does not confim that it is an elementary reaction.