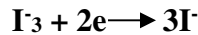


5.2: REDUCTION OF I_3^- 

Reaction mechanism:



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

Anodic & cathodic currents are not equal

Consider Step-3 as RDS: Slow electrochemical equilibrium.

$\gamma^{\leftarrow} = 0$; $\gamma^{\rightarrow} = 0$ (There are no electrochemical steps before or after rds) $v = 2$; $r = 1$

$$\text{Therefore, } \alpha^{\leftarrow} = (\gamma^{\leftarrow}/v) + r - r\beta = 0 + 1 - 1(1/2) = 1/2$$

$$\alpha^{\rightarrow} = (\gamma^{\rightarrow}/v) + r\beta = 0 + 1(1/2) = 1/2$$

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.

$$i = nF(v^{\leftarrow} - v^{\rightarrow}) = 1.F \{ k_{-3}[I^-] e^{(1-\beta)\Delta\phi F/RT} - k_3 [I] e^{-\beta\Delta\phi F/RT} \}$$

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)

$$[I] = \{K_2 [I_2]\}^{1/2} = K_2 \{K_1 [I_3^-]/[I^-]\}^{1/2}$$

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

$$i = F (k_{-3} [I^-] e^{(1-\beta)\Delta\phi F/RT} - k_3 K_2 K_1^{1/2} [I_3^-]^{1/2} [I^-]^{-1/2} e^{-\beta\Delta\phi F/RT})$$

5.2: Reduction of I_3^-

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

The cathodic orders w.r.t $I^- = -1/2$ & $I_3^- = 1/2$

The above equation after replacing $\Delta\phi$ by $\Delta\phi_e + \eta$ becomes $i = i_0 [e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$

Hence, comparing with $i = i_0 [e^{\alpha \eta F/RT} - e^{-\alpha \eta F/RT}]$

Hence, the sum of the coefficients of $\eta F/RT$ is found to be one $\alpha \leftarrow = 1/2$ & $\alpha \rightarrow = 1/2$

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

$\alpha \leftarrow + \alpha \rightarrow > 1$ confirms multistep reaction process. But, this being equal to one does not confirm that it is an elementary reaction.