5.5(b): ELECTRONATION OF O_2

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

For the plot of **η vs log i** in both acidic and alkaline solution the slope are found to be 0.12 for reduction and 0.04 for oxidation

$$\text{i.e., } 2.303RT/\overrightarrow{\alpha}F = 0.12 \quad ; \quad \overrightarrow{\alpha} = ½ \textit{ (Reduction, cathodic)}$$

$$2.303RT/\overleftarrow{\alpha}F = 0.4 \qquad \overleftarrow{\alpha} = 1½ \textit{ (Oxidation , anodic)}$$

Therefore,

$$\nu = n / (\overrightarrow{\alpha} + \overleftarrow{\alpha}) = 4/2 = 2$$

From the above data we can determine $\overleftarrow{\gamma}$ and $\overrightarrow{\gamma}$

Note the following relations:

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

$$\overleftarrow{\alpha} = (\overleftarrow{\gamma} / \nu) + r - r\beta$$

$$r = n - (\overleftarrow{\gamma} + \overrightarrow{\gamma})$$

$$\overleftarrow{\gamma} = n - \overrightarrow{\gamma} - r\nu$$

For electronation of O_2

$$\overrightarrow{\alpha} = ½ = (\overrightarrow{\gamma}/2) + [4 - (\overleftarrow{\gamma} + \overrightarrow{\gamma})]$$

$\overleftarrow{\gamma} + \overrightarrow{\gamma}$ can be 4 , 3 not 2 or 1 as they will give negative value for $\overrightarrow{\gamma}$

But $(\overleftarrow{\gamma} + \overrightarrow{\gamma})$ = Total electron transferred in all the steps except rds must be an integer & must be less than or equal to n

5.5(b):Electronation of Oxygen

$(\overleftarrow{\gamma} + \overrightarrow{\gamma}) = 4$; $\overrightarrow{\gamma} = 1$ (RDS is non electrochemical)

Similarly, for oxygen evolution: we have $\beta = ½$, $n = 4$, $\overleftarrow{\alpha} = 1½$, $\nu = 2$

$$\overleftarrow{\alpha} = 1½ = (\overleftarrow{\gamma}/\nu) + r - r\beta$$

$$= (\overleftarrow{\gamma}/\nu) + r(1 - \beta)$$

$$= (\overleftarrow{\gamma}/\nu) + [4 - (\overleftarrow{\gamma} + \overrightarrow{\gamma})](1 - \beta)$$

$\overleftarrow{\gamma} + \overrightarrow{\gamma}$ can be 4 or 3

There are three possible paths for the electronation of O_2 with the charge transfer step as the rds .

Mechanism: A

$$O_2 + 2M \longrightarrow MO$$

$$2MO + 2H^+ + 2e^- \longrightarrow 2\,MOH$$

$$2MOH + 2H^+ + 2e^- \longrightarrow 2\,M + H_2O$$

Mechanism:B

$$O_2 + 2M \longrightarrow 2MO$$

$$MO + H_2O \longrightarrow MO\text{-}H\text{-}OH$$

$$2MO\text{-}H\text{-}OH + 2e^- \longrightarrow 2MO\text{-}H\text{-}OH^-$$

$$H\text{-}OH^- + H^+ \longrightarrow MOH + H_2O$$

$$2MOH + 2H^+ + 2e^- \longrightarrow 2\,M + 2H_2O$$

Mechanism:C

$$O_2 + 2M \longrightarrow 2MO$$

$$2MO + 2e^- \longrightarrow 2MO^-$$

$$MO^- + H^+ \longrightarrow MOH$$

$$2MOH + 2H^+ + 2e^- \longrightarrow 2M + 2H_2O$$

NOTE: The type of mechanism & rds depends on the nature of the electrode used.