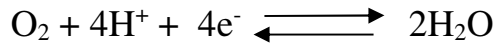


5.5 (b) :Electronation of Oxygen

5.5(b): ELECTRONATION OF O₂



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

$$\text{i.e., } 2.303RT / \bar{\alpha} F = 0.12 ; \quad \bar{\alpha} = 1/2 \text{ (Reduction, cathodic)}$$

$$2.303RT / \bar{\alpha} F = 0.4 \quad \bar{\alpha} = 1/2 \text{ (Oxidation, anodic)}$$

Therefore,

$$v = n / (\bar{\alpha} + \bar{\alpha}) = 4 / 2 = 2$$

From the above data we can determine $\bar{\gamma}^{\leftarrow}$ and $\bar{\gamma}^{\rightarrow}$

Note the following relations:

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

$$\bar{\alpha}^{\leftarrow} = (\bar{\gamma}^{\leftarrow} / v) + r - r\beta$$

$$r = n - (\bar{\gamma}^{\leftarrow} + \bar{\gamma}^{\rightarrow})$$

$$\bar{\gamma}^{\leftarrow} = n - \bar{\gamma}^{\rightarrow} - rv$$

For electronation of O₂

$$\bar{\alpha}^{\rightarrow} = 1/2 = (\bar{\gamma}^{\rightarrow} / 2) + [4 - (\bar{\gamma}^{\leftarrow} + \bar{\gamma}^{\rightarrow})]$$

$\bar{\gamma}^{\leftarrow} + \bar{\gamma}^{\rightarrow}$ can be 4, 3 not 2 or 1 as they will give negative value for $\bar{\gamma}^{\rightarrow}$

But $(\bar{\gamma}^{\leftarrow} + \bar{\gamma}^{\rightarrow}) =$ 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

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

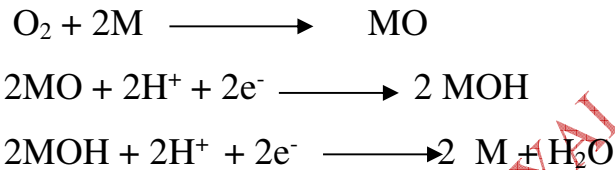
Similarly, for oxygen evolution: we have $\beta = 1/2$, $n = 4$, $\overleftarrow{\alpha} = 1 1/2$, $\nu = 2$

$$\begin{aligned} \overleftarrow{\alpha} = 1 1/2 &= (\overleftarrow{\gamma}/\nu) + r - r\beta \\ &= (\overleftarrow{\gamma}/\nu) + r(1 - \beta) \\ &= (\overleftarrow{\gamma}/\nu) + [4 - (\overleftarrow{\gamma} + \overrightarrow{\gamma})](1 - \beta) \end{aligned}$$

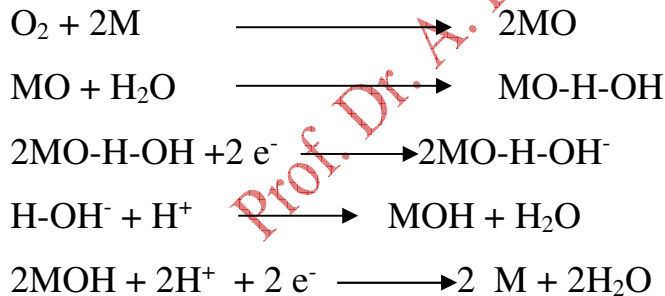
$\overleftarrow{\gamma} + \overrightarrow{\gamma}$ can be 4 or 3

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

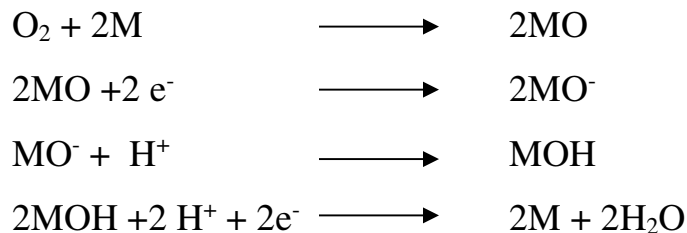
Mechanism: A



Mechanism: B



Mechanism: C



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