

5.5 (a) .Oxygen Evolution

5.5 (a). OXYGEN EVOLUTION

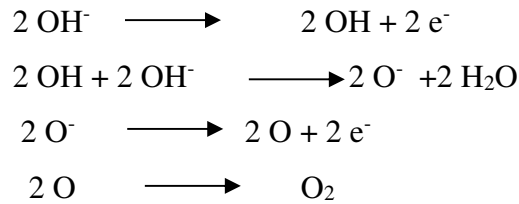
Oxygen is usually evolved on the oxidized metal surface at potentials more positive than its SRP. (SRP = 1.23V), depending on the pH of the medium.

- i. $4 \text{ OH}^- \longrightarrow 2 \text{ H}_2\text{O} + \text{O}_2 + 4\text{e}^-$ (Alkaline solution-Fe group metals)
- ii. $2 \text{ H}_2\text{O} \longrightarrow 4 \text{ H}^+ + \text{O}_2 + 4\text{e}^-$ (Acid solution-Pt group metals)

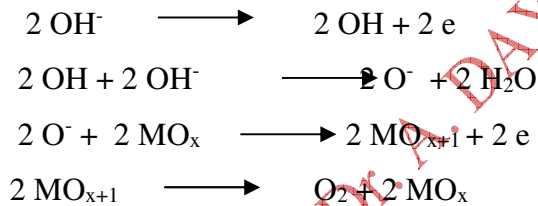
The evolution of O_2 is a complex mechanism and occurs with side reactions.

Some possible mechanisms

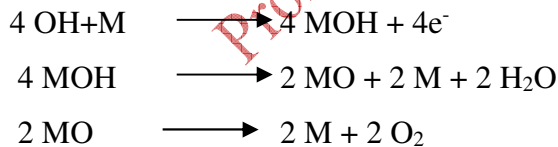
Mechanism-I



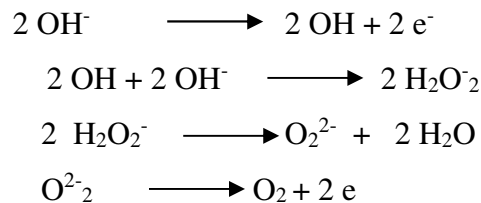
Mechanism-II



Mechanism-III



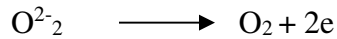
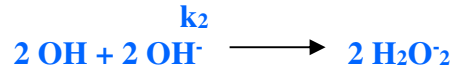
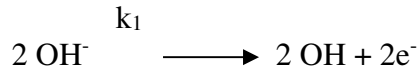
Mechanism-IV



One has to construct the experimental anodic Tafel plot and compare it with the theoretical values.

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Consider mechanism: IV



Consider , **step-2** (non electrochemical) **RDS**

$$\text{Rate} = v_2 = k_2 [\text{OH}]^2 [\text{OH}]^2$$

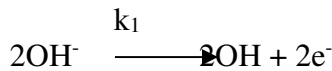
This should be eliminated for [OH] and incorporated with current

Therefore,

$$[\text{OH}] = \frac{v_2^{1/2}}{k_2^{1/2} [\text{OH}]} \dots\dots\dots 1$$

NOTE: *The non-electrochemical rds will also have its effect on the over all current (rate) of the process.*

Considering the preceding electrochemical step (**Step-1**).



$$i = 2F k_1 [\text{OH}] e^{(1-\beta) \Delta\Phi_F/RT} \dots\dots\dots 2$$

Substituting for [OH] in equation-2 as given by the rds step above in equation-1

$$i = 2F k_1 \frac{v_2^{1/2}}{k_2^{1/2} [\text{OH}]} e^{-\beta \Delta\Phi_F/RT} \dots\dots\dots 3$$

$$= (2F)^{1/2} k_1 \frac{v_2^{1/2} (2F)^{1/2}}{k_2^{1/2} [\text{OH}]} e^{(1-\beta) \Delta\Phi_F/RT} \quad ; \quad 2F \text{ can be written as } (2F)^{1/2} (2F)^{1/2}$$

We know that $i = nFv$

Hence, $v_2^{1/2} (2F)^{1/2} = i^{1/2}$ for the 2nd step which is same as that for the first step

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Therefore, equation-3 becomes

$$i = (2F)^{1/2} k_1 \frac{i^{1/2}}{k_2^{1/2} [\text{OH}]} e^{(1-\beta) \Delta\Phi F/RT}$$

$$i^{1/2} = (2F)^{1/2} k_1 \frac{1}{k_2^{1/2} [\text{OH}]} e^{(1-\beta) \Delta\Phi F/RT}$$

Squaring both sides we get,

$$i = (2F) k_1^2 \frac{1}{k_2 [\text{OH}]^2} e^{2(1-\beta) \Delta\Phi F/RT}$$

$$= \frac{2F k_1^2 e^{2(1-\beta) \Delta\Phi F/RT}}{k_2 [\text{OH}]^2} \dots\dots\dots 4$$

$$= i_o e^{2(1-\beta)\eta F/RT} \dots\dots\dots 5$$

$$\log i = \log i_o + \frac{2(1-\beta)\eta F}{2.303 RT}$$

$$\frac{2.303 RT}{2(1-\beta)F} \log i = \frac{2.303 RT}{2(1-\beta)F} \log i_o + \eta$$

$$\text{Slope} \frac{(\Theta\eta)}{(\Theta \log i)} = 2.303RT / \{2(1-\beta)F\} = b_o$$

NOTE: The species [OH] is an intermediate & must be eliminated to get the order with respect stable species.

HW: Alternatively step-2 of mechanism-IV could be considered as fast equilibrium

$$F.2.k_1 e^{(1-\beta) \Delta\Phi F/RT} [\text{OH}^-] = F.2.k_{-1} e^{-\beta \Delta\Phi F/RT} [\text{OH}]$$

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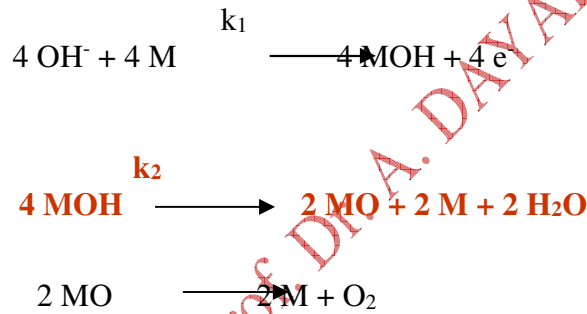
$$[OH] = K_2 e^{\Delta\Phi_F/RT} [OH^-]$$

$$= \frac{2Fk_1^2 e^{2(1-\beta)\Delta\Phi_F/RT}}{k_2 K_2^2 e^{2\Delta\Phi_F/RT} [OH^-]^2}$$

$$= \frac{2Fk_1^2 e^{-2\beta\Delta\Phi_F/RT}}{k_2 K_2^2 [OH^-]^2}$$

$$i = i_o e^{-2\beta\eta_F/RT}$$

Consider Mechanism III, step – 2 as rds



$$v_2 = k_2 (MOH)^4 \dots\dots\dots 6$$

and $i = 4 Fv_2$

$$[MOH] = \theta_{MOH} = (v_2 / k_2)^{1/4} \dots\dots\dots 7$$

For step-1 (fast equilibrium); cathodic rate = anodic rate

$$4 F k_{-1} \theta_{MOH} e^{-\beta \Delta\Phi_F/RT} = 4 F k_1 (1-\theta_{MOH}) [OH^-] e^{(1-\beta) \Delta\Phi_F/RT}$$

Hence, for $\theta_{MOH} \ll 1$, we get

$$\theta_{MOH} = MOH = K_1 [OH^-] e^{\Delta\Phi_F/RT} \dots\dots\dots 8$$

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Hence,

$$\theta_{\text{MOH}} = K_1 (v_2 / k_2)^{1/4} e^{\Delta\Phi F/RT}$$

Substituting θ_{MOH} , anodic current is given as,

$$i = 4F k_{-1} k_1 [(i/4F) / k_2]^{1/4} e^{(1-\beta) \Delta\Phi F/RT}$$

$$i^{3/4} = \frac{(4F)^{3/4} k_{-1} k_1 e^{(1-\beta) \Delta\Phi F/RT}}{(k_2)^{1/4}}$$

$$i = \frac{(4F k_{-1} k_1)^{4/3} e^{4/3 (1-\beta) \Delta\Phi F/RT}}{(k_2)^{1/3}}$$

$$\log i = \log i_0 + \frac{4(1-\beta)\eta F}{3(2.303 RT)}$$

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