5.4: DEPOSITION OF IRON

❖ Need to study this reaction-Rusting of iron

❖ Conventional analysis-Overall reaction-**"$Fe^{2+}+ 2e \rightarrow Fe$"** Two faradays current for every one mole of iron deposited from Fe^{2+}.

❖ One can look for the transfer coefficients and electrochemical reaction orders.

❖ The **anodic Tafel slope** of the plot **of "ΔΦ vs logi"** OR "(η vs logi)" was found to be **0.04**

$$\frac{d\,\Delta\Phi}{d\log i} = \frac{2.303RT}{\overleftarrow{\alpha}\,F} = 0.04 \quad ; \quad \overleftarrow{\alpha} = 1\tfrac{1}{2}$$

Note:

$i = i_o\, e^{\overleftarrow{\alpha}\,\eta F/RT}$ (Anodic process)

$\ln i = \overleftarrow{\alpha}\,\eta F / RT + \ln i_o$

$$\eta = \frac{2.303RT}{\overleftarrow{\alpha}\,F}\log i - \frac{2.303RT}{\overleftarrow{\alpha}\,F}\log i_o$$

❖ Similarly the magnitude of the **cathodic Tafel slope** of the plot of **ΔΦ vs logi** (η vs logi) was found to be **0.12**

$$\frac{d\,\Delta\Phi}{d\log i} = \frac{2.303RT}{\overrightarrow{\alpha}\,F} = 0.12 \quad ; \quad \overrightarrow{\alpha} = \tfrac{1}{2}$$

$$\nu = \frac{n}{\overleftarrow{\alpha} + \overrightarrow{\alpha}} = \frac{2}{1\tfrac{1}{2} + \tfrac{1}{2}} = 1$$

NOTE: *The conventional plot should be **log i vs η** . In which case the expression for slope would be the reciprocal of what are mentioned above.*
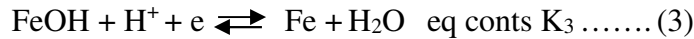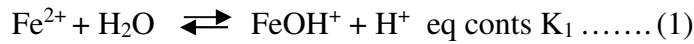
❖ Therefore, the rds occurs once per the occurrence of the overall reaction since, $\nu = 1$.

❖ The discharge reaction was found to be is **1st order** with respect to **Fe^{2+}** and **OH^-** .

❖ Thus the mechanism proposed for iron dissolution reaction must account for the following :

$\overleftarrow{\alpha} = 1\tfrac{1}{2},\quad \overrightarrow{\alpha} = \tfrac{1}{2},\quad \nu = 1,$ The reaction order: $\rho_{OH^-} = 1$(on both direction) and

$$\rho_{Fe^{2+}} = 1$$

❖ Consider the following mechanism.

$$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+ \quad \text{eq conts } K_1 \dots(1)$$

$FeOH^+ + e \rightleftharpoons FeOH \qquad \text{eq conts } K_2 \dots (2)*$

$$FeOH + H^+ + e \rightleftharpoons Fe + H_2O \quad \text{eq conts } K_3 \dots(3)$$

Step-1: Fast chemical equilibrium

Law mass action & Equilibrium constant

Step-2: Slow electrochemical equilibrium-RDS **(Actual rds)**

Anidic & cathodic currents are not equal; Nett current is not equal zero

Step-3: Fast electrochemical equilibrium

Anidic & cathodic currents are equal

The equation for the multistep step reaction is

$$i = i_0[e^{\overleftarrow{\alpha}F\,\eta/RT} - e^{-\overrightarrow{\alpha}\,F\,\eta/RT}]$$

NOTE:-

➢ *Equlibrium step (RDS) nett c.d is not zero, if it is electrochemical*

➢ *Equlibrium step (Not RDS) nett c.d is zero, if it is electrochemical*

I. Assume **STEP-3** as **RDS**.

Rate = Rate of rds = Magnitude of net c.d. of rds ,

$i_{rds} = i_a - i_c$

$$i = 1.F[\, k_{-3}(1-\Theta_{FeOH})e^{(1-\beta)\,\Delta\Phi F\,/\,RT} - k_3\,\Theta_{FeOH}\,[H^+]e^{-\beta\Delta\Phi F\,/\,RT}]\dots(4)$$

$$=1.F[k_{-3}e^{(1-\beta)\Delta\Phi F/RT}-k_3\Theta_{FeOH}[H^+]e^{-\beta\Delta\Phi F/RT}];\text{for}\Theta_{FeOH}<<1 \dots (4a)$$

Step-3 assumed to be RDS. Hence net current is not equal

The intermediate FeOH could be considered as a precipitate .Hence,the surface of Fe will be covered with a coating of FeOH. Therefore, the activity of **Fe** *will not be one.But (1-θ_{FeOH}) and the activity (concentration) of* **FeOH** *will be θ_{FeOH}.*

Note: θ_{FeOH} *in* equation-4(a) must be eliminated.

The **2nd step** is a fast electroequilibrium electrochemical process $v_{-2} = v_2$ or $i_{-2} = i_2$

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$$k_{-2} \theta_{FeOH} e^{(1-\beta) \Delta F / RT} = k_2[FeOH^+]e^{-\beta \Delta \Phi F / RT} \dots\dots\dots\dots\dots\dots (5)$$

The species $FeOH^+$ will be in solution

$$\theta_{FeOH} = K_2[FeOH^+]e^{-\beta \Delta \Phi F/RT} \quad \text{---} (6)$$

The concentration of $FeOH^+$ can be determined from the chemical **step-1**. (Eq-1) as follows:

$$[FeOH^+] [H^+][Fe^{2+}]^{-1} = K_1$$

$$\text{Therefore, } \mathbf{[FeOH^+]} = K_1[H^+]^{-1}[Fe^{2+}]\dots\dots\dots\dots\dots (7)$$

Hence, substitute $[FeOH^+] = K_1[H^+]^{-1}[Fe^{2+}]$ in eqation-(6)

$$\mathbf{\theta_{FeOH}} = K_1K_2[Fe^{2+}][H^+]^{-1}e^{-\Delta\Phi F/RT} \dots\dots\dots\dots\dots\dots\dots\dots (8)$$

Substituting for $[FeOH^+]$ & θ_{FeOH} in equation-4a

$$i = F\{k_{-3} e^{(1-\beta)\Delta\Phi F / RT} - k_3 K_1K_2[Fe^{2+}]e^{-\Delta\Phi F/RT}e^{-\beta\Delta\Phi F / RT} \}\dots\dots\dots\dots (9)$$

The dissolution reaction (cathodic reaction) order looks to be zero w.r.t. H^+ & OH^- and 1 w.r.t Fe^{2+} .

But , it has been found to be first – order w.r.t H^+ .

Moreover, the final equation could be written as

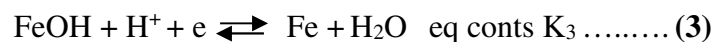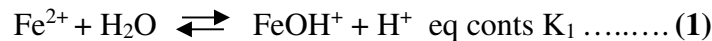$$\mathbf{i = i_o [e^{(1-\beta)\eta F / RT} - e^{-(1+\beta)\eta/RT}]}$$

Hence, $\overleftarrow{\alpha} = \frac{1}{2}$ and $\overrightarrow{\alpha} = 1\frac{1}{2}$

But, the values have been found to be

$\overleftarrow{\alpha} = 1\frac{1}{2}$ and $\overrightarrow{\alpha} = \frac{1}{2}$

"Therefore STEP-3 is not rds !!!!".

II. **Assume Step - 2 as RDS.**

$$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+ \quad \text{eq conts } K_1 \dots\dots (1)$$

$$\mathbf{FeOH^+ + e \rightleftharpoons FeOH} \qquad \mathbf{eq \ conts \ K_2 \dots\dots (2)*}$$

$$FeOH + H^+ + e \rightleftharpoons Fe + H_2O \quad \text{eq conts } K_3 \dots\dots (3)$$

The B.V. eq for the rds (step-2) is

$$\mathbf{i = Fk_{-2}\theta_{FeOH} e^{(1-\beta)\Delta\phi F/ RT} - k_2 [FeOH^+]e^{-\beta\Delta\phi F/ RT}} \text{ for } \theta_{FeOH} << 1 \textbf{....(4)}$$

Step-2(slow electrochemical equilibrium) is assumed to be RDS. Hence net current is not equal

NOTE : *The terms ,* θ_{FeOH} & $[FeOH^+]$ *in equation-4 must be eliminated*

From the electrochemical equilibrium **step- 3**. $v_a = v_c$

i.e., $F k_{-3}(1-\theta_{FeOH}) e^{(1-\beta)\Delta\phi F/ RT} = Fk_3\theta_{FeOH}[H^+]e^{-\beta\Delta\phi F/ RT}$

$F k_{-3}e^{(1-\beta)\Delta\phi F/ RT} = Fk_3\theta_{FeOH}[H^+]e^{-\beta\Delta\phi F/ RT}$ **; for** $\theta_{FeOH} << 1$

$$\theta_{FeOH} = \frac{1}{K_3}\ [H^+]^{-1}\ e^{\Delta\phi F/ RT}$$

$[H^+][OH^-] = K_W = 1 \times 10^{-14}$

$$[H^+]^{-1} = \frac{[OH^-]}{K_W}$$

$$\boldsymbol{\theta_{FeOH}} = \frac{1}{K_3\ K_w}\ [OH^-]e^{\Delta\phi F/ RT} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(5)$$

The expression for [FeOH⁺] can be obtained as follows:

From **step-1(Fast chemical equilibrium)**,

$$[FeOH^+] = \frac{K_1 [Fe^{2+}][H^+]}{[Fe^{2+}]}\ ; \text{(Law of mass action)} \ldots\ldots\ldots\ldots\ldots\ldots..(6)$$

$$\text{But, } [H^+] = \frac{[OH^-]}{K_W}$$

$$\textbf{Therefore, } [FeOH^+] = \frac{K_1 [Fe^{2+}][OH^-]}{K_W}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(7)$$

Substituting for $\boldsymbol{\theta_{FeOH}}$ and **[FeOH⁺] , from equations-5 & 7 ,** in Eq-4 , the

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B.V. eq for rds becomes

$$i = k[OH^-]e^{(2-\beta)\Delta\phi F/RT} - k'[Fe^{2+}][OH^-]\, e^{-\beta\Delta\phi F/RT} \quad \ldots\ldots\ldots\ldots(8)$$

Therefore, the anodic order is 1 w.r.t : OH^- ; cathodic order is 1 w.r.t both Fe^{2+} and OH^-

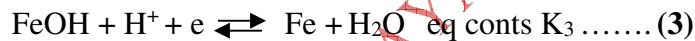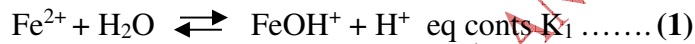Replacing $\Delta\Phi$ by $\Delta\Phi_e + \eta$, and thereby factorizing the exchange current density, i_0 we get

$$i = i_0[e^{(2-\beta)\eta F/RT} - e^{-\beta\eta F/RT}] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Hence, the anodic and cathodic transfer coefficients are $\overleftarrow{\alpha} = 1\frac{1}{2}$ and $\overrightarrow{\alpha} = \frac{1}{2}$

Therefore, the mechanism with " Step-2 as rds" is the correct one

The transfer coefficients can be evaluated theoretically.

$$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+ \quad \text{eq conts } K_1 \ldots\ldots(1)$$
$$FeOH^+ + e \rightleftharpoons FeOH \quad \text{eq conts } K_2 \ldots\ldots(2)$$
$$FeOH + H^+ + e \rightleftharpoons Fe + H_2O \quad \text{eq conts } K_3 \ldots\ldots(3)$$

Note:

$$\overleftarrow{\alpha} = (\overleftarrow{\gamma}/\upsilon) + r - r\beta \quad \& \quad \overrightarrow{\alpha} = (\overrightarrow{\gamma}/\upsilon) + r\beta$$

$\overrightarrow{\gamma}$: No. of electrochemical step(s) before rds

$\overleftarrow{\gamma}$: No. of electrochemical step(s) after rds

Step-3 rds : Not ok

$$\overleftarrow{\gamma} = 0 \; ; \; \overrightarrow{\gamma} = 1 \; ; \; \upsilon = 1 \; ; \; r = 1 \; ; \overleftarrow{\alpha} = \frac{1}{2} \; \& \; \overrightarrow{\alpha} = 1$$

Step-2 rds : OK

$$\overleftarrow{\gamma} = 1 \; ; \overrightarrow{\gamma} = 0 \; ; \; \upsilon = 1 \; ; \; r = 1 \; ; \overleftarrow{\alpha} = \frac{3}{2} \; \& \; \overrightarrow{\alpha} = \frac{1}{2}$$

Step-1 rds: Not ok

$$\overleftarrow{\gamma} = 2 \; ; \overrightarrow{\gamma} = 0 \; ; \; \upsilon = 1 \; ; \; r = 0 \; ; \overleftarrow{\alpha} = 2 \; \& \; \overrightarrow{\alpha} = 0$$

HW: Calculate the theoretical Anodic & Cathodic Tafel slope of **"lni vs η"** in each case