5.3: DISSOLUTION OF IRON

$Fe + H_2O \rightleftharpoons FeOH + H^+ + e^-$; Eq Const K_1…… 1

$FeOH \rightleftharpoons FeOH^+ + e^-$; Eq Const K_2…….. 2*(OK)

$FeOH^+ + H^+ \rightleftharpoons Fe^{2+} + H_2O$; Eq Const K_3 ……3

Let us **assume step-2 as rds**.

Hence, the B.V.Eq : $i = i_a - i_c$, for the rds is

$i = F[k_2\theta_{FeOH}\, e^{(1-\beta)\Delta\phi F/RT} - k_{-2}[FeOH^+]e^{-\beta\Delta\phi F/RT}]$ …….…… 4

The terms: θ_{FeOH} & $[FeOH^+]$ must be eliminated

From the equilibrium step-1

Anodic rate = Cathodic rate

$Fk_1e^{(1-\beta)\Delta\phi F/RT} = F\, k_{-1}\, \theta_{FeOH}[H^+]\, e^{-\beta\Delta\phi F/RT}$

$$\theta_{FeOH} = [FeOH] = \frac{e^{\Delta\phi F/RT}}{K_1[H^+]}$$

$$= \frac{1}{K_1 K_W}[OH^-]e^{\Delta\phi F/RT} \quad \text{……5}$$

From step-3 and expressions for K_W we get $[FeOH^+]$ as,

$$[FeOH^+] = \frac{[Fe^{2+}]}{K_3[H^+]}$$

$$= \frac{[Fe^{2+}][OH^-]}{K_3K_W} \quad \text{---------- 6}$$

Hence, from equation-5 & 6 , substituting the expression for θ_{FeOH} and $[FeOH^+]$ in the B.V.Eq for rds **(Eq-4)** , it becomes

$$i = F\left[k_2 \frac{1}{K_1K_W}[OH^-]e^{\Delta\phi F/RT}\, e^{(1-\beta)\Delta\phi F/RT} - k_{-2}\frac{[Fe^{2+}][OH^-]}{K_3K_W} e^{-\beta\Delta\phi F/RT}\right]$$ ……..……7

Prof. Dr. A. DAYALAN

i.e., $i = i_o[e^{(2-\beta)\eta F/RT} - e^{-\beta\eta F/RT}]$ 8

Hence, the anodic and the cathodic transfer coefficients are respectively 1½ & ½ in agreement with the experimental values. ***Therefore, the mechanism with "Step-2 as rds", is the correct one.***

From the B.V.Eq for the step-2 rds **(Eq-5)** it is seen that the orders are as observed.

The other possible mechanisms for the dissolution of iron.

Mech : A

$Fe + OH^- + FeOH \rightleftharpoons (FeOH)_2 + e$

$FeOH)_2 \rightleftharpoons 2\ FeOH$

$FeOH \rightleftharpoons FeOH^+ + e$

$FeOH^+ \rightleftharpoons Fe^{2+} + OH^-$

Mech : B

$Fe + OH^- \rightleftharpoons FeOH^+ + 2e$

$FeOH^+ \rightleftharpoons Fe^{2+} + OH^-$

Mech : C

$Fe + H_2O \rightleftharpoons FeOH + H^+ + e$

$FeOH \rightleftharpoons FeOH^+ + e$

$FeOH^+ + Fe \rightleftharpoons Fe_2OH^+$

$Fe_2OH^+ \rightleftharpoons Fe^{2+} + FeOH + e$

$FeOH + H^+ \rightleftharpoons Fe^{2+} + H_2O + e$

Mech : D

$Fe + OH^- \rightleftharpoons FeOH + e$

$FeOH + OH^- \rightleftharpoons FeO + H_2O + e$

$FeO + OH^- \rightleftharpoons HFeO_2^-$

$HFeO_2^- + H_2O \rightleftharpoons Fe(OH)_2 + OH^-$

$Fe(OH)_2 \rightleftharpoons Fe^{2+} + 2OH^-$

Note: In Mech – C , two "Fe" are involved becoming two Fe^{2+} thereby loosing 4e.

Mech: E

$Fe + H_2O \rightleftharpoons FeOH + H^+ + e$

$FeOH \rightleftharpoons FeOH^+ + e$

$FeOH^+ + OH^- \rightleftharpoons Fe^{2+} + H_2O$

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