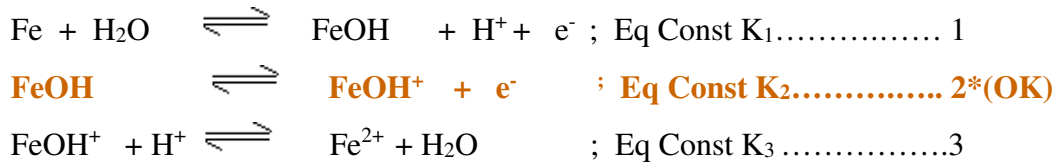


5.3: Dissolution of Iron

5.3: DISSOLUTION OF IRON



Let us assume step-2 as rds.

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

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

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

From the equilibrium step-1

Anodic rate = Cathodic rate

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

$$\begin{aligned}
 \theta_{\text{FeOH}} = [\text{FeOH}] &= \frac{e^{\Delta\phi F/RT}}{K_1[\text{H}^+]} \\
 &= \frac{1}{K_1 K_w} [\text{OH}^-]e^{\Delta\phi F/RT} \dots\dots\dots 5
 \end{aligned}$$

From step-3 and expressions for K_w we get $[\text{FeOH}^+]$ as,

$$\begin{aligned}
 [\text{FeOH}^+] &= \frac{[\text{Fe}^{2+}]}{K_3[\text{H}^+]} \\
 &= \frac{[\text{Fe}^{2+}][\text{OH}^-]}{K_3K_w} \dots\dots\dots 6
 \end{aligned}$$

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

$$i = F\left[k_2 \frac{1}{K_1 K_w} [\text{OH}^-]e^{\Delta\phi F/RT} e^{(1-\beta)\Delta\phi F/RT} - k_{-2} \frac{[\text{Fe}^{2+}][\text{OH}^-]}{K_3 K_w} e^{-\beta\Delta\phi F/RT} \right] \dots\dots\dots 7$$

5.3: Dissolution of Iron

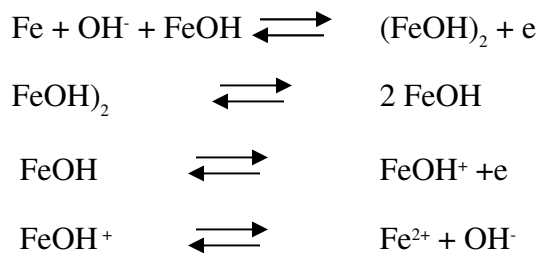
i.e., $i = i_0[e^{(2-\beta)\eta F/RT} - e^{-\beta\eta F/RT}] \dots\dots\dots 8$

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.*

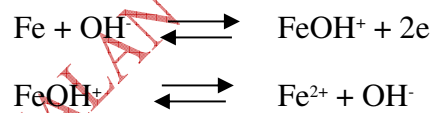
From the B.V.Eq for the step-2 rds (Eq-5) it is seen that the orders are as observed.

The other possible mechanisms for the dissolution of iron.

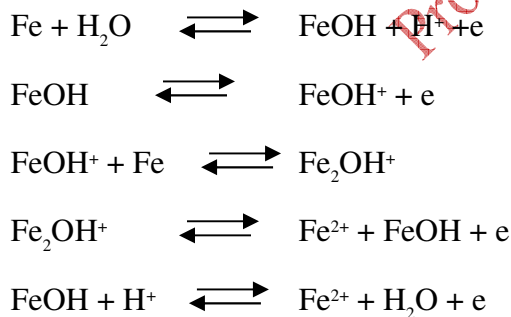
Mech : A



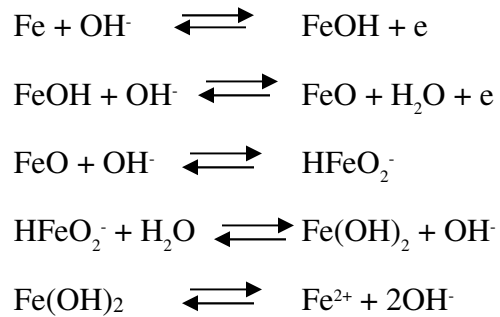
Mech : B



Mech : C



Mech : D



Note: In Mech – C , two “Fe” are involved becoming two Fe²⁺ thereby losing 4e.

Mech: E

