HOMEWORK # 5

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30/30

: 3.8

Problem # 3.8 Given the following one electron half cell reaction, derive Nernst Equ. from Butler-Volmer equation.

Anode: $\frac{1}{2} H_2 \longleftrightarrow H^+ + e^-$ (A)

Cathode: $H^+ + e^- + \frac{1}{4} O_2 \longleftrightarrow \frac{1}{2} H_2O$ (C)

using equation 3.51 (textbook) for anode (A):

$$j^A = j_0^A \left(\left(\frac{C_{H_2}^{*A}}{C_{H_2}^{o*A}}\right)^{1/2} \exp(1\alpha^A F\eta^A/RT) - \left(\frac{C_{H^+}^{*A}}{C_{H^+}^{o*A}}\right)^1 \left(\frac{C_{e^-}^{*A}}{C_{e^-}^{o*A}}\right)^1 \exp(-(1-\alpha)F\eta^A/RT) \right)$$

for cathode:

$$j^C = j_0 \left[\left(\frac{C_{O_2}^{*C}}{C_{O_2}^{o*C}}\right)^{1/4} \left(\frac{C_{H^+}^{*C}}{C_{H^+}^{o*C}}\right)^1 \left(\frac{C_{e^-}^{*C}}{C_{e^-}^{*oC}}\right)^1 \exp(1\cdot\alpha^C F\eta^C/RT) - \left(\frac{C_{H_2O}^{*C}}{C_{H_2O}^{o*C}}\right)^{1/2} \exp(-(1-\alpha^C) F\eta^C/RT) \right]$$

At equilibrium, $j^A = j^C = 0$

$$\Rightarrow \left(\frac{C_{H_2}^{*A}}{C_{H_2}^{o*A}}\right)^{1/2} \exp(\alpha^A F\eta^A/RT) = \left(\frac{C_{H^+}^{*A}}{C_{H^+}^{o*A}}\right)\left(\frac{C_{e^-}^{*A}}{C_{e^-}^{o*A}}\right) \exp(-(1-\alpha)F\eta^A/RT)$$

taking natural logarithm function

$$\frac{1}{2}\ln\left(\frac{C_{H_2}^{*A}}{C_{H_2}^{*oA}}\right) + \frac{\alpha^A F\eta^A}{RT} = \ln\left(\frac{C_{H^+}^{*A}}{C_{H^+}^{*oA}}\right) + \ln\left(\frac{C_{e^-}^{*A}}{C_{e^-}^{o*A}}\right) - \frac{(1-\alpha)F\eta^A}{RT}$$

Rearranging:

$$\frac{F\eta^A}{RT} = \frac{-1}{2}\ln\left(\frac{C^{*A}_{H_2}}{C^{0*A}_{H_2}}\right) + \ln\left(\frac{C^{A}_{H^+}}{C^{0*A}_{H^+}}\right) + \ln\left(\frac{C^{*A}_{e^-}}{C^{0*A}_{e^-}}\right)$$

using definition of activity

$$\eta^A = \frac{RT}{2F}\left(-\frac{1}{2}\ln(a^{*A}_{H_2}) + \ln(a^{*A}_{H^+}) + \ln(a^{*A}_{e^-})\right)$$

$$\boxed{\eta^A = \frac{RT}{F}\left(-\frac{1}{2}\ln(a^{*A}_{H_2}) + \ln(a^{*A}_{H^+}) + \ln(a^{*A}_{e^-})\right)}$$

Similarly for cathode.

$$\boxed{\eta^C = \frac{RT}{F}\left(-\ln(a^{*C}_{H^+}) - \ln(a^{*C}_{e^-}) - \ln(a^{*C}_{O_2})^{1/4} + \ln(a^{*C}_{H_2O})^{1/2}\right)}$$

At equilibrium, $\eta^A + \eta^C = E^0 - E$

net overvoltage = (actual voltage − reference voltage)

$$\Rightarrow \eta^A + \eta^C = E^0 - E = \frac{RT}{F}\left(\ln\left[\frac{(a^{*C}_{H_2O})^{1/2}}{(a^{*C}_{O_2})^{1/4}(a^{*A}_{H_2})^{1/2}}\right] - \ln\left(\frac{a^{*C}_{H^+}}{a^{*A}_{H^+}}\right) - \ln\left(\frac{a^{*C}_{e^-}}{a^{*A}_{e^-}}\right)\right)$$

(for one electron) ~~this~~ is the required form of Nernst equation

($\ln(a^{*C}_{H^+}/a^{A}_{H^+})$ & $\ln(a^{C}_{e^-}/a^{A}_{e^-})$ are small at equilibrium)

On rearranging

$$E^0 - E = \frac{RT}{2F}\left(\ln\left(\frac{a^{C}_{H_2O}}{(a^{C}_{O_2})^{1/2} a^{A}_{H_2}}\right) - \ln\left(\frac{a^{C}_{H^+}}{a^{A}_{H^+}}\right)^2 - \ln\left(\frac{a_{e}^{C}}{a_{e}}\right)^2\right)$$

Problem # 3.10

Anode: $R \longleftrightarrow P$

$$j = j_0\left(\frac{C_R^*}{C_R^{0*}}\exp(\alpha n F \eta/RT) - \frac{C_P^*}{C_P^{0*}}\exp(-(1-\alpha)nF\eta/RT)\right)$$

Given: Reference concentrations C_R^{0*} & C_P^{0*} (not equal to concentrations at zero current density (C_R^{**} & C_P^{**})

At equilibrium, $C_R^* = C_R^{**}$ & $C_P^* = C_P^{**}$

Let η_A = activation overvoltage at anode at equilibrium

such that $\eta = \eta_A$ at equilibrium

at equilibrium $j_1 = j_2$

$$\Rightarrow \quad \cancel{j_0}\frac{C_R^{**}}{C_R^{0*}}\exp(\alpha n F\eta_A/RT) = \cancel{j_0}\frac{C_P^{**}}{C_P^{0*}}\exp\left(-(1-\alpha)\frac{nF\eta_A}{RT}\right)$$

$\Rightarrow$ taking logarithm function:

$$\ln\left(\frac{C_R^{**}}{C_R^{0*}}\right) + \frac{\alpha n F\eta_A}{RT} = \ln\left(\frac{C_P^{**}}{C_P^{0*}}\right) - \frac{(1-\alpha)nF\eta_A}{RT}$$

$$\Rightarrow \quad \frac{nF\eta_A}{RT} = \ln\left(\frac{C_P^{**}}{C_P^{0*}}\right) - \ln\left(\frac{C_R^{**}}{C_R^{0*}}\right)$$

$$\Rightarrow \quad \eta_A = \frac{RT}{nF} \ln\left(\frac{C_P^{**} \cdot C_R^{o*}}{C_P^{o*} \cdot C_R^{**}}\right) \longleftarrow \text{Ans } 3.10(a)$$

3.10 (b)

given new overvoltage: $\eta' = \eta - \eta_A$.

Rewriting Butler-Volmer equation using η'

(let j_0^{**} is exchange current density, corresponds to C_R^{**} & C_P^{**})

$$j = j_0^{**}\left(\frac{C_R^*}{C_R^{**}} \exp\left(\frac{\alpha n F \eta'}{RT}\right) - \frac{C_P^*}{C_P^{**}} \exp\left(-\frac{(1-\alpha) n F \eta'}{RT}\right)\right)$$

where j_0^{**} can be found as follows

at $C_R^* = C_R^{o*}$ & $C_P^* = C_P^{o*}$, $j = j_0$

$$\Rightarrow \quad j_0 = j_0^{**}\left(\frac{C_R^{o*}}{C_R^{**}} \exp\left(\frac{\alpha n F \eta'}{RT}\right) - \frac{C_P^{o*}}{C_P^{**}} \exp\left(\frac{(1-\alpha) n F \eta'}{-RT}\right)\right)$$

$$\Rightarrow \quad j_0^{**} = \frac{j_0}{\left(\frac{C_R^{o*}}{C_R^{**}} \exp\left(\frac{\alpha n F \eta'}{RT}\right) - \frac{C_P^{o*}}{C_P^{**}} \exp\left(-\frac{(1-\alpha) n F \eta'}{RT}\right)\right)}$$

'5'

Problem 3.15 net current density is given by following:

$$j = j_0 \left(\frac{C_R^*}{C_R^{0*}} \exp\left(\frac{\alpha n f \eta}{RT}\right) - \frac{C_P^*}{C_P^{0*}} \exp\left(-\frac{(1-\alpha) n f \eta}{RT}\right) \right)$$

where $j_0 = A \exp\left(-\frac{\Delta G^\ddagger}{RT}\right)$

assuming 'A' to be independent of T

Case-1: Let us study the effect of ~~doubling~~ the temperature assuming overvoltage (η) is sufficiently high

$\Rightarrow \eta \in (50 - 120\ mV)$ $\eta >> 1\ mV$

at T: $j_T = j_0 \exp\left(\frac{\alpha f n \eta}{RT}\right) = A \exp\left(\frac{\alpha n f \eta - \Delta G^\ddagger}{RT}\right)$

at 2T: $j_{2T} = A \exp\left(\frac{\alpha n f \eta - \Delta G^\ddagger}{2RT}\right)$

$$\boxed{\frac{j_{2T}}{j_T} = \exp\left(\frac{\Delta G^\ddagger - \alpha n f \eta}{2RT}\right)} \quad \text{--- (1)}$$

now if $\Delta G^\ddagger > \alpha n f \eta \Rightarrow$ current increases with increasing temperature.

& $\Delta G^\ddagger < \alpha n f \eta \Rightarrow$ current decreases with increasing temperatures.

Case 2: halving the activation barrier $\Delta G^{\ne} \to \frac{\Delta G^{\ne}}{2}$

$$j_{\Delta G^{\ne}} = A \exp\left(\frac{\alpha F n \eta - \Delta G^{\ne}}{RT}\right)$$

$$j_{\frac{\Delta G^{\ne}}{2}} = A \exp\left(\frac{2\alpha F \eta n - \Delta G^{\ne}}{2RT}\right)$$

$$\boxed{\frac{j_{\frac{\Delta G^{\ne}}{2}}}{j_{\Delta G^{\ne}}} = \exp\left(\frac{\Delta G^{\ne}}{2RT}\right)} \Rightarrow \frac{j_{\frac{\Delta G^{\ne}}{2}}}{\cancel{}} \text{ always positive}$$

(2)

$\Rightarrow$ $j_{\Delta G^{\ne}}$ current density always increases with halving of ~~to~~ activation barrier.

Next, assuming $\Delta G^{\ne} > \alpha F \eta$, Comparing eqn (1) & (2) (with $\Delta G^{\ne} > \alpha n F \eta$)

$\Downarrow$

because $\exp\left(\frac{\Delta G^{\ne}}{2RT}\right) > \exp\left(\frac{\Delta G^{\ne} - \alpha n F \eta}{2RT}\right)$

Ans $\Rightarrow$ $\Rightarrow$ halving of activation barrier affects the current density more significantly than doubling of temperature (assuming $\Delta G^{\ne} > \alpha n F \eta$)