Chem 558 – Kinetics Homework

1] In class we considered the current-potential characteristics of a system where MT effects were not important. That equation breaks down to the Nernst equation (why?) when equilibrium conditions prevail. In B+F there is an equation that expressed the i-E characteristics when MT effects are apparent in the electrochemical cell.

$$i = i_0 \left[\frac{C_{ox}(0,t)}{C_{ox}^b} \exp \frac{-\alpha n F \eta}{RT} - \frac{C_{red}(0,t)}{C_{red}^b} \exp \frac{(1-\alpha) n F \eta}{RT} \right] \qquad (3.4.10)$$

Show how this equation breaks down the Nernst equation under equilibrium conditions. What does the say about the potential of the solution vs. electrode surface when MT effects are important?

2] The Butler-Volmer equation follows as:

$$i_{total} = i_0 \left(\exp\left(\frac{-\alpha F \eta}{RT} \right) - \exp\left(\frac{(1-\alpha) F \eta}{RT} \right) \right) \qquad (3.4.11)$$

Using the identity $e^x \approx 1 + x$ for small values of x. Show that for small values of η, i vs. η is linear.

3] What is the derived unit of the slope for the relationship discovered in the problem above? What effect does i_0 have on this slope?

4] The Tafel characteristics for a solution of Fe^{2+}/Fe^{3+} was obtained and the results shown below. The area of the platinum electrode was 1.5 cm^2. Calculate α and i_0 for this syste.

η(V)	i (mA)
0.02	3.20
0.05	9.95
0.07	17.03
0.10	35.18
0.012	55.89
0.15	110.78
0.20	343.62

5] If i_0 = 2.5e-5 A/m^2 and α = 0.5 for the $Cu^{2+} + 2e^- = Cu$ system, calculate the overpotential required to deposit Cu(s) from a 1 M Cu^{2+} solution at i = 5e-3 A/m^2.

Answers

1] For equilibrium let i = 0;

$$0 = i_0\left[\frac{C_{ox}(0,t)}{C_{ox}^b}\exp\frac{-\alpha nF(E-E_{Nernst})}{RT} - \frac{C_{red}(0,t)}{C_{red}^b}\exp\frac{(1-\alpha)nF(E-E_{Nernst})}{RT}\right]$$

$$\frac{C_{ox}(0,t)}{C_{ox}^b}\exp\frac{-\alpha nF(E-E_{Nernst})}{RT} = \frac{C_{red}(0,t)}{C_{red}^b}\exp\frac{(1-\alpha)nF(E-E_{Nernst})}{RT}$$

at equilibrium we should realize that $\alpha = ½$

$$\frac{C_{ox}(0,t)}{C_{ox}^b}\exp\frac{-\frac{1}{2}nF(E-E_{Nernst})}{RT} = \frac{C_{red}(0,t)}{C_{red}^b}\exp\frac{\frac{1}{2}nF(E-E_{Nernst})}{RT}$$

$$\frac{C_{ox}(0,t)}{C_{red}(0,t)} = \frac{C_{ox}^b}{C_{red}^b}\exp\frac{nF(E-E_{Nernst})}{RT}$$

note that $E_{Nernst} = E^0 + \frac{RT}{nF}\ln\frac{C_{ox}^b}{C_{red}^b}$ or $\frac{C_{ox}^b}{C_{red}^b} = \exp\frac{nF(E_{Nernst}-E^0)}{RT}$ sub this into above we have

$$\frac{C_{ox}(0,t)}{C_{red}(0,t)} = \exp\frac{nF(E_{Nernst}-E^0)}{RT}\exp\frac{nF(E-E_{Nernst})}{RT}$$

$\frac{C_{ox}(0,t)}{C_{red}(0,t)} = \exp\frac{nF(E-E^0)}{RT}$ or simply

$$E = E^0 + \frac{RT}{nF}\ln\frac{C_{ox}(0,t)}{C_{red}(0,t)}$$

Note that this is the SURFACE potential is different than $E_{Nernst} = E^0 + \frac{RT}{nF}\ln\frac{C_{ox}^b}{C_{red}^b}$ which reflects the potential in the BULK of the solution. This indicates that the two potentials are different when MT effects are in place.

2] $i_{total} = i_0\left(\exp\left(\frac{-\alpha F\eta}{RT}\right) - \exp\left(\frac{(1-\alpha)F\eta}{RT}\right)\right)$ using $e^x \approx 1 + x$

$$i_{total} = i_0\left(1 - \frac{\alpha F\eta}{RT} - 1 + \frac{(1-\alpha)F\eta}{RT}\right)$$

$$i_{total} = i_0 \frac{\alpha F\eta}{RT}$$

3] For the plot of i vs. η the slope = $i_0 \frac{\alpha F}{RT}$. Remember that $\frac{RT}{F} = volts$, and Ohm's law is E = iR. This means that the slope has units of 1/Ω.

The inverse of the slope is $\frac{RT}{i_0 \alpha F}$, which has units of ohms! This is referred to as the charge transfer resistance (R_{CT}). Note as i_0 decreases, R_{CT} increases as should expect.

4] Tafel eqn. $\eta = \frac{-0.0592}{\alpha}\log i_0 - \frac{0.0592}{\alpha}\log i$

plot log i vs. η   slope = -9.89 = α/0.0592   α = 0.59

intercept = 0.39 = log i_0 i_0 = 2.46 mA/cm^2

5] Using $\eta = \frac{-0.0592}{\alpha}\log i_0 - \frac{0.0592}{\alpha}\log i$

$$\eta = -\frac{0.0592}{0.5}\log 2.5\times10^{-5} - \frac{0.0592}{0.5}\log 5\times10^{-3} = 0.272 \text{ V}$$