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.

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

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.