For the following electrochemical cell, what are the redox half reactions, the net cell reaction, $E_{\text{cell}}$, $\Delta G_{\text{rxn}}$ and $K_{eq}$? This cell had a resistance of 4.00 ohms. Calculate the potential when it is producing a current of 0.100 mA.

$$\text{Cd} | \text{Cd}^{2+}(0.100 \text{m}) \parallel \text{Cu}^{2+} | \text{Cu}$$

$\text{Cd} \rightleftharpoons \text{Cd}^{2+} + 2e^-$ c Deluxe $E^0 = -0.403 \text{V}$

$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu} \text{ c cathode } E^0 = 0.334 \text{V}$

$\text{Cu}^{2+} + \text{Cd} \rightleftharpoons \text{Cd}^{2+} + \text{Cu}$

$E_a = -0.403 \text{V} + \frac{0.0592 \log (0.100)}{2} = -0.433 \text{V}$

$E_c = 0.334 \text{V} + \frac{0.0592 \log (0.100)}{2} = 0.304 \text{V}$

$E_{\text{cell}} = E_c - E_a = 0.304 \text{V} - (-0.433 \text{V}) = 0.737 \text{V}$

$$\Delta G_{\text{rxn}} = nFE_{\text{cell}} = -(2)(96,480 \text{Coul} / \text{mol}) (0.737 \text{V}) = -1.42 \times 10^5 \text{ J/mol}$$

$K_{eq} = -\frac{RT \ln K_{eq}}{nFE_{\text{cell}}} = \Delta G_{\text{rxn}}$

$$E_{\text{cell}} = E_c - E_a - \ell R = 0.737 - (0.100 \times 10^{-3} \text{A})(4.00 \text{V}) = 0.737 - 4.0 \times 10^{-5} \text{V}$$

$\ell R = (1.0 \times 10^{-4} \text{A})(4.0) = 4.0 \times 10^{-4} \text{V}$

$E_{\text{cell}} = E_{\text{cell, rev}} - \ell R = 0.737 - 4.0 \times 10^{-5} \text{V} = 0.737 \text{V}$

Essentially recharge
2 (25 pts). Describe (use sketches) the structure of an electric double layer formed at a Au electrode in KCl at a potential well negative of the point of zero charge. Be sure to illustrate how the potential, \( \phi \), varies through the solution layer. Finally, sketch the current-voltage curves for a reduction reaction (Ox + e = Red) when \( \Delta \phi \) exists almost entirely across the compact layer and when only about 50% of \( \Delta \phi \) occurs across the compact layer.

Double layer effects, lower \( \Delta \phi \) at place 9
Closest approach will cause \( E_2 \) to shift Negative. Classical double layer effect.
3 (25 pts). Researchers studying the electron transfer kinetics of a novel redox reaction (BM$_{ox}$ + 2e = BM$_{red}$) at a clean carbon electrode determined some kinetic parameters: ($\alpha$=0.5 and $k^0 = 4.3 \times 10^5 \text{ s}^{-1}$). For an electrode area of 0.5 cm$^2$ and [BM$_{ox}$]=[BM$_{red}$]=10 $\mu$M, what exchange current is predicted? What exchange current density is predicted?

\[
I_0 = nFAk^0 C(1-\alpha)C^\alpha = nFAk^0 C
= (2)(96,500 \text{ Coul} / \text{mol})(0.5 \text{ cm}^2)(4.3 \times 10^5 \text{ s}^{-1})(1.0 \times 10^{-9} \text{mol/cm}^3)
= 4.1 \times 10^{-8} \text{ A} \text{ or } 8.2 \text{ nA/cm}^2
\]

A plot of log i vs. $\eta$, known as a Tafel plot, is useful for evaluating kinetic parameters. What is the predicted Tafel slope for the cathodic reaction assuming the reaction follows Butler-Volmer kinetics?

\[
\text{Slope} = \frac{2.303RT}{\alpha nF} \quad \text{assuming $\alpha$ = 0.5 and $n$ = 2}
\]

Then slope is 0.059 V/decade

Explain why there is an expected log i vs. $\eta$ relationship for redox reactions following Butler-Volmer kinetics.

The next current is predicted to increase exponentially with $\eta$ ($E$-$E^0$). This is because the activation barrier for ET decreases with increasing overpotential. This is reflected in the Arrhenius equation.

\[
\text{Rate} = \frac{k}{A} \exp \left( -\frac{\Delta G^\circ}{RT} \right)
\]

$\Delta G^\circ = \Delta G^\circ + nFE(E-E^0) \quad \text{assuming forward run is cathodic, i.e.}

2 \text{ Ox} + 2 \epsilon \rightleftharpoons \text{ Red}
4 (25 pts). What are the three modes of mass transport? What are Fick’s 1st and 2nd laws of diffusion?

\[
J = \frac{\dot{n}}{nFA} = -D \frac{\partial C}{\partial x} \bigg|_{x=0} \quad \text{1st law}
\]

\[
\frac{\partial C}{\partial t} \bigg|_{x=0} = D \left( \frac{\partial^2 C}{\partial x^2} \right) \bigg|_{x=0}
\]

Really, \[
J = \frac{\dot{n}}{nFA} = -D \left( \frac{\partial C(x,t)}{\partial x} \right) \bigg|_{x=0} \quad \text{and} \quad \frac{\partial C(x,t)}{\partial t} \bigg|_{x=0} = D \left( \frac{\partial^2 C(x,t)}{\partial x^2} \right) \bigg|_{x=0}
\]

For the following current-voltage curve, sketch the concentration-distance profiles and describe why the current increases or decreases.

At pt. #2 current increases steeply as there is a step curve gradient \( \left( \frac{\partial C}{\partial x} \right) \bigg|_{x=0} \) up, thicker depletion layer.

#3, #4 decreasing curve, gradient \( \left( \frac{\partial E}{\partial x} \right) \bigg|_{x=0} \) down.