Problem!

Cathode : $H_2O(l) + e^- \rightleftharpoons \frac{1}{2} H_2 (g, 1.0 bar) + OH^- (aq, 0.10M)$

$E° = -0.828V$

Anode : $Br^- (aq, 0.10M) \rightleftharpoons \frac{1}{2} Br_2 (l) + e^-$ $E° = 1.078V$

$\frac{1}{2} Br_2 (l) + e^- \rightleftharpoons Br^- (aq, 0.10M)$

a) Calc voltage needed to drive net rxn if current neglible

b) Cell resistance of 2.0 Ohm & current of 100mA. How much V is needed to overcome the cell resistance (ohmic potential)?

c) Anode rxn has overpotential of 0.20v & cathode over potential of 0.40v. What Voltage is needed to overcome these effects combined with those parts a + b

d) [ ] polarization occurs [OH⁻] at the cathode surface ↑ to 1.0M and [Br⁻] at anode surface ↓ to 0.010M. What V is needed to overcome these effects combined with those of (b) & (c)?

a) $E = E_{cath} - E_{ANODE}$

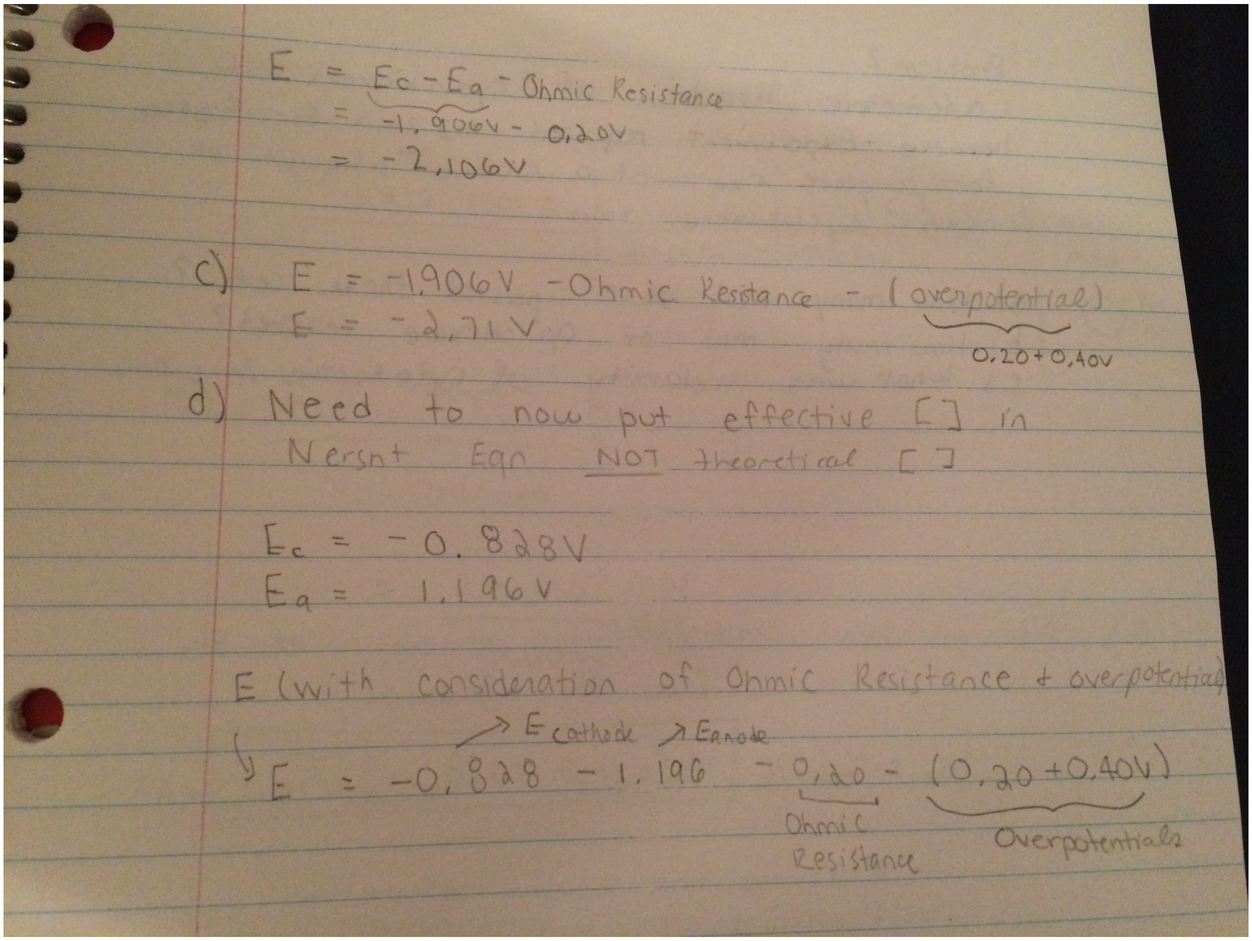
$= \{ E_c° - 0.05916 \log P_{H_2}^{1/2} [OH^-] \} - \{ E_a° - 0.05916 \log [Br^-] \}$

$E = -1,906V$

b) use Ohm's law → $U = R \cdot I = 0,100A \cdot 2,0 \Omega$

$= 0,20V$

(ohmic resistance of soln)



$E = \underbrace{E_c - E_a} - \text{Ohmic Resistance}$

$= -1,906V - 0,20V$

$= -2,106V$

c) $E = -1,906V - \text{Ohmic Resistance} - (\underbrace{\text{overpotential}}_{0,20 + 0,40V})$

$E = -2,71V$

d) Need to now put effective [ ] in Nersnt Eqn <u>NOT</u> theoretical [ ]

$E_c = -0.828V$

$E_a = 1.196V$

E (with consideration of Ohmic Resistance + overpotential)

$E = \overset{E_{cathode}}{-0,828} - \overset{E_{anode}}{1.196} - \underbrace{0,20}_{\text{Ohmic Resistance}} - \underbrace{(0,20 + 0.40V)}_{\text{Overpotentials}}$

Problem 2

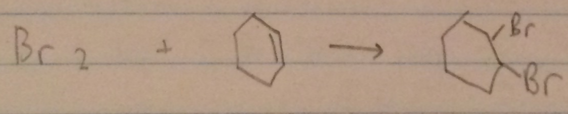
Coulometric Titration of cyclohexene with bromine. Experiment required 5.32 mA for 964 sec for complete rxn of a 5.00 mL aliquot of unkwn cyclohexene soln.

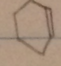
a) How many mol of e^- passed thru cell?
b) How many mol of cyclohexane reacted?
c) What was molarity of cyclohexene in unkwn

a) KBr in soln → Electrolytic generation of Br_2 from the Bromine

$2Br^- \rightarrow Br_2 + 2e^-$ (964 sec, 5.32 mA)

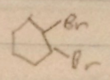
= determines the amount of insitu then know how much product produced

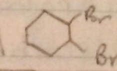


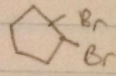
1 mol e^- reacts with ½ mole of Br_2 which in turn reacts with ½ 

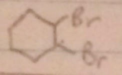
⇨ moles e^- produced $= \frac{I \times t}{F} = \frac{(5.32 \times 10^{-3}\ C/s) \times 964\ s}{1 \cdot e^- \times 96485\ C/mol}$

$\boxed{\text{mole } e^- = 5.32 \times 10^{-5}\ \text{mol}}$
passed thru cell

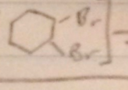
b) mole e^- produces $2,66 \times 10^{-5}$ mol 

$5,32 \times 10^{-5}$ mol e^- | 1 mol Br^2 / 2 mol e^- | 1 mol  / 1 mol Br_2 = $\boxed{2,66 \times 10^{-5} \text{ mol}}$



c) moles  / Vol aliquot = [ ]

$$= \frac{2,66 \times 10^{-5} \text{ mol}}{5,00 \times 10^{-3} \text{ L}}$$

[] = $5,32 \times 10^{-3}$ M

More advantage since can count e^- easily

→ why electroanalysis with insitu titrant

Problem 3

Suppose that the diffusion current in a polarogram for reduction of Cd^{2+} at a mercury electrode is 14 μA.
If soln contains 25 mL of 0.5 mM Cd^{2+} what % of Cd^{2+} is reduced in the 3.4 min required to scan from $\underbrace{-0.6 \text{ to } -1.2\text{V}}$?

voltage sweep (half-wave potential) → determines that it is Cd

diffusion current → current produces by signal due to reduction of Cd^{2+} at electrode

Duration of process: e^- flowing for 3.4 min of 14 μA

$$\text{mol } e^- = \frac{14 \times 10^{-6}\ \text{C/s} \times 60\text{s} \times 3.4\text{min}}{96485\ \text{C/mol}}$$

$$\boxed{\text{mol } e^- = 2.96 \times 10^{-8}\ \text{mol}}$$

$Cd^{2+} + 2e^- \rightarrow Cd(s)$ at Hg electrode

⇨ 1.48×10^{-8} mol Cd^{2+} that are reduced

Initial: 25 mL of 0.5 mM soln

Initial moles of Cd^{2+} in soln: $25\text{mL}\left(\frac{1\text{L}}{1000\text{mL}}\right)(0.5\text{mM})$
$= 1.25 \times 10^{-5}$ mol

Fraction: $\frac{1.48 \times 10^{-8}\text{mol (reduced)}}{1.25 \times 10^{-5}\text{mol (intial)}} \times 100 = 0.12\%$

Prblm 4

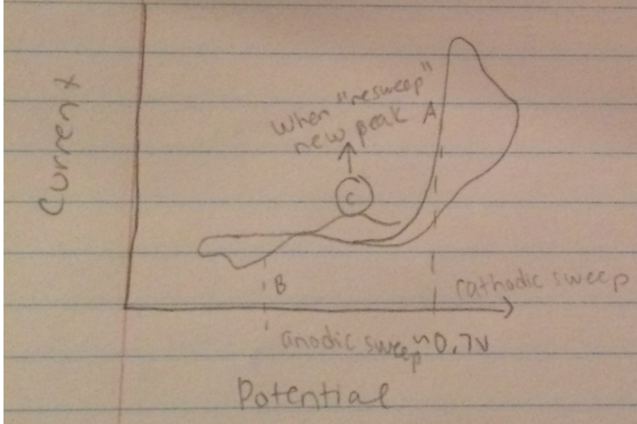
Cyclic voltammogram of antibiotic chloramphenicol shown here.
1st cathodic scan goes from 0 to -1.0V
1st cathodic wave A from rxn

$$RNO_2 + 4e^- + 4H^+ \rightarrow RNHOH + H_2O$$

Peak B in reverse anodic scan could be assigned to

$$RNHOH \rightarrow RNO + 2H^+ + 2e^-$$

2nd cathodic scan +0.9 to -0.4V, new peak C appears. Write rxn peak C + explain why peak C was not seen in initial scan.



Reverse anodic scan = forms new product (RNO)

When rescan cathodic sweep = RNO reacts and forms RNHOH hence the appearance of peak C