Problem 1 – 3.1, 3.3, 3.6, 4.3 from the B&F text:

20 pts 3.1

a) The equation to use for this problem is 3.4.6:

$$i_0 = FAk^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$$

6 pts for the right equations

And therefore:

$$j_0 = \frac{i_0}{A} = Fk^0 C_O^{*(1-\alpha)} C_R^{*\alpha}$$

We were given values for all of these variables, so:

$$j_0 = \frac{9.64853 \times 10^4 C}{\cancel{mol}} \times \frac{10^{-7} cm}{s} \times \frac{(10^{-3})^{0.7} \cancel{mol^{0.7}}}{\cancel{L^{0.7}}} \times \frac{(10^{-3})^{0.3} \cancel{mol^{0.3}}}{\cancel{L^{0.3}}} \times \frac{1\ \cancel{mL}}{1\ cm^3} \times \frac{1\ \cancel{L}}{10^3\ \cancel{mL}}$$
$$= 9.648 \times 10^{-9} \frac{A}{cm^2}$$

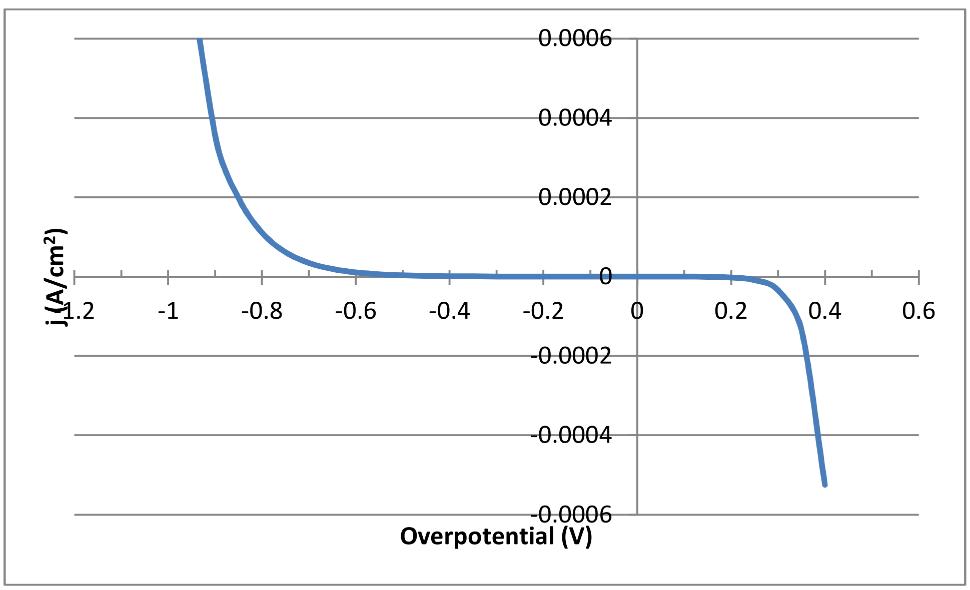
2 pts for correct number, 2 pts for correct units

b) Neglecting mass transfer, we can use 3.4.11:

$$j = j_0\left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}\right]$$

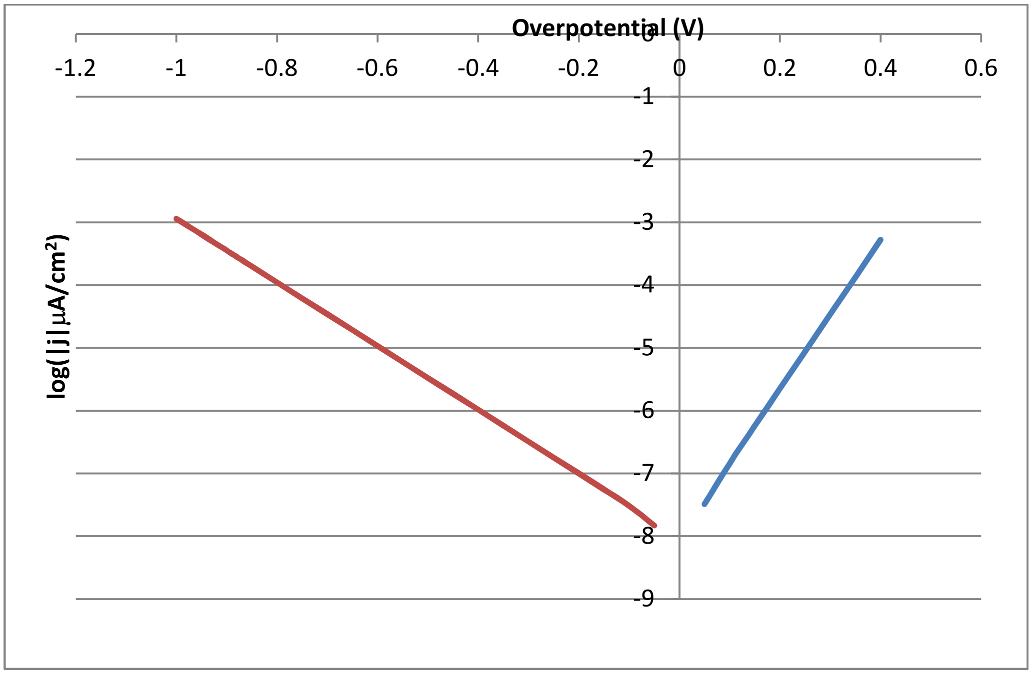
Which gives us the plot shown below:

5 points for this graph



c) Taking the log, we obtain this plot:

5 pts for this graph



3.3a To use the given equation, we first need to calculate i_0, $i_{l,c}$ and $i_{l,a}$ (see Bard 1.4.9 and 1.4.17):

20 pts

$$i_0 = FAk^0 C_O^{*(1-\alpha)} C_R^{*\alpha} = 9.65 \times 10^{-4} A$$

$$i_{l,c} = nFA\, m_O C_O^* = 9.65 \times 10^{-1} A$$

$$i_{l,a} = -nFAm_R C_R^* = -9.65 \times 10^{-3} A$$

10 pts for these equations and values and units

We also need to calculate the Nernstian potential of the solution, so that we can calculate the overpotential:

$$\eta = E - E_{eq}$$

$$E_{eq} = E^0 + \frac{RT}{nF} ln\left(\frac{C_O^*}{C_R^*}\right) = -0.5\ V + 0.118\ V = -0.382\ V$$

Thus, all of the plots should go through zero current at E = -0.382 V. Note that you will get the same value for E if you use equation 1.4.20 where i=0 (at equilibrium) because m_O=m_R and because when i=0 $i_{l,c}$ divided by $i_{l,a}$ will give the bulk concentration terms as above.

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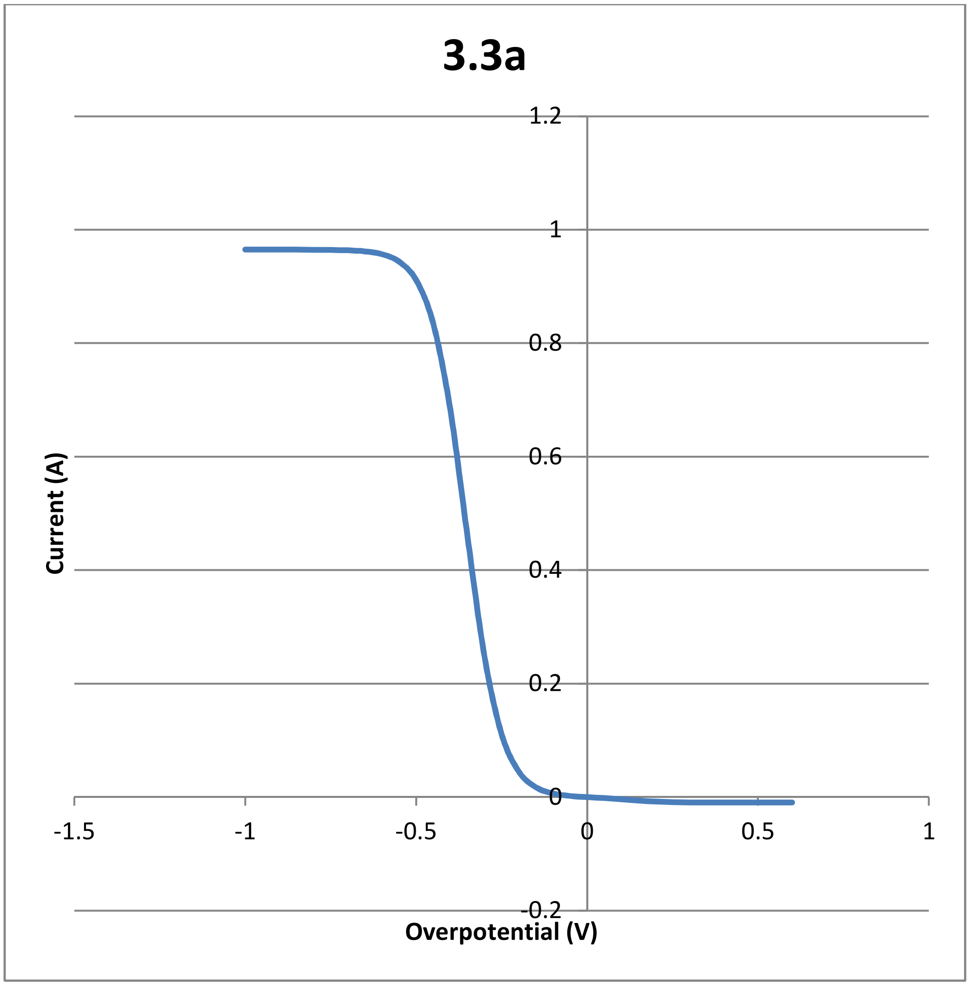
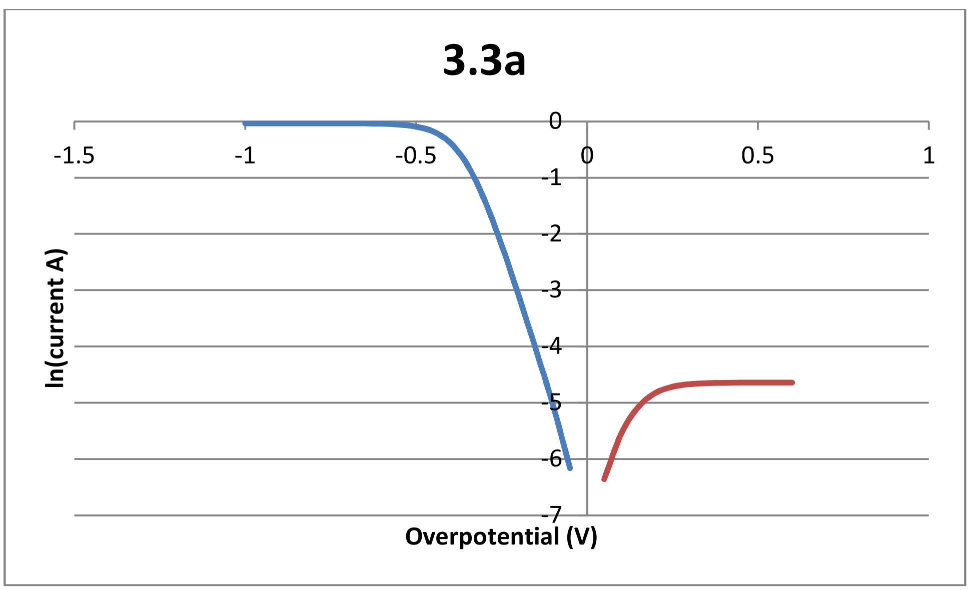
3.3a (cont'd) Table of values:

E	Current (A)	ln(abs(i))	Overpotential (V)
-1.382	0.96485	-0.0358	-1
-1.332	0.96484	-0.0358	-0.95
-1.282	0.96483	-0.0358	-0.9
-1.232	0.96479	-0.0358	-0.85
-1.182	0.96469	-0.0360	-0.8
-1.132	0.96441	-0.0362	-0.75
-1.082	0.96369	-0.0370	-0.7
-1.032	0.96179	-0.0390	-0.65
-0.982	0.95678	-0.0442	-0.6
-0.932	0.94376	-0.0579	-0.55
-0.882	0.91096	-0.0933	-0.5
-0.832	0.83421	-0.1813	-0.45
-0.782	0.68207	-0.3826	-0.4
-0.732	0.45998	-0.7766	-0.35
-0.682	0.24700	-1.3984	-0.3
-0.632	0.11093	-2.1988	-0.25
-0.582	0.04506	-3.0997	-0.2
-0.532	0.01743	-4.0495	-0.15
-0.482	0.00649	-5.0381	-0.1
-0.432	0.00210	-6.1636	-0.05
-0.382	0.00000	#NUM!	0
-0.332	-0.00173	-6.3591	0.05
-0.282	-0.00389	-5.5482	0.1
-0.232	-0.00625	-5.0750	0.15
-0.182	-0.00801	-4.8267	0.2
-0.132	-0.00896	-4.7151	0.25
-0.082	-0.00938	-4.6696	0.3
-0.032	-0.00954	-4.6519	0.35
0.018	-0.00961	-4.6451	0.4
0.068	-0.00963	-4.6425	0.45
0.118	-0.00964	-4.6415	0.5
0.168	-0.00965	-4.6412	0.55
0.218	-0.00965	-4.6410	0.6

5 pts for a table, particularly with values such that $E-\eta = -0.382V$ as calculated above



5 points for both graphs (combined)



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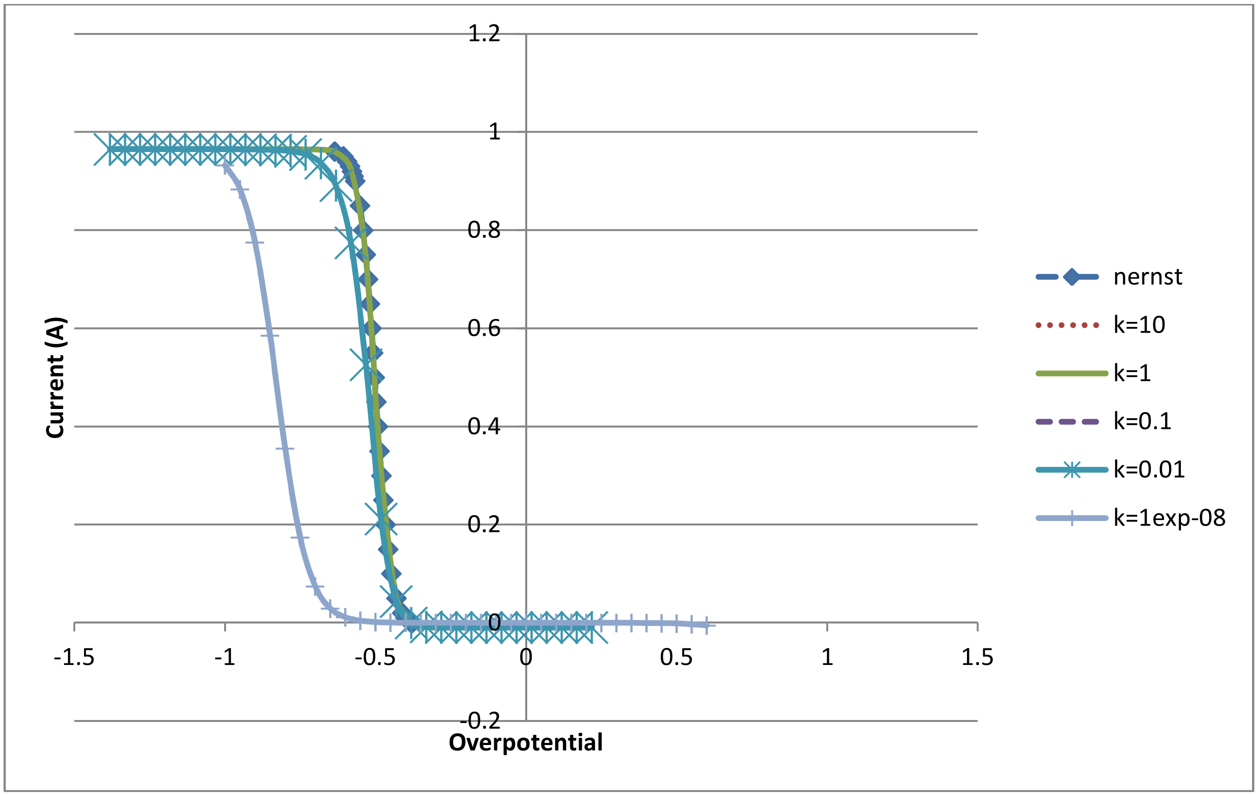
3.3 b Now we just need some plots where we've varied k^0. Also, since the problem asks to compare to the Nernstian curve, we can plot the Nernstian curve using Eq. 1.4.20:

$$E = E^{0\prime} - \frac{RT}{nF} ln \frac{m_O}{m_R} + \frac{RT}{nF} ln \left(\frac{i_{l,c} - i}{i - i_{l,a}} \right)$$

5 pts for this graph and answering the question

The plots look like this, converging to the Nernstian curve as k^0 increases:



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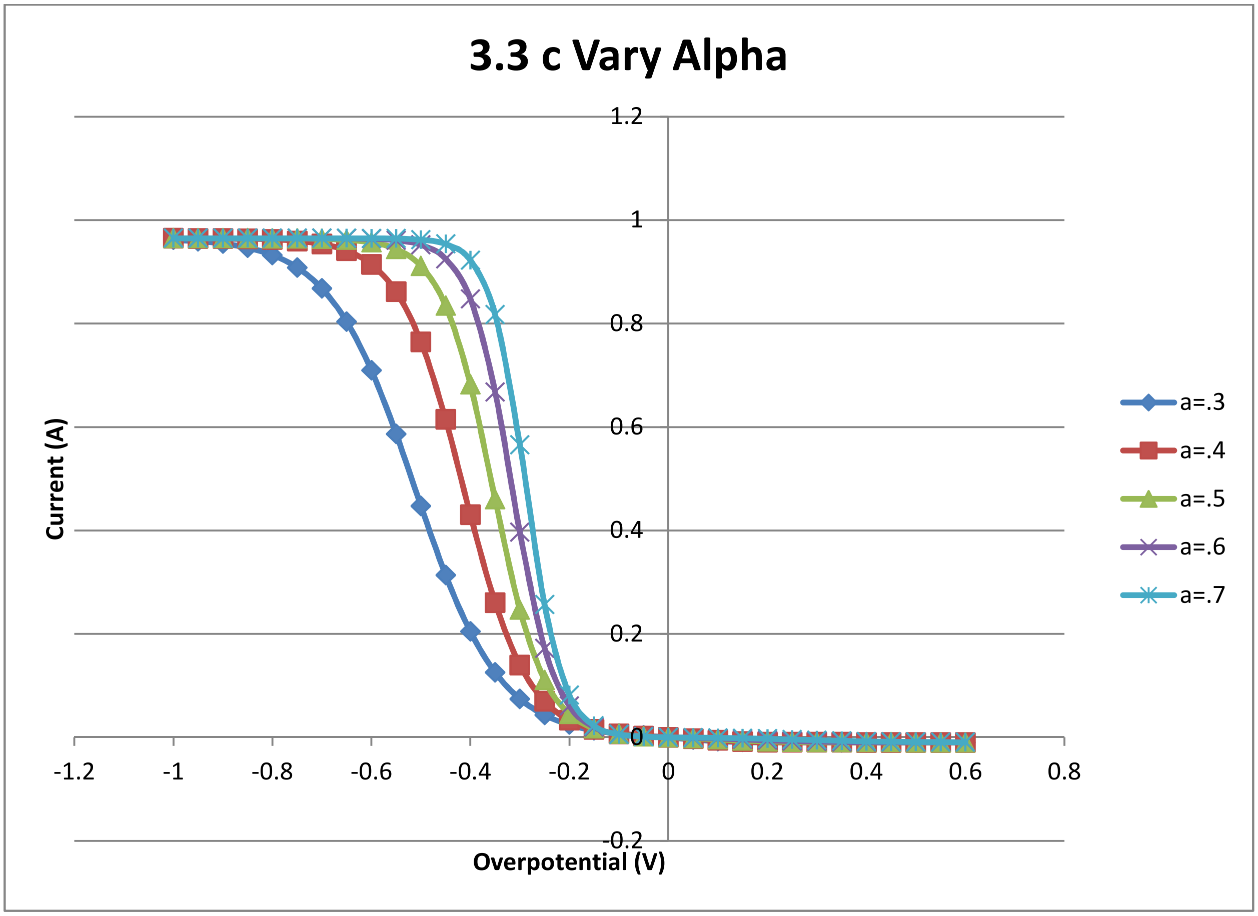
5 pts for a graph like this

c) Varying α within the range of typical values gives curves looking like this:



3.6

20 pts

a) We can rearrange Eq 3.4.6 to get:

$$k^0 = \frac{i_0}{FAC_O^{*(1-\alpha)}C_R^{*\alpha}} =$$

10 pts

$$\frac{2\times10^{-3}A}{cm^2}\times\frac{mol}{9.65853\times10^4C}\times\frac{L^{0.5}}{(2\times10^{-3}\ mol)^{0.5}}\times\frac{L^{0.5}}{(2\times10^{-3}mol)^{0.5}}\times\frac{1000cm^3}{L} = 1\times10^{-2}cm/s$$

b) Using the value of k0 from part a, and just changing the concentrations using Eq 3.4.6, we find for solutions with 1 M concentrations, j_0=1.0 A/cm^2

5 pts

c) We calculate i0 again using Eq 3.4.6 and the given concentrations, to get i_0=9.648 μA, and then use Eq 3.4.13 to calculate R_{CT}:

$$R_{CT} = \frac{RT}{Fi_0} = \frac{8.31447\,J}{mol\ \mathrm{K}}\times298K\times\frac{mol}{9.64853\times10^4C}\times\frac{s}{9.648\times10^{-6}C} = 2.67k\Omega$$

5 pts

4.3 Use Eq. 4.4.3 to find the thickness of a diffusion layer:

20 pts

$$\overline{\Delta} = \sqrt{2Dt} = \sqrt{2 \times 100s \times 1 \times 10^{-5}\frac{cm^2}{s}} = 0.045\ cm$$

Thus, to have at least 5 diffusion-layer thicknesses, the distance is at least 0.224 cm (2.24 mm).

20 pts

Problem 2

Given the RC time constant, we first calculate the length of time that we must wait before there is negligible contribution from double-layer charging. Typically we can use 5 times the RC constant as a rule of thumb. Thus, t = 5 ms. At this time, the smallest current that we can detect using our potentiostat is 0.1 μA/cm^2. We can rearrange the Cottrell equation to obtain the desired concentration:

$$i(t) = \frac{nFAD_0^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

15 pts

$$C_O^* = \frac{j\pi^{\frac{1}{2}}t^{\frac{1}{2}}}{nFD_O^{\frac{1}{2}}} = \frac{0.1 \times 10^{-6}A}{cm^2} \times \pi^{\frac{1}{2}} \times (5 \times 10^{-3}s)^{\frac{1}{2}} \times \frac{mol}{9.648 \times 10^4 C} \times \frac{1}{\left(1 \times 10^{-5}\frac{cm^2}{s}\right)^{\frac{1}{2}}}$$

$$= 4.1 \times \frac{10^{-8}mol}{L}$$

If 3RC is used instead of 5RC, then 31.8 nM is obtained as the smallest detectable concentration.

5 pts