

CH 117 PS3

Solutions

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Revisions, Notes, etc. Feb 22, 2017 KMP

Problem 1

25 pts

A) In order to determine if this is a mass-limited process, we should compare its behavior to the integrated Cottrell equation:

$$Q_f(t) = \frac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}} + Q_{dl} + nF\Gamma_O \quad (1)$$

2 pts for this relationship

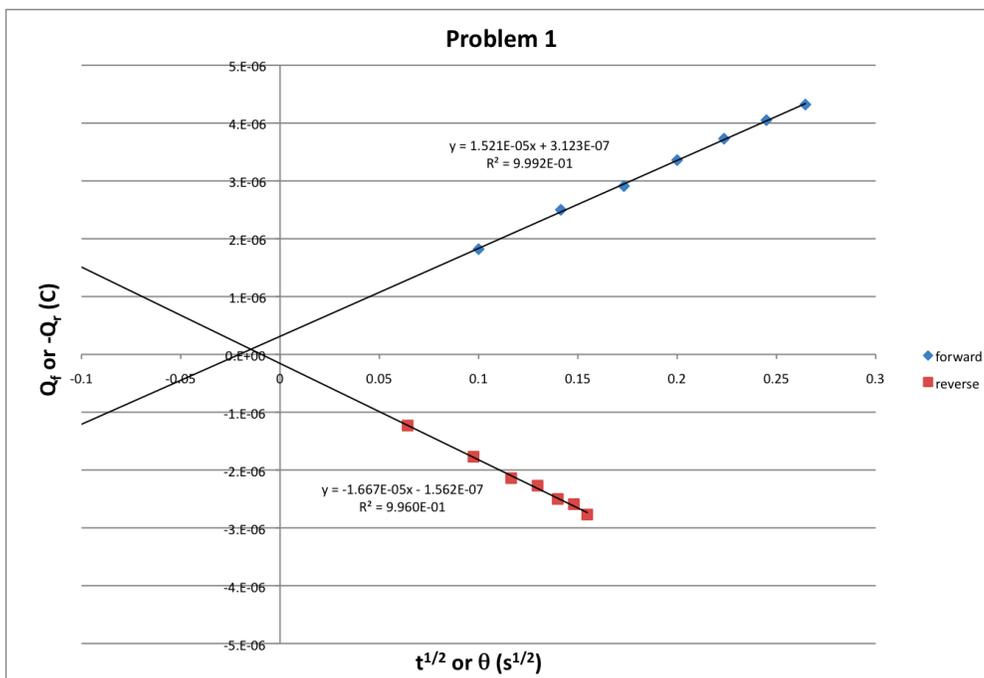
Thus, we expect a plot of $Q(t)$ vs. $t^{1/2}$ to be linear. Measuring several values of $Q(t)$ from the printed plot, we obtain the plot shown below of $Q_f(t)$ vs. $t^{1/2}$ (ignore Q_r for now). From this plot, we can see that the data fit a line well, so the process is likely to be diffusion limited. We find the following values for the slope and intercept.

$$\text{slope} = \frac{2nFAD_O^{1/2}C_O^*}{\pi^{1/2}} = 1.52 \times 10^{-5} \text{ C s}^{-1/2}$$

$$\text{y-intercept} = Q_{dl} + nF\Gamma_O = 3.12 \times 10^{-7} \text{ C}$$

6 pts, 4 for making a graph,
2 for intercept with units

This is the right thing to do, but the values for the slope and intercept are going to have a very strong dependence on the exact data points. What you do here is also going to affect the other parts of this question. So, for grading purposes, I am only looking at procedure and units.



B) In order to determine if the process involves adsorption of Cd ions at the Hg interface before the oxidation process, we need to eliminate the contribution from the double layer above. Using the reverse step, we can calculate the value of Q_{dl} . First, we measure the values of Q with t from the plot given. Then we calculate the values of $Q_r(t) = Q(\tau) - Q(t > \tau)$, where τ is the time of the second potential step ($\tau \approx 74.5$ ms in this case). We can then plot $Q_r(t)$ vs. θ , where $\theta \equiv \tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}$, to obtain a linear plot (Bard 5.8.6):

$$Q_r(t > \tau) = \frac{2nFAD_O^{1/2}C_O^*}{\pi^{1/2}}\theta + Q_{dl} \quad (2)$$

2 points for this equation

The plot of $-Q_r(t)$ vs. θ is shown above. We've plotted it this way so that the graph is comparable to the sort of graph usually seen in the literature. Notice from this plot that intercept is slightly larger for the forward step than the reverse step, indicating the presence of some contribution from adsorbed species. Also note that the intersection of the two lines is above the t axis.

We will now quantify this effect. From the fit, we have:

$$\text{slope} = \frac{2nFAD_O^{1/2}C_O^*}{\pi^{1/2}} = 1.67 \times 10^{-5} \text{ C s}^{1/2}$$

$$\text{y-intercept} = Q_{dl} = 1.57 \times 10^{-7} \text{ C}$$

6 pts, 4 for a graph, 2 for an intercept with units

Thus, we have independently measured Q_{dl} , and we can then calculate the value of $nFA\Gamma_O$ from above. Note that this is only valid if we assume no surface adsorption of the reduced Cd species and if the reverse jump returns to the initial potential. Both should be valid assumptions in this case. Using the intercept above, we can calculate:

$$\Gamma_O = \frac{3.13 \times 10^{-7} - Q_{dl}}{nFA} = 2.53 \times 10^{-11} \text{ mol/cm}^2 = 1.67 \times 10^{13} \text{ molecules/cm}^2$$

4 pts for answering yes if your intercepts don't match. The question didn't ask us to actually calculate how much adsorption

This indicates a small amount of adsorbed molecules, probably significantly less than one monolayer (for comparison, there are about $10^{15}/\text{cm}^2$ surface sites on Si surface). Given that the data are measured from a small graph by hand and that the intercept is an extrapolated value, this is probably within the error of the experiment. Thus, answers will vary depending on how the plot is measured.

This is an important point about error. The conclusion of the original paper was that there was no adsorption, and the number here is very sensitive to the values in your plot (and the linear regression thereof). So, ~1% of a monolayer (as Jim calculated here) is probably within experimental error of 0% (i.e., the same things as far as we can tell).

C) We calculated Q_{dl} above, so we have:

5 pts

$$Q_{dl}/A = \frac{1.57 \times 10^{-7} \text{ C}}{0.032 \text{ cm}^2} = 4.91 \text{ } \mu\text{C/cm}^2$$

NOTE: the electrode used in this case was spherical, but the linear equations are used. Anson makes the case in the paper that at short times, this is still valid, but at long times it becomes a significant consideration. However, it should be noted that this makes our finding above that a very small amount of Cd^{2+} ions are adsorbed during the reduction process even more suspect.

Problem 2 - Bard Problems

25 pts

6.9

We first calculate the relevant values for each wave. The results are shown below:

First Wave								
ω (mV/s)	$\log \omega$	$i_{p,c}$ (μ A)	$i_{p,a}$ (μ A)	$-E_{p,c}$	$-E_{p,a}$	$i_{p,c}/\omega^{1/2}$	$i_{p,a}/i_{p,c}$	$\Delta E_{p/2}/\Delta \log \omega$
430	2.63	8	8	1.42	1.36	0.39	1	
298	2.47	6.7	6.7	1.42	1.36	0.39	1	0
203	2.31	5.2	5.2	1.42	1.36	0.36	1	0
91	1.96	3.4	3.4	1.42	1.36	0.36	1	0
73	1.86	3	2.9	1.42	1.36	0.35	0.97	0

Second wave								
ω (mV/s)	$\log \omega$	$i_{p,c}$ (μ A)	$-E_{p,c}$	$-E_{p/2}$	$i_{p,c}/\omega^{1/2}$	$\Delta E_{p/2}/\Delta \log \omega$	Average ω	
430	2.63	7	2.1	2	0.34			
298	2.47	6.5	2.09	2	0.38		0	364
203	2.31	4.7	2.08	2	0.33		0	250.5
91	1.96	3	2.07	1.99	0.31		0.03	147
73	1.86	2.8	2.06	1.98	0.33		0.10	82

8 pts for the plot and slope

First Wave: Recall that we can plot $i_p/\omega^{1/2}$ in place of the current function. We see that the current function is approximately constant, the peak ratio is approximately 1, and there is no shift in the peak potential with scan rate. These indicate mechanism I from Nicholson and Shain, the totally reversible mechanism. Therefore, we know that:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^* \omega^{1/2}$$

Watch out for units here. B&F don't tell you the units on the 2.69E5 number. If you work it out, the units are $\text{Cmol}^{-1}\text{V}^{-0.5}$

We can then plot i_p vs. $\omega^{1/2}$ and calculate D_O using the slope of the resulting linear fit and $A = 0.0154 \text{ cm}^2$, $n = 1$, and $C_O^* = 6.8 \times 10^{-7} \text{ mol/cm}^2$.

$$D_O = \left(\frac{\text{slope}}{(2.69 \times 10^5) A C_O^*} \right)^2 = 2.16 \times 10^{-5} \text{ cm}^2/\text{s}$$

4 pts

Repeating this procedure for the reverse wave, we find $D_R = 2.23 \times 10^{-5} \text{ cm}^2/\text{s}$, which is equal to D_O within experimental error.

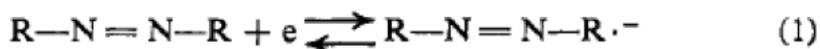
Second Wave: In this case, there is no anodic wave, so the mechanism must be one of II, IV, or VIII from Nicholson and Shain. We notice that again the current function is constant with scan rate. This implies that mechanism

II is correct. Noting also that $\Delta E_{p/2}/\Delta \log \omega$ is also nearly flat, we see that mechanism II is indeed the correct choice. Thus, the second peak is a totally irreversible wave. Given this information, we can determine α using:

$$E_p - E_{p/2} = \frac{47.7\text{mV}}{\alpha} \approx 86\text{mV} \implies \alpha = 0.55 \quad \text{B\&F Eq 6.3.11}$$

13 pts

Although the data above argue for mechanism II, only a limited range of scan rates was measured. If we assume that we are in the low scan rate portion of the plots shown in Nicholson and Shain, the results are consistent with a reversible charge transfer followed by a very fast, irreversible chemical transformation, mechanism VI. In this case, a possible chemical mechanism for the observed behavior is:



The question doesn't actually say we need to speculate this far

Where HS is any proton donor.

6.12

25 pts

a) Our first objective is to calculate ψ . We can as shown below (recall that $D_O = D_R$ in this case):

$$\psi = \Lambda \pi^{-1/2} = \frac{\left(\frac{D_O}{D_R}\right)^{\alpha/2} k^0}{(\pi D_O f \omega)^{1/2}} = \frac{k^0}{(\pi D_O f \omega)^{1/2}}$$

We can thus obtain a table of ψ values and use table 6.5.2 from Bard to calculate ΔE_p . The results are shown below. The value of ΔE_p for $\omega = 3$ mV/s was just taken to be the reversible value.

ω (V/s)	ψ	ΔE_p (mV)
3	46.84	59.2
30	14.81	62
100	8.11	63
200	5.74	64
300	4.68	65
500	3.63	66

20 pts

Values for E_p are a bit larger than this according to B&F and when I did the calculation

b) The values shown here for ΔE_p are higher than predicted in part a. One likely explanation for these results is the significant iR losses expected at high scan rates. This is particularly likely given that the supporting electrolyte concentration was reduced from 0.5 M in part a to 0.1 M in part b.

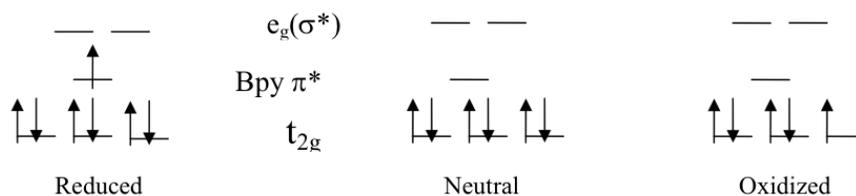
5 pts for any reasonable speculation

Problem 3

This was a poorly posed problem. Generous with credit for all reasonable attempts.

25 pts

A) The bpy ligand is reduced in the reduction wave and the metal is oxidized during the oxidation wave. The following diagram shows the correct MO scheme (this diagram was shown in the lecture on $W(\text{bpy})(\text{CO})_4$).



5 pts

B) This question is stupid because the diffusion limited current is a function of time (as you should know by now). Maybe Bocarsly was after something else, but I don't see what. In any case, you don't have to do it.

Skipped this
one per email

C) The double layer capacitance can be found from $i_c = AC_d\omega$, where i_c is the current above zero in the baseline. We can estimate this current by taking the difference in the baselines in the middle panel and dividing by two. Since we know that the scan rate is 100 mV/s, we can calculate AC_d the double layer capacitance. I measure $i_c = 4.2 \mu\text{A}$. This gives $AC_d = 42 \mu\text{F}/\text{cm}^2$.

5 pts

D) Without looking at the scan rate dependence, we only have two pieces of information at our disposal— ΔE_p and $i_{p,c}/i_{p,a}$. By measuring the plots, we find that $i_{p,c} \approx i_{p,a}$, suggesting that these are reversible peaks. The ΔE_p values, shown in the table below, are a bit high for reversible waves, but they are expected to be somewhat large due to the high resistance of the medium used.

5 pts

Metal	ΔE_p
Cr	118 mV
Mo	98 mV
W	82 mV

Without further evidence, we can conjecture that these might be reversible peaks, but we can't be sure.

E) Since the problem asks you speculate, credit will be given for reasonably cogent speculations. Again, I'm not certain what Bocarsly was originally after. It is possible that there is some difference in the binding of Cr to CO as compared to Mo and W. There may also be significant differences because Cr is a first-row transition metal, and they tend to have significantly different chemistry compared to second and third row transition metals.

5 pts

F) With the data given, we can only calculate two of the three diagnostics recommended by Nicholson and Shain ($i_{p,a}/i_{p,c}$ and $i_p/\omega^{1/2}$). Therefore, if we get it wrong, they can't be held responsible. We obtain the plots shown below. It is difficult to draw conclusions from these plots. Mechanism V is the only one that seems to fit the current function plot, since V is the only mechanism that increases with increasing scan rate. However, we expect to see a decrease in $i_{p,a}/i_{p,c}$ with increasing scan rate for mechanism V, and we see an increase in the data. Only mechanisms V and VI show values of $i_{p,a}/i_{p,c} < 1$, so it is likely one of these two. These are both EC mechanisms. Thus the data point to a chemical reaction (either reversible or irreversible) following the reduction, but the results are far from conclusive. Again, any reasonably cogent speculation about the mechanism will be accepted.

5 pts

