Ch117 – Electrochemistry
Final Exam Solution Set

there was a typo here originally

20 pts 1) A solution contains 2.0×10^{-3} M Fe^{3+} and 1.0×10^{-3} M Sn^{4+} in 1 M HCl (aqueous). The solution is examined by voltammetry at a rotating platinum disk electrode of area 0.30 cm^2. At the rotation rate employed, both Fe^{3+} and Sn^{4+} have mass-transfer coefficients, *m*, of 10^{-2} cm/s. For this problem, assume that the electrode reactions are Nernstian and that no changes to the bulk concentrations occur.

This problem is essentially B&F 1.3.

a. What are the three most important reactions that will occur if the potential of the Pt disk electrode is scanned from +1.2 V to -0.10 V? Include the standard potentials for those reactions in your answer.

Use Table C.1 to answer this question. In this window, we expect:

$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ E^0=0.771 V vs NHE 2 pts each

$Sn^{4+} + 2e^- \rightleftarrows Sn^{2+}$ E^0=0.150 V vs NHE

$2H^+ + 2e \rightleftarrows H_2$ E^0=0.000 V vs NHE

b. Calculate the limiting current for the reduction of Fe^{3+} and for the reduction of Sn^{4+} under these conditions.

The limiting current is given by Eq 1.4.9:

$$i_l = nFAm_O C_O^*$$

Note that the limiting current will be the same for both species because the difference in concentrations is cancelled out by the difference in n.

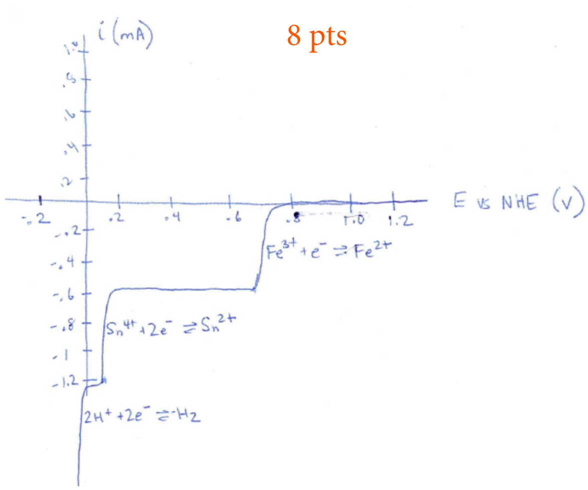
6 pts, 3 ea for Fe^{3+} and Sn^{4+}

Plugging in our variables, we get:

$$i_l = 1 \times \frac{96485C}{mol} \times 0.30cm^2 \times \frac{10^{-2}cm}{s} \times \frac{2\times10^{-3}mol}{1000\ cm^3} = 5.8\times10^{-4}A \text{ or } 580\mu A$$

c. Apply your answers to parts a and b to make a labelled, qualitatively correct sketch of the current versus potential curve that would be obtained from a potential scan from +1.2 V to -0.10 V versus NHE for this system. Be sure to label the axes and to use a correct sign convention. Also label reactions associated with any inflection points on the sketch.

8 pts



20 pts

2) For the system Pt/H_2 (1 atm)/Na^+, OH^- (0.1 M)//Na^+, OH^- (0.1 M)/O_2 (0.2 atm)/Pt:

a. Write the half reactions and the full cell reaction including the standard potentials.

This is B&F 2.4a.

$O_2 + 2H_2O + 4e^- \rightleftarrows 4OH^-$ E^0=0.401 V 3 pts

$H_2 + 2OH^- \rightleftarrows 2H_2O + 2e^-$ E^0=-0.828 V 3 pts

$O_2 + 2H_2 \rightleftarrows 2H_2O$ E=1.229 V 3 pts

b. What is the emf for the cell (assuming standard conditions)?

$$E_{right} = 0.401\ V + \frac{0.059V}{4} \times log\frac{0.2}{0.1^4} = 0.449\ V$$ 3 pts

$$E_{left} = -0.828V + \frac{0.059V}{2} \times log\frac{1}{1 \times 0.1^2} = -0.769\ V$$ 3 pts

Emf = 0.449V—0.769 V=1.218 V 2 pts

c. Is the cell reaction spontaneous and how do you know?

Yes. The emf is positive (meaning ΔG is negative). 3 pts

3) The following data were obtained for the reduction of species R to R^- in a stirred solution at a 0.1 cm^2 electrode; the solution contained 0.01 M R and 0.01 M R^-, and E_{eq} was 535 mV:

20 pts

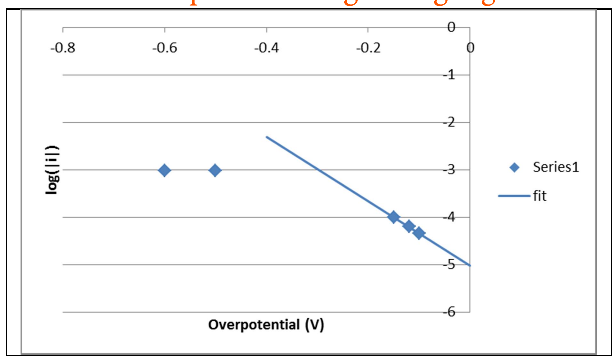
E (mV)	435	415	385	35	-65
i (μA)	-45.9	-62.6	-100	-965	-965

a) Make a Tafel plot for the data. Use an appropriate fit of the data to calculate i_0, k^0, and α.

This is adapted from 3.11

Here is the Tafel plot:

Deduct 10 pts for fitting wrong region of curve



The slope of the fit to the Tafel plot is -6.765 log(A)/V.

$i_0 = 10^{(-5.0149)}$ A = -9.662 ×10^{-6} A. 5 pts

$$slope = \frac{-\alpha F}{2.3RT}$$

$$\alpha = \frac{-2.3RT \times slope}{F}$$

$$\alpha = \frac{-2.3 \times 8.3J \times 298K \times -6.765mol}{molKV96485C} = 0.399$$ 5 pts

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

$$k^0 = \frac{i_0}{FA\ {}_O^{*(1-\alpha)} C_R^{*\alpha}} = \frac{9.662 \times 10^{-6} Cmol1000cm^3}{s96485C0.1cm^2 0.01mol} = 1 \times 10^{-4} cm/s$$ 5 pts

b) What is the charge-transfer resistance for this system?

$$R_{CT} = \frac{RT}{Fi_0} = \frac{8.3J298Kmol}{molK96485C9.662 \times 10^{-6}A} = 2.65k\Omega$$ 5 pts

20 pts

4) The effective time scale for kinetic measurements at a rotating disk electrode is ~1/ω.

a. What range of effective times is available for the usual range of rotation rates of an RDE?

$$\frac{1}{\omega} = \frac{1min}{10000rotations} \times \frac{60s}{min} \times \frac{rotations}{2\pi} = 9.5 \times 10^{-4}\, s$$

According to B&F section 9.3.6, the ranges of f are limited in most RDE studies to 100-10,000 rpm. So, the range of times is 0.95 ms ≤ t ≤ 95 ms. 7 pts

b. Ultramicroelectrodes provide an alternative steady-state electrode system for electrochemical studies. What range of UME radii yields the same effective time range as that calculated for the RDE? (Use B&F Figure 9.7.1 to answer this question.)

From the figure, this corresponds to radii ≥ 10μm. 7 pts

c. Can stationary UMEs be extended to even shorter times than an RDE at its maximum useful rotation rate? If yes, how? If no, why?

Yes, by using UMEs with smaller radii (< 5μm). 6 pts

20 pts

5) A disk UME gives a plateau current of 2.32 nA in the steady-state voltammogram for a species known to react with n=1 and to have a concentration of 1 mM and a diffusion coefficient of 1.2×10^{-5} cm^2/s. What is the radius of the electrode?

$$r_0 = \frac{i_{ss}}{4nFD_O C_O^*}$$

$$= \frac{2.32\times10^{-9}A}{4\times1}\times\frac{mol}{96500C}\times\frac{s}{1.2\times10^{-5}cm^2}\times\frac{1000\ cm^3}{1\times10^{-3}mol} = 5\times10^{-4}cm$$

deduct 5 pts for incorrect units