Ch117 – Electrochemistry

Final Exam

Due Thursday, March 16 by 4:00 p.m.

This exam is due to the box outside 210A Noyes no later than 4:00 p.m. on Thursday, March 16. The exam is untimed. You may consult the Bard & Faulkner text, your notes, anything posted on the course website (http://sunlight.caltech.edu/chem117), your past homework sets, and lab assignments.

You may not collaborate or talk about the exam with anyone or use any additional outside resources. You may use a calculator and spreadsheet program for calculations and plots, but you must show all work explicitly and you must include a printout of any work done by computer.

The exam consists of five questions either adapted or directly from the B&F text. The questions will be weighted equally toward the total grade (i.e., each of the five questions is worth 1/5 of the final exam grade).

1) [Based on B&F Q1.3]
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.

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.

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

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.

2) [This question is based on B&F Q2.4a]
For the aqueous 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.

b. What is the emf for the cell?

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

3) [This question is adapted from B&F Q3.11]
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:

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

Calculate i_0, k^0, α, R_{ct}, and i_l,using fit(s) from plot(s) of the data where appropriate.

4) [Based on B&F Q9.9]
The effective time scale for kinetic measurements at a rotating disk electrode is ~$1/\omega$.

a. What range of effective times corresponds to the practical limits of the range of useful rotation rates of an RDE?

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.)

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?

5) [B&F Q5.4]
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?