Key for Voltammetry Final

The final exam for voltammetry consists of three parts: questions that require relatively shorter responses; questions that require relatively longer responses; and questions that require calculations. You are free to use your textbook, the library, web resources, your work on take-home assignments, handouts, and your notes as you work on this exam. You are not free to discuss any portion of this exam with other students or with faculty members other than the instructor.

Your responses are due by 4:00 pm on Wednesday, November 15th. As you have access to lots of resources and ample time to work on the exam, your final product should be organized and neat. Answers to questions that require a written response must be typed, thoughtful, rich in detail, and written in complete sentences and, where required, in well-developed paragraphs. You may wish to annotate your response with appropriate figures drawn from resources available to you.

For questions that require calculations, organize your work so that the logic of your approach is clear. Please be sure that your work is neat and easy to follow, and that your final answer is clear. You may wish to annotate your work with short written descriptions that explain your approach to the problem.

Questions that draw on the paper "Spectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 1. Demonstration of Concept with Ferricyanide" by Shi, Slaterbeck, Seliskar, and Heineman refer to the SSSH paper. If you need a copy of the paper, you can access it by entering the following DOI into a browser: https://doi.org/10.1021/ac970322u.

The exam has 200 points, distributed as follows: Part I has 32 points; Part II has 96 points; Part III has 72 points.

Part I: Questions with Relatively Shorter Responses

Question IA. Figures 6c1 and 6c2 in the SSSH paper are cyclic voltammograms that correspond to the transmittance data in Figures 6b1 and 6b2. Prepare a new set of figures (6d1 and 6d2) that shows the current vs. time curves that correspond to the transmittance data in Figure 6a1 and 6a2. Explain how you arrived at your answer.

Answer. Figure 6a1 and Figure 6a2 use a potential step and are, therefore, chronoamperometry experiments. The following figure, created using `caSim` shows a general comparison of the two experiments; note: the relative relationship between the currents is correct, but the absolute values of the currents are not correct as they are based on the default conditions for `caSim`.
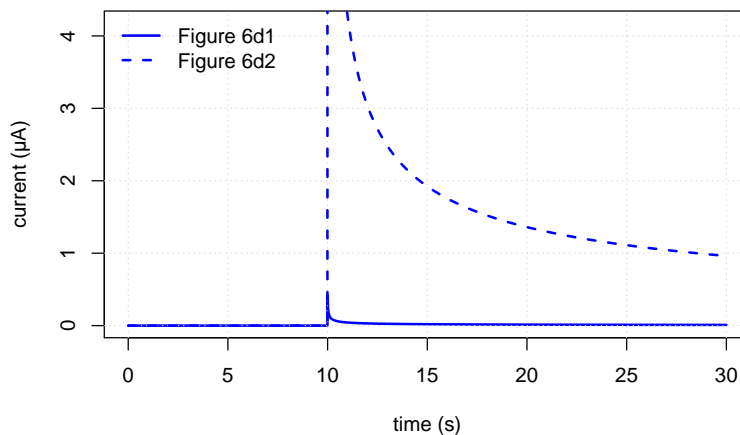
Question IB. Figure 4b in the SSSH paper shows a series of cyclic voltammograms recorded during the sensor's uptake of 1.0 mM $Fe(CN)_6^{4-}$. Draw a plot that shows how the peak current changes as a function of

the number of scans (from 1–50 scans). Explain how you arrived at your answer.

Answer. The authors note on page 3683 that after approximately 42 scans the current becomes fairly constant; thus, a plot of current vs. scans should show a linear increase through the first roughly 30-40 scans and should then level off to a relatively constant value thereafter.

Question IC. Are the data in Figure 6a1 and 6a2 of the SSSH paper consistent with the expected linear relationship of $-\log T = k[\text{Fe(CN)}_6^{4-}]$. Defend your answer with both appropriate calculations and a written explanation. If the data are not consistent with this equation, then explain why.

Answer. The data in these two figures are not consistent with Beer's law. At a concentration of 2.5×10^{-5} M, the transmittance is approximately 0.60, which gives $k = 8874$ M^{-1} s^{-1}. Substituting this value into Beer's law along with a concentration of 2.5×10^{-3} M gives an absorbance of 22 and an expected transmittance of 0; as the actual transmittance is approximately 0.10, the value of k must not be constant. The limitation here is that Beer's law fails when the concentration of the absorbing species is too large, which is consistent with the authors' observation that the linear range extends to approximately 5.0×10^{-5} M.

## Part II: Questions with Relatively Longer Written Responses

Question IIA. Use the function cvSim to determine how the cathodic peak current in cyclic voltammetry depends bulk concentration of Ox (C), the number of electrons in the reduction of Ox to Red (n), the electrode's surface area (A), the diffusion coefficient (D) for Ox, and the scan rate (ν). Document your work carefully with appropriate figures and propose a general equation that relates the cathodic peak current to these parameters. Do some research to find the known theoretical relationship between the peak current and these parameters and compare your result to this theoretical relationship.

Answer. Using cvSim, you should find that the current is a linear function of C and of A, that it is a linear function of $D^{1/2}$ and of $\nu^{1/2}$, and that it is a linear function of $n^{3/2}$. Putting this together gives us an overall equation of

$$i = k \times n^{3/2} \times D^{1/2} \times \nu^{1/2} \times C \times A$$

where k is a proportionality constant. The actual relationship is known as the Randles–Sevcik equation, for which $k = 268600$. If you measure the peak current using cvSim for known values of C, n, A, D, and ν, you should be able to obtain a value for k that is reasonably similar to the known value.

Question IIB. The plot below shows a set of four cyclic voltammograms obtained at scan rates of 0.1 V/s, 1 V/s, 5, V/s, and 10 V/s for an electroactive species that undergoes an EC mechanism with a forward chemical rate constant of 10 s^{-1} and a reverse chemical rate constant of 0 s^{-1}. Estimate values for the peak current ratio and for ΔE and discuss how these values are why they are consistent with an EC mechanism.
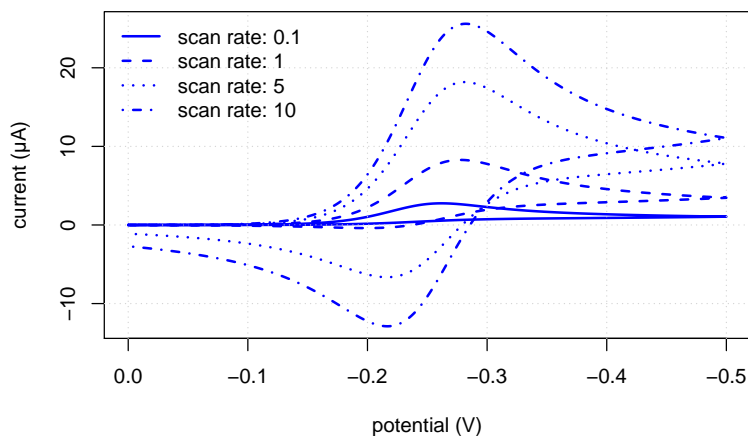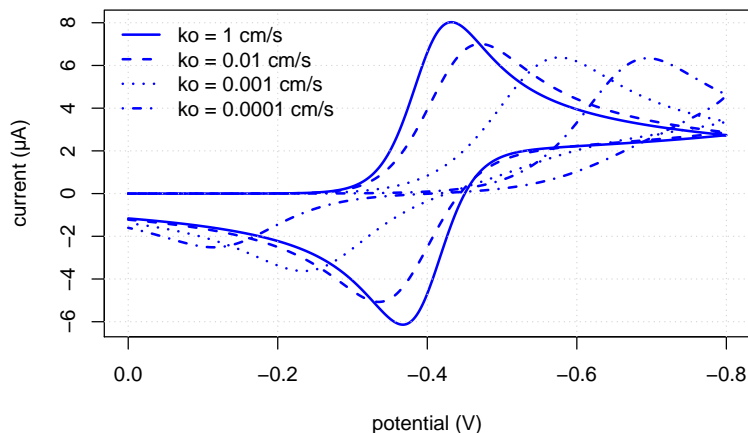

Estimated values for ΔE and for the peak current ratio are summarized below.

scan rate (V/s)	Delta E (V)	current ratio
0.1	NA	NA
1.0	0.08	0.3
5.0	0.065	0.6
10.0	0.065	0.8

For a system that is both chemically reversible and electrochemically reversible, we expect that ΔE is approximately 60 mV (although this value is somewhat larger in a `cvSim` simulation due to the limitations of the diffusion grid) and the peak current ratio is 1. For an EC mechanism of an Ox to Red reaction, where the chemical step is not reversible, the longer it takes to complete the forward scan the smaller the concentration of Red and the smaller the peak current on the return scan and the less chemically reversible the system. We see this behavior clearly with the decrease in the current ratio at slower scan rates. We also see that the system is less electrochemically reversible at slower scan rates—thus, the increase in ΔE—as no Red is available to convert back to Ox, which means that the system can no longer maintain a true thermodynamic equilibrium between Ox and Red.

Question IIC. The figure below shows four cyclic voltammograms for Ox to Red with a formal potential of –0.4 V. The mechanism in each case is E only with the standard heterogeneous electron transfer rate constant (k^o) taking on values of 1 cm/s, 0.01 cm/s, 0.001 cm/s, and 0.0001 cm/s. Explain the shapes of these curves in terms of the change in k^o. As part of your answer, clearly explain what k^o represents. The scan rate for all four cyclic voltammograms is 1 V/s.

Estimated values for ΔE and for the peak current ratio are summarized below.

rate constant (cm/s)	Delta E (V)	current ratio
1.000	0.06	0.98
0.010	0.14	0.95
0.001	0.34	0.7
0.001	0.58	NA

The heterogeneous electron-transfer rate constant, k^o, is the rate constant for the transfer of an electron from the solution species to the electrode or for the transfer of an electron from the electrode to a solution species. If the heterogeneous electron transfer rate constant is sufficiently large then the reactions Ox to Red and Red to Ox remain in equilibrium and the CV shows both chemical and electrochemical reversibility with $\Delta E \approx 60 mV$ and a peak current ratio of approximately 1. When the rate of electron becomes smaller (0.01), the reaction during the reverse scan no longer is in equilibrium with the forward reaction; the result is a loss of electrochemical reversibility but not, to any great extent, of chemical reversibility. For even smaller values of k^o, the CV also shows a loss of chemical reversibility as there is insufficient time to convert Red back to

Ox during the reverse scan.

Part III: Questions that Require Calculations

Question IIIA. The zinc from a 2.50-g sample of plant tissue is extracted into an aqueous solution and diluted to 50 mL in a volumetric flask. The sample is analyzed by voltammetry with a limiting current of 0.583 mA. A 5.00-mL aliquot of a 1.2×10^{-3} M solution of zinc is added, resulting in a limiting current of 1.35 mA. Calculate the amount of zinc in the plant tissue, reporting your result as µg zinc per gram of tissue.

Answer. This is an example of a standard addition. To find the concentration in the sample as analyzed, we note that

$$\frac{0.583 \text{ mA}}{C} = \frac{1.35 \text{ mA}}{C \times \frac{50.00}{55.00} + 0.0012 \text{ M} \times \frac{5.00}{50.00}}$$

where C is the concentration before the standard addition. Solving for C gives 7.76×10^{-5} M. To find the concentration of Zn in the plant sample, we account for how the original sample was prepared for analysis; thus

$$\frac{(7.76 \ times10^{-5} \text{ mol/L}) \times (0.05000 \text{ L}) \times (65.38 \text{ g/mol}) \times (10^6 \text{ µg/g})}{2.50 \text{ g}} = 101 \text{ µg/g}$$

Question IIIB. A sample of pottery being considered for import is leached for 24 hours using 50.0 mL of 4% acetic acid A 40.00-mL aliquot is transferred to an electrochemical cell and 10.00 mL of a 0.200 mM standard solution of Cd^{2+} is added. A stripping analysis of the solution yields peak currents of 1.81 µA for lead and 2.18 µA for cadmium. Analysis of a standard solution that is 0.0600 mM in Pb^{2+} and 0.0500 mM in Cd^{2+} gives peak currents of 2.39 µA and 2.71 µA, respectively. What is the concentration of Pb^{2+} in the original leachate?

Answer. This is an example of an internal standardization. For the standard, we have $\frac{2.39 \text{ µA}}{2.71 \text{ µA}} = K \times \frac{0.0600 \text{ mM}}{0.0500 \text{ mM}}$, which gives k as 0.735. For the sample, we then have

$$\frac{1.81 \text{ µA}}{2.18 \text{ µA}} = 0.735 \times \frac{C \times \frac{40.00 \text{ mL}}{50.00 \text{ mM}}}{0.20 \text{ mM} \times \frac{10.00 \text{ mL}}{50.00 \text{ mL}}}$$

which gives C as 0.0565 mM Pb^{2+}.

Question IIIC. The following data were obtained for the reduction of an analyte using steady-state voltammetry (linear sweep voltammetry while stirring the solution). Show that this data is consistent with an electrochemically reversible reaction.

Applied Potential (V)	Current (mA)
–0.385	0.0
–0.444	1.0
–0.465	2.0
–0.489	4.0
–0.511	6.0
–0.535	8.0
–0.556	9.0
–0.573	10.0
–0.596	10.0

Answer. To show that the system is reversible, we plot the potential, E, versus $\log\left(\frac{i}{i_l - i}\right)$ using 10.00 as the limiting current. As we see here
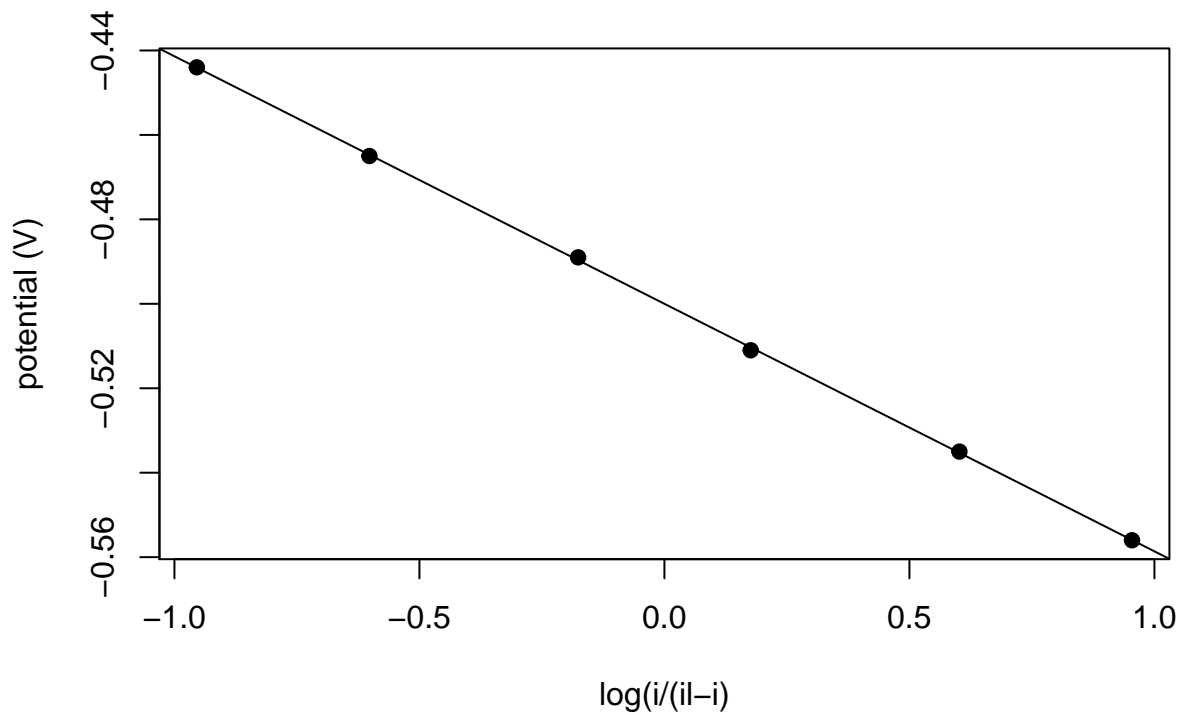
this yields a straight-line, which means that the reaction is reversible. Regression analysis gives the equation of the line as

$$E = -0.5 + (-0.0586) \times \log\left(\frac{i}{i_l - i}\right)$$

The slope is equivalent to $-0.0596/n$, which gives $n as 1.