

# Experiment 1

## AN INTRODUCTION TO CYCLIC VOLTAMMETRY

### Description

The goal of this experiment is to become familiar with using a modern electrochemical potentiostat, to determine the concentration of hexaammineruthenium(III) chloride, 99%,  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ , in an unknown solution, and to measure the diffusion coefficient for the hexaammineruthenium(III) cation,  $\text{Ru}(\text{NH}_3)_6^{+3}$ . This procedure illustrates how the current observed in a cyclic voltammetry experiment depends upon experimental parameters such as concentration and sweep rate.

### Experimental Apparatus

- Pine Instrument Company AFCBP1 Bipotentiostat
- Pine Instrument Company ASCBP1 **PineChem**<sup>TM</sup> software package
- Pine Instructional Three Electrode Cell
- Pine Disposable Printed Electrode Card
- Three 10 mL volumetric flasks
- Pipettes (1, 2, and 5 mL)

### Reagents and Chemicals

Description	per expt	per 20 expts*
<b>Supporting Electrolyte</b> 1.0 <u>M</u> potassium chloride (KCl)	100 mL	2 L
<b>Analyte Stock Solution</b> 6.0 <u>mM</u> hexaammineruthenium(III) chloride prepared using 1.0 <u>M</u> KCl as the solvent.	20 mL	500 mL

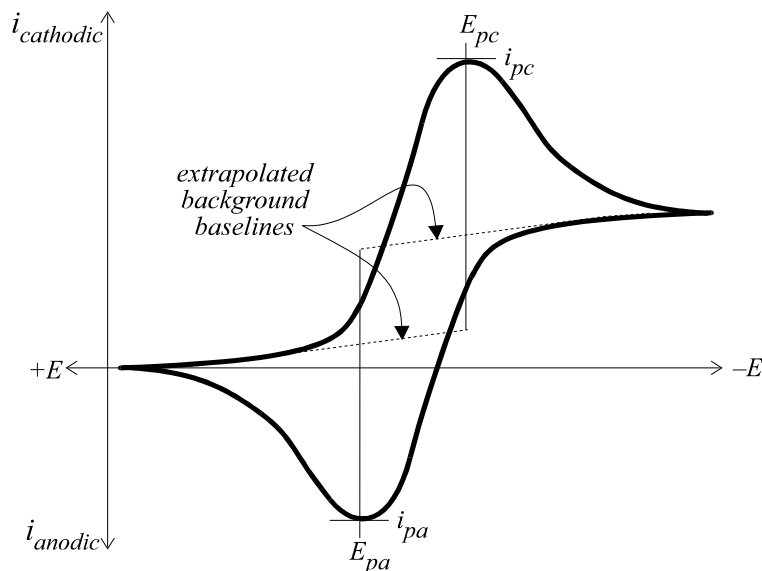
\* includes amounts needed by instructor to prepare stock and unknown solutions for entire group.

### Discussion

For several decades, cyclic voltammetry has been a very popular and often used electroanalytical technique. A cyclic voltammogram (or CV) is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential,  $E^0$ , of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration.

The equipment required to perform cyclic voltammetry consists of a conventional three-electrode potentiostat connected to three electrodes (working, reference, and auxiliary) immersed in a test solution. The potentiostat applies and maintains the potential between the working and reference electrode while at the same time measuring the current at the working electrode. (During the experiment, charge flows between the working electrode and the auxiliary electrode.) A recording device (such as a computer or plotter) is used to record the resulting cyclic voltammogram as a graph of current versus potential.

Figure 1.1 depicts a generic cyclic voltammogram. The potential is graphed along the x-axis with more positive (or oxidizing) potentials plotted *to the left*, and more negative (or reducing) potentials *to the right*. The current is plotted on the y-axis of the voltammogram, with cathodic (*i.e.*, reducing) currents plotted *up* along the positive direction, and anodic (*i.e.*, oxidizing) currents plotted *down* in the negative direction. (A voltammogram is almost always plotted in this fashion by North American electrochemists, but in Europe, the axes are typically reversed.)



**FIGURE 1.1: A TYPICAL CYCLIC VOLTAMMOGRAM**

The peaks appearing in a voltammogram are similar to those found in a spectrum or chromatogram. Each peak corresponds to a particular electroactive analyte in the test solution, and the height of a peak is proportional to the concentration of that analyte. The peaks in a cyclic voltammogram are asymmetric, with the leading side being very steep and the trailing side falling off gradually. The peaks observed during the reverse sweep have the same general shape as those seen in the forward sweep, but they are inverted because the direction of current flow is reversed. The first sweep in a cyclic voltammetry experiment may be in either the positive (anodic) direction or in the negative (cathodic) direction.

There is a great deal of quantitative information that can be gleaned from a good cyclic voltammogram. First, it can be a test to see if a redox couple is indeed

reversible. The peak potential for the anodic sweep,  $E_{pa}$ , and the peak potential for the cathodic peak,  $E_{pc}$ , can be directly read from the voltammogram, and the difference between them,  $\Delta E_{peak}$ , can be calculated. If the redox couple is reversible, then the relationship,

$$n \Delta E_{peak} = 59 \text{ mV} \quad (1.1)$$

holds true, where  $n$  is the number of electrons involved in the redox couple (usually just one).

Direct observation of the relationship in equation 1.1 is not possible with the printed electrodes used in this introductory experiment. The surface characteristics of inexpensive printed electrodes are not pristine enough to record an undistorted, fully reversible cyclic voltammogram. To do this, it is necessary to use more expensive precious metal electrodes (such as mirror polished platinum or gold electrodes). Nevertheless, the inexpensive electrodes used in this experiment will provide a voltammogram useful for instructional purposes.

In addition, the cyclic voltammogram for a reversible redox couple has an anodic peak current,  $i_{pa}$ , that is equal to the cathodic peak current,  $i_{pc}$ , so that the relationship,

$$i_{pa} / i_{pc} = 1 \quad (1.2)$$

also holds true. It is important to note that the peak currents are not measured using the  $x$ -axis as a baseline. Rather, a background current baseline must first be extrapolated out to the peak potential (see Figure 1.1). Then, the peak current is measured (vertically) from the peak down to the extrapolated baseline.

The background current is always present, even in a test solution that contains no electroactive analyte. It is due to a *double layer* of ions in the solution immediately adjacent to the surface of the electrode. This double layer behaves like a capacitor, alternately being charged and discharged as the potential is swept back and forth. Thus, the background current is sometimes referred to as a *charging current*.

The formal potential,  $E^0$ , for a reversible redox couple is easily determined as the average of the two peak potentials as follows.

$$E^0 = (E_{pa} + E_{pc}) / 2 \quad (1.3)$$

Formal potentials measured using cyclic voltammetry are usually accurate to within 50 mV of the true value. More accurate values can be obtained using other electrochemical techniques and precious metal electrodes.

Quantitative information regarding analyte concentration can be obtained from the voltammogram using the Randles-Sevcik equation (Eqn. 1.4). This equation specifies the peak current,  $i_p$  (either anodic or cathodic), in terms of the analyte concentration,  $C$ .

$$i_p = 0.4463 n F A C (n F v D / R T)^{1/2} \quad (1.4)$$

In this equation,  $n$  is the number of electrons appearing in half-reaction for the redox couple,  $v$  is the rate at which the potential is swept (V / sec),  $F$  is Faraday's constant (96485 C / mol),  $A$  is the electrode area (cm<sup>2</sup>),  $R$  is the universal gas constant (8.314 J / mol K),  $T$  is the absolute temperature (K), and  $D$  is the analyte's diffusion coefficient (cm<sup>2</sup>/sec). Note that if the temperature is assumed to be 25°C (298.15K), the Randles-Sevcik can be written in a more concise form,

$$i_p = (2.687 \times 10^5) n^{3/2} v^{1/2} D^{1/2} A C \quad (1.5)$$

where the constant is understood to have units (*i.e.*, 2.687x10<sup>5</sup> C mol<sup>-1</sup> V<sup>-1/2</sup>).

Note that the peak current is directly proportional to the analyte concentration. Also note that if the analyte concentration is a known quantity, then cyclic voltammetry can be used to measure the analyte's diffusion coefficient. The diffusion coefficient is a measure of how fast the analyte moves through the solution as a result of random collisions with other molecules.

## Procedure

All glassware used for electrochemistry should be as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. It is a good idea to use deionized, ultrafiltered (DIUF) water or "conductivity water" or "HPLC grade water" for the final rinsing of glassware and for all solution preparation.

### A. SOLUTION PREPARATION

- 1) These stock solutions should be provided to a group of 20 students:

#### **1.0M potassium chloride (2 liters)**

[KCl formula mass is 74.56 g/mol; CAS number 7447-40-7]

Saturated solutions of *potassium chloride* available directly from chemical manufacturers may be diluted and used as electrolyte solutions for cyclic voltammetry. Alternately, the *potassium chloride solution* can be prepared by dissolving 149.12 grams of KCl in enough ultrapure water to obtain a 2.0 liter final volume.

#### **6.0 mM hexaammineruthenium stock solution (500 mL)**

[Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> formula mass is 309.61 g/mol; CAS number 14282-91-8]

This stock solution can be prepared by dissolving 928.8 milligrams of Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> in enough 1.0M *potassium chloride solution* to make 500 mL of solution. The resulting solution has a hexaammineruthenium(III) concentration near 6.0 mM.

### Unknown solution (250 mL)

To prepare enough unknown solution for twenty (20) students, pipette anywhere from 25 to 125 mL of the *hexaammineruthenium stock solution* into a 250 mL volumetric flask and dilute “to the line” using 1.0M *potassium chloride solution*. Alternately, individual unknowns may be prepared by pipetting anywhere from 1 to 9 mL of the *iron stock solution* into 10 mL flasks and diluting “to the line” with 1.0M *potassium chloride solution*.

- 2) Each individual student should prepare four standard solutions with various concentrations of hexaammineruthenium(III) ranging from 0.5 to 6.0 mM. One of the standard solutions should be the stock solution itself (6.0 mM). The other three solutions can be prepared by pipetting various volumes of the stock solution into a series of three 10 mL volumetric flasks. When filling each flask “to the line,” be sure to use the 1.0M *potassium chloride solution* rather than water. The table below is meant to serve as a guide in making these five solutions. The concentrations listed in the table assume that the *hexaammineruthenium stock solution* has a concentration of 6.0 mM. Students should verify this assumption and compute the concentrations again if needed.

pipette volume (mL)	flask volume (mL)	standard concentration (mM)
1	10	0.6
2	10	1.2
5	10	3.0

## B. SETTING UP THE SOFTWARE

- 3) From the INSTRUMENT STATUS panel of the **PineChem** software package, adjust the IDLE CONDITIONS as shown in Figure 1.2. Confirm that the AFCBP1 Bipotentiostat is in DUMMY (NOT NORMAL) mode, and then make all necessary electrical connections between the electrodes and the potentiostat. Also, adjust the front panel voltmeter of the AFCBP1 so that it is displaying the working electrode potential (E1). It should confirm that the K1 electrode is idling near 200 millivolts.

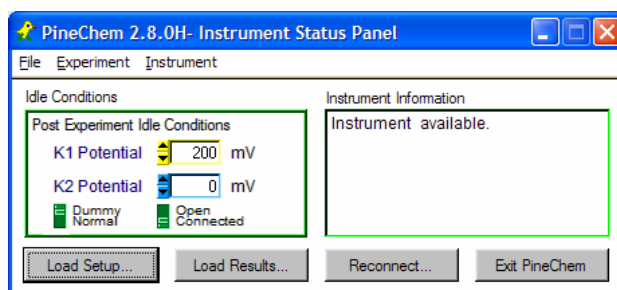


FIGURE 1.2: INITIAL INSTRUMENT STATUS PANEL SETTINGS

- 4) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and then enter the experimental parameters shown in Figure 1.3

below. Note that these settings are only suggested starting points for performing a cyclic voltammogram. The ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.

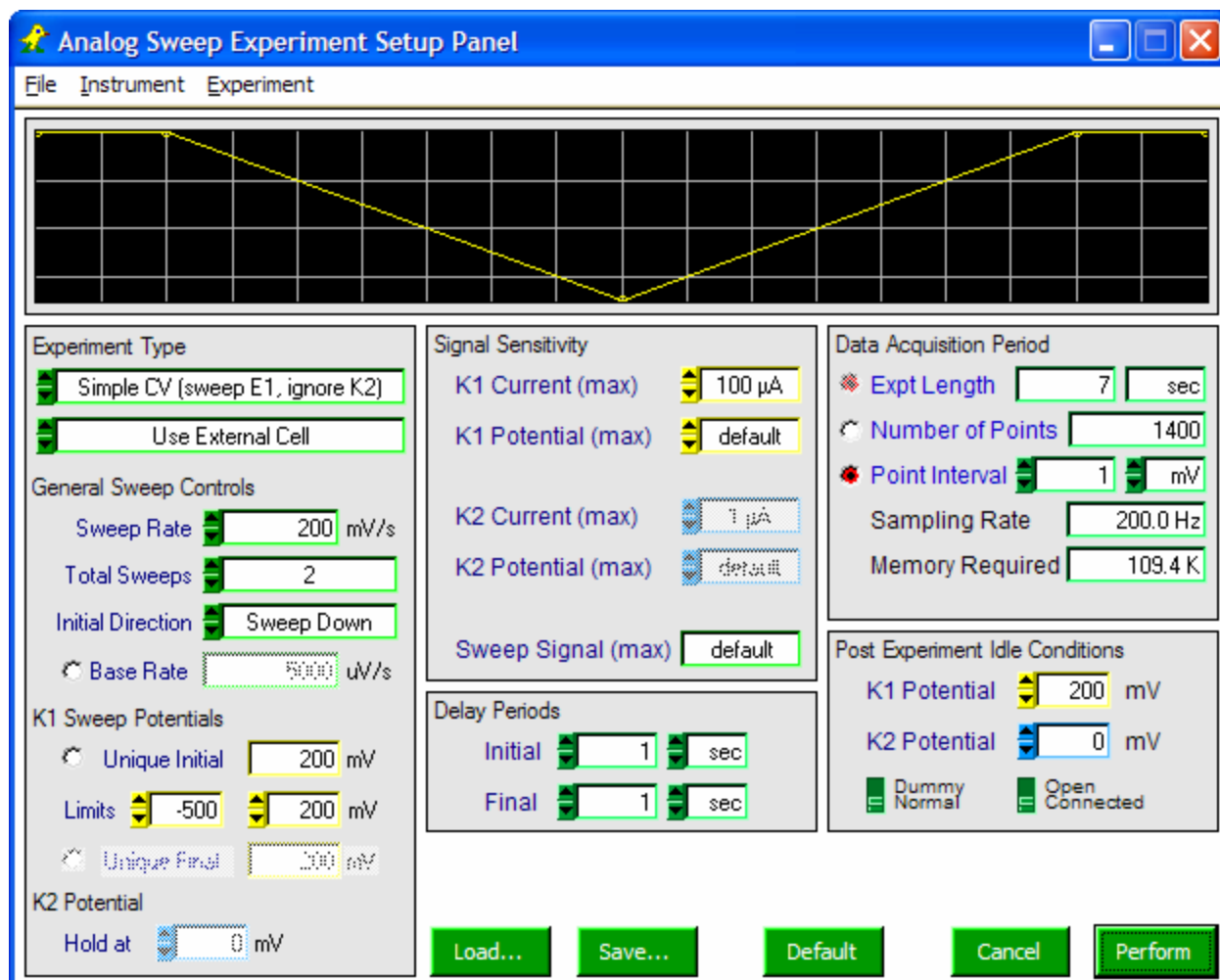


FIGURE 1.3: EXPERIMENTAL SETUP FOR CYCLIC VOLTAMMETRY

### C. THE EFFECT OF CONCENTRATION

In this part of the experiment, several cyclic voltammograms are obtained with solutions of varying concentration. Four standard solutions with concentrations ranging from 0.6 to 6.0 mM should be used. The standards should be prepared using 1.0M potassium chloride solution as the solvent.

- 5) Obtain a clean 20 mL glass vial and a special cap for mounting the Disposable Printed Electrode Card.

- 6) Fill the glass vial with 10.0 mL of the standard solution which has the lowest hexaammineruthenium(III) concentration.
- 7) Place the special cap on the vial and then mount the electrode card in the special cap. Make sure that all three electrodes on the card are immersed in the solution.
- 8) Before making electrical connections between the cell and the potentiostat, it is a good idea to make sure the AFCBP1 Bipotentiostat is in DUMMY mode. This can be done using the controls on the INSTRUMENT STATUS panel (see Figure 1.2).
- 9) Use the special cable to connect the potentiostat to the electrode card. Note that the various colored banana plugs on the cable are connected to the various electrodes as follows:
  - The yellow banana plug is the working electrode. Made from carbon ink, the working electrode appears as a black dot in the middle of the card.
  - The red banana plug is the auxiliary electrode. Made from carbon ink, the auxiliary electrode appears as a wide black band around the outside of the card.
  - The white banana plug is the reference electrode. Made from silver chloride ink, the reference electrode appears as a thin grey line on the card. A BNC-to-banana adapter may be required to make this connection to the potentiostat.
  - The blue banana plug is an alternate connection to the working electrode that **should not** be connected to the potentiostat.
- 10) After the cell has been properly configured, use the INSTRUMENT STATUS panel of the **PineChem** software package to adjust the IDLE CONDITIONS as shown in Figure 1.4. Note that the K1 electrode potential should idle at about +200 mV, a potential which is *more positive* than the formal potential for the *hexaammineruthenium* redox couple. Use the front panel voltmeter to confirm the K1 electrode potential (E1). Note also that the AFCBP1 should be placed in NORMAL mode at this time.

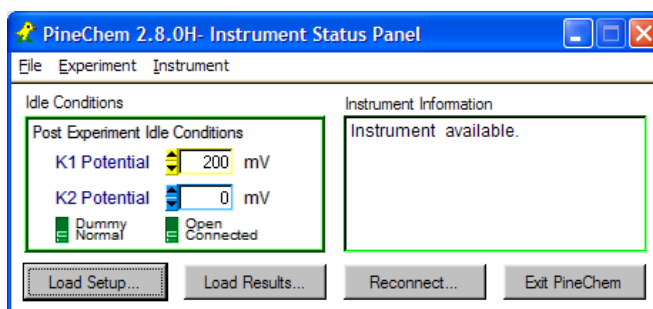
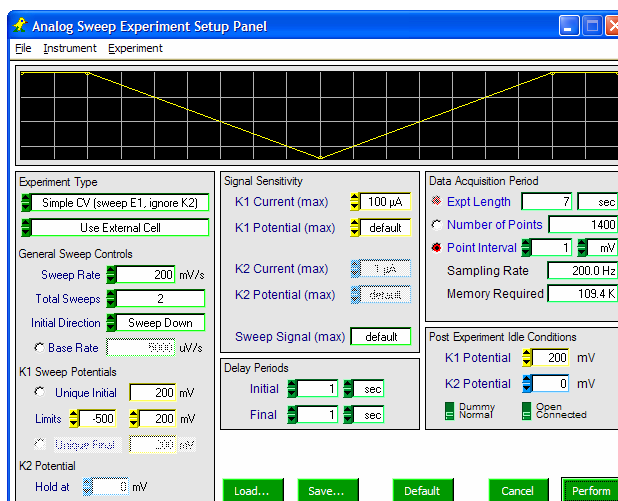


FIGURE 1.4: SWITCH CELL CONDITION FROM “DUMMY” TO “NORMAL”



**FIGURE 1.5: PRESS THE PERFORM BUTTON ON THIS SCREEN TO START**

- 11) Once the experiment settings have been adjusted to match those in Figure 1.5, click on the **PERFORM** button to initiate the experiment. A fairly prominent cathodic wave should appear during the sweep from +200 mV to -200 mV millivolts. On the return sweep, an anodic wave of roughly equal size should appear.
- 12) After acquiring a satisfactory voltammogram, save it on the disk and/or print it out on the printer.
- 13) Plot the voltammogram as a current versus time graph by choosing the **I1 vs. t** option from the **Plot** menu. Then, use the **Peak Height Tool** found in the **Toolbox** menu to measure the height of the cathodic peak as shown in Figure 1.6. Note that the cathodic peak is the first peak and that the peak is in the negative direction. The software presents the peak height result as a negative number, but you should record it as a positive number in your lab notebook.
- 14) Acquire similar voltammograms for the remaining standard solutions in order of increasing concentration. Use the same sweep rate (200 mV/s) for all solutions. Clean the cell between solutions.
- 15) After the last standard solution has been studied, *leave it in the cell* and use it for the next part of the experiment.

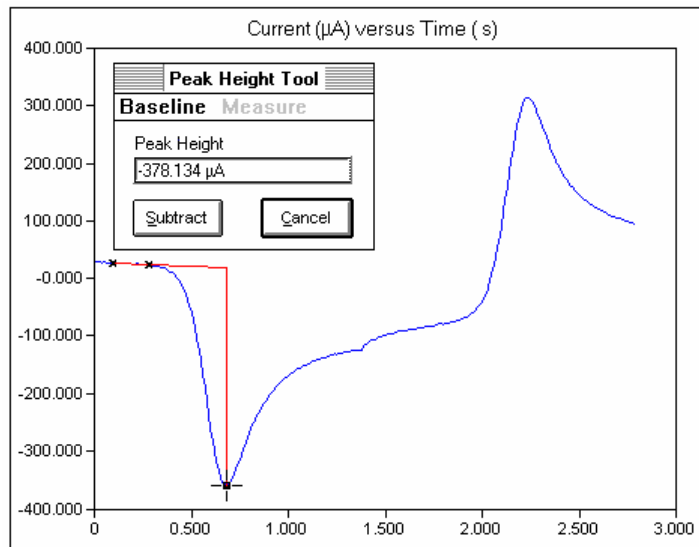


FIGURE 1.6: MEASURING THE PEAK HEIGHT

## D. THE EFFECT OF SWEEP RATE

Using the standard iron solution with the highest concentration, a series of cyclic voltammograms should be acquired at various sweep rates. The peak current observed in these voltammograms should exhibit a noticeable dependence on the sweep rate.

- 16) Using sweep parameters similar to those in Figure 1.3, acquire voltammograms at the following sweep rates: 50, 100, 200, 500, and 1000 mV/s. Be sure to save each voltammogram on a disk and/or print it out on the printer. In addition, use the **Peak Height Tool** to measure the height of the cathodic peak from each voltammogram. Note that the ELECTRODE SENSITIVITY may need to be adjusted from time to time as progressively higher sweep rates are used.

## E. THE UNKNOWN SOLUTION

The instructor may provide a solution which has an unknown concentration. This solution should be examined using the same sweep rate as that used to examine the series of standard solutions in Part C of this procedure (200 mV/s). Because the unknown solution has a concentration on the same order as your standard solutions, it may be examined directly as supplied by the instructor.

- 17) Using sweep parameters similar to those in Figure 1.6, acquire a voltammogram of the unknown iron solution using a 200 mV/s sweep rate. Be sure to save the voltammogram on a disk and/or print it out on the printer. In addition, use the **Peak Height Tool** to measure the height of the cathodic peak in the voltammogram. Note that the ELECTRODE SENSITIVITY may need to be adjusted to a value different than that shown in Figure 1.3.

# Data Analysis

## Concentration Study

- a) Using the cathodic peak currents for the series of standard solutions, prepare a plot of peak current versus concentration. (Make sure that each of the voltammograms was acquired using the same sweep rate.)
- b) Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.
- c) Use the slope of the line to calculate the diffusion coefficient for the hexaammineruthenium(III) cation.

## Unknown Solution

- d) Using the equation from (b), above, compute the concentration of hexaammineruthenium(III) cation in the unknown solution. Report your result in moles per liter using three significant figures.

## Sweep Rate Study

- e) Using the cathodic peak currents measured from the series of voltammograms acquired at different sweep rates, prepare a plot of peak current versus the square root of the sweep rate. (Make sure that each of the voltammograms was acquired using the same standard solution.)
- f) Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.
- g) Use the slope of the line to calculate the diffusion coefficient for the hexaammineruthenium(III) cation.
- h) Using the voltammogram obtained using the slowest sweep rate, determine the formal potential,  $E^{\circ}$ , for the iron(III/II) redox couple. Express the result in volts versus the silver/silver chloride (Ag/AgCl) reference electrode, and compare your result to an accepted value from the scientific literature.

# Report Questions

- 1) Explain, in terms of what happens in the diffusion layer immediately adjacent to the electrode surface, why faster sweep rates give higher peak currents.
- 2) When a group of molecules or ions are randomly diffusing through a solution, the average distance,  $x$ , that they move in a period of time,  $t$ , can be estimated using  $x = (2 D t)^{1/2}$ , where  $D$  is the diffusion coefficient. Using your experimental result for the diffusion coefficient, show that it takes more than a day for a group of hexaammineruthenium(III) cations to diffuse just one centimeter.

# Prelab Questions

Answer the following questions before beginning the lab experiment.

- 1) In section C of the lab procedure above, you are encouraged to examine the standard solutions in order of increasing concentration. Why is it a good idea to do this?
- 2) A 4.500 mM standard solution of an analyte is prepared and studied using cyclic voltammetry at 25.0°C. A platinum disk electrode with diameter 5.0 mm is used. The analyte exhibits a simple one electron redox couple ( $n = 1$ ) and has a diffusion coefficient,  $D$ , equal to  $7.56 \times 10^{-5} \text{ cm}^2/\text{s}$ . The sweep rate is 200.0 mV/s. Using the Randles-Sevcik equation (Eqn. 1.4), calculate the peak current that should be observed.