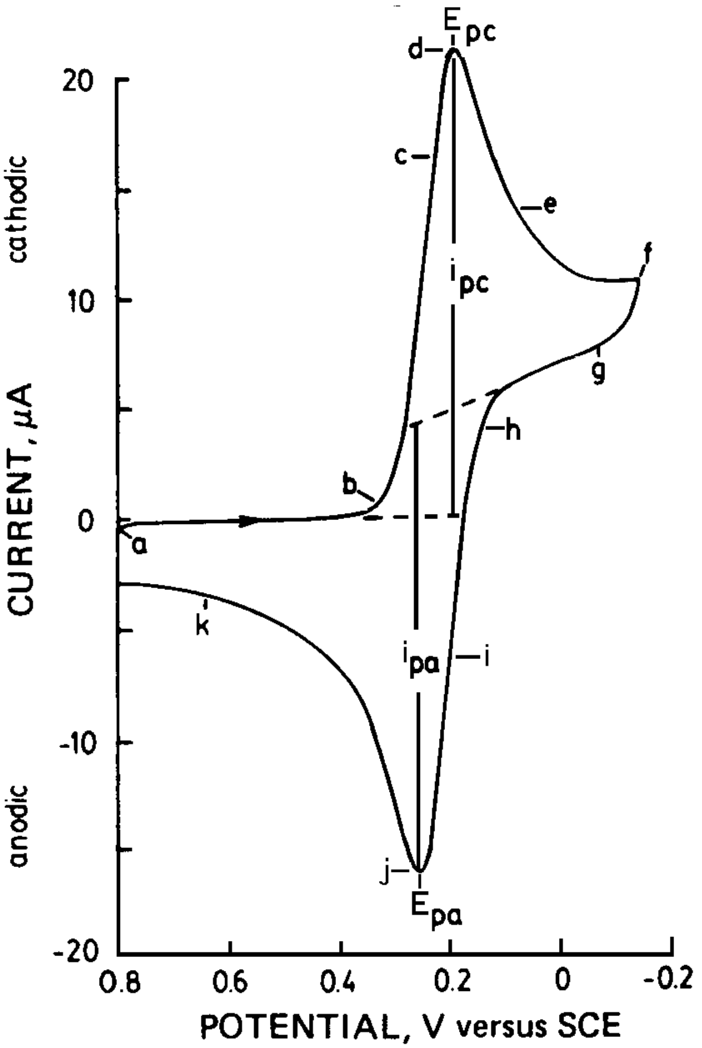
# Cyclic Voltammetry of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$

## Introduction

Cyclic voltammetry (CV) is a very useful electroanalytical technique. Many inorganic compounds contain elements that may take on several different oxidation states. The CV experiment can provide important information about the oxidation state of an element in a compound as well as the compound's stability in the solvent system in which it is studied. When conditions provide stable oxidized and reduced forms during the time required to obtain a voltammogram (current-potential curve) CV is a simple and direct method for measuring the formal potential of a half-reaction. The $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ couple is an example of a well-behaved electrochemically reversible system in aqueous solution. This experiment will demonstrate the general CV method and show how it can be used to obtain the formal reduction potential ($E^{o\prime}$); the number of electrons transferred in the redox process ($n$); the diffusion coefficient ($D$); electrochemical reversibility; and the effects of varying concentration and scan rate.

The CV apparatus is computer controlled. It consists of a potentiostat with scan capability and contains a display of current versus potential (voltage). A three electrode system is used. The electrodes in this experiment consist of a working electrode (platinum), a platinum auxiliary electrode, and a Ag/AgCl or saturated calomel (SCE) reference electrode. Potentials will be referenced versus SCE. The cell contains holes for the electrodes and one for a tube for deoxygenating the solution by bubbling a stream of nitrogen. The surface of the working electrode may be polished with powdered alumina and rinsed with distilled water as a pretreatment. Nitrogen should be passed through the solution for 10 minutes before any measurement is made. After bubbling nitrogen through the solution the tip of the deoxygenation tube should be raised above the surface of the liquid and a flow of nitrogen continued throughout the experiment. During the course of the CV the solution should remain quiescent and be oxygen free.

The diagram on the next page shows a typical CV for an electrochemically reversible reaction at the working electrode ($Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ couple). The initial potential (point *a*) at 0.80 V shows no current and therefore no electrolysis when the electrode is switched on. The electrode is scanned toward a more negative potential (forward scan) toward point *b*. As the potential is made more negative between points *b* and *c* the electrode is now a sufficiently strong reductant to reduce the $Fe^{III}(CN)_6^{3-}$. The concentration of the complex ion decreases rapidly at the electrode surface and the cathodic current increases. At point *d* the concentration of $Fe^{III}(CN)_6^{3+}$ is substantially diminished causing the current to peak. From point *d* to *e* the current decays as $Fe^{III}(CN)_6^{3-}$ becomes more depleted and $Fe^{II}(CN)_6^{4-}$ surrounds the electrode. The scan is then reversed at –0.15 V indicated by point *f* (switching potential). Between points *f* and *h* the cathodic current continues because the potential is still sufficiently negative to reduce $Fe^{III}(CN)_6^{3-}$. At point *i* the electrode is a sufficiently strong oxidant to oxidize $Fe^{II}(CN)_6^{4-}$, which has accumulated adjacent to the electrode and the reaction: $Fe^{II}(CN)_6^{4-} \rightarrow Fe^{III}(CN)_6^{3-} + e^-$ occurs on the electrode surface. The anodic current rapidly increases to point *j* until the surface concentration of $\mathrm{Fe^{II}(CN)_6^{4-}}$ is diminished causing the current peak. From point *j* to *k* the current decays as solution surrounding the electrode is depleted of $\mathrm{Fe^{II}(CN)_6^{4-}}$. One CV cycle has now been completed. The quantities $E_{pa}$, $E_{pc}$, $i_{pa}$, and $i_{pc}$ may be obtained directly from CV diagrams similar to that shown here or computed using specific modeling software. The use of a supporting electrolyte in CV experiments is to suppress migration of charged reactants and products.



A redox couple in which both species rapidly exchange electrons with the working electrode is called an electrochemically reversible couple. The formal reduction potential ($E^{o\prime}$) for a reversible couple is centered between the anodic ($E_{pa}$) and cathodic ($E_{pc}$) peak potentials.

$$E^{o\prime} = (E_{pa} + E_{pc})/2$$

## Procedure

From 1 M $KNO_3$ solution available in the lab prepare a 100 mL stock solution of approximately 10 mM $K_3Fe(CN)_6$. Note that this solution is 1 M in $KNO_3$ supporting electrolyte. From this solution prepare 25-mL quantities of approximately 2, 4, 6, and 8 mM $K_3Fe(CN)_6$ that are also 1 M in $KNO_3$ (use 1 M $KNO_3$ for the dilutions). In addition prepare 25 mL of approximately 4 mM $K_3Fe(CN)_6$ that is 1M in $Na_2SO_4$. All solution concentration must be accurately known to three significant figures, so use analytical methods (weigh on analytical balance, use volumetric flasks, and pipets). An unknown $K_3Fe(CN)_6$ will also be provided by the instructor. (Be certain of your solution concentrations: 1 mM = 1 mmol/L. A 100 mL volume of 10 mM solution will contain 1 mmol solute.)

The instructor will familiarize the students with the operation of the computer program interfaced to the CV and the proper procedure for introducing and removing solutions from the cell. Fill the cell with 1M $KNO_3$. While the system is being deoxygenated and the working electrode is disconnected, set the initial potential to 0.80 V and the scan limits to 0.80 V and –0.15 V. The scan should be initiated in a negative direction with a scan rate of 20 mV/s. After the deoxygenation is complete switch on the working electrode and wait for approximately 10 s until the current has reached a constant value. Initiate the potential scan and a background CV of the supporting electrolyte is obtained. Similar scans with longer ranges are done in all CV experiments because they provide the operational limits of potential at which the experiment can be run. For example in 1M $KNO_3$ at one extreme of potential the solvent (water) will be oxidized and at the other extreme the solvent will be reduced. Thus, a “window” for which CV experiments can be performed in that medium is obtained.

After turning off the working electrode, wash the cell with several small volumes of distilled water and refill with 4 mM $K_3Fe(CN)_6$ in 1 M $KNO_3$. Following the same procedure as above to obtain a CV of the $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ couple. Measure and record $i_{pc}$ and $i_{pa}$ using the computer software. Make a hard copy of the CV with the $E_{pc}$ and $E_{pa}$ clearly indicated.

The same solution is used to observe the effect of sweep rate ($\nu$). Gently move the working electrode up and down in the solution being careful not to introduce oxygen to the system. This process restores the electrode surface to the initial conditions. Repeat CVs at the following rates: 20, 50, 75, 100, 125, 150, 175, and 200 mV/s performing the restorative process between scans. Measure and record $i_{pc}$ and $i_{pa}$ for every scan. Care should be taken that no bubbles remain on the electrodes. Make a hard copy of each CV which includes values of $E_{pc}$ and $E_{pa}$.

The next section of the experiment illustrates how concentration affects the magnitude of peak current. Obtain scans of the 2, 6, 8, and 10 mM $K_3Fe(CN)_6$ solutions using a sweep rate of 20 mV/s. You have already obtained a CV of the 4 mM solution. Also obtain a voltammogram of the unknown solution. Make hard copies of all the CVs.

Record a voltammogram of 4 mM $K_3Fe(CN)_6$ in 1 M $Na_2SO_4$ to determine the effect of supporting electrolyte on the appearance of a CV. Make a hard copy of the CV.

**Laboratory Report**

1. Using the data generated from the CV scans of the 4 mM $K_3Fe(CN)_6$ in 1 M $KNO_3$ report the values of $E_{pa}$, $E_{pc}$, $i_{pa}$, $i_{pc}$, and $E^{o\prime}$.

2. The effect of scan rate ($\nu$) on the CV can be described by the Randle-Sevcik equation

$$i_p = (2.69 \text{ x } 10^5) n^{3/2} A\, D^{1/2}\, C\, \nu^{1/2}$$

   where
   $i_p$ is the peak current ($i_{pa}$ anodic and $i_{pc}$ cathodic)
   $n$ is the electron stoichiometry
   $A$ is the electrode area ($cm^2$)
   $D$ is the diffusion current
   $C$ is the concentration ($mol/cm^3$)
   $\nu$ is the scan rate (V/s)

   Make a plot of $i_{pc}$ and $i_{pa}$ versus $\nu^{1/2}$ and report the diffusion coefficient for the system. The value of A will be given by the instructor.

3. Evidence of electrochemical reversibility can be ascertained by the independence of $\Delta E_p$ on $\nu$. From the experiment, using variable scan rate, show that this system is electrochemically reversible.

4. The number of electrons transferred in the electrode reaction ($n$) for a reversible couple is given by

$$\Delta E_p = \quad E_{pa} - \; E_{pc} \cong 0.059/n$$

   Calculate the values of $\Delta E_p$ and $n$ using the data from the 4 mM $K_3Fe(CN)_6$ in 1 M $KNO_3$ experiment. What should be the value of $n$ for this system? Comment?

5. Use the Randle-Sevcik equation and the value of D calculated in question 2 to calculate the concentration of the unknown solution. Calculate $C_{unknown}$ from a least squares line of $i_{pa}$ or $i_{pc}$ versus $C$ constructed from the data obtained at different concentrations.

6. Calculate $E^{o\prime}$ for the $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ couple in 0.1 M $Na_2SO_4$. What conclusions do you draw from comparison of this value with the one obtained in 0.1 M $KNO_3$?

## References

1. Kissinger, P. T., Heineman, W. R., *J. Chem. Educ*., **1983**, *60*, 702.

2. Van Benschoten, J. J., Lewis, J. Y., Heineman, W. R., Roston, D. A., Kissinger, P. T., *J. Chem. Educ*., **1983**, *6o*, 772.

3. Evans, D. H., O'Connell, K. M., Petersen, R. A., Kelly, M. J., *J. Chem. Educ*., **1983**, *60*, 290.

Some good WEB sites describe some of the fundamentals:
http:/www.epsilon-web.net/Ec/manual/Techniques/CycVolt/cv_analysis.html
http://www.bath.ac.uk/~chsact/solartron/electro/html/cv.htm
http://soulcatcher.chem.umass.edu/web/downloads/cyclicv.html (a very nice simulation package from U.Mass Amherst)
http://poohbah.cem.msu.edu/courses/cem419/cem372cyclicvoltammetry.pdf
http://www.biol.paisley.ac.uk/macro/Enzyme_Electrode/Chapter1/Cyclic_Voltammetry1.htm

Any modern instrumental analysis or analytical text book will also provide sufficient background information.