

# Study of Ferricyanide by Cyclic Voltammetry Using the CV-50W

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*This article describes an experiment for an undergraduate chemistry laboratory to introduce cyclic voltammetry prior to studies of more complex systems. It also serves as a general introduction to computer-based instrumentation.*

Cyclic voltammetry is the most versatile electroanalytical technique for the study of electroactive species, and it is widely used in industrial applications and academic research laboratories. However, there are few cyclic voltammetry experiments designed to introduce students to this technique. In this article, the  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  couple is used as an example of an electrochemically reversible redox system in order to introduce some of the basic concepts of cyclic voltammetry (1,2). The CV-50W is ideal for teaching purposes. The instrument is simple to use, and its Windows-based software can be quickly mastered by students with little or no background in electrochemistry.

The experiment outlined below demonstrates the determination of the following: the formal reduction potential ( $E^0$ ); the number of electrons transferred in the redox process ( $n$ ); the diffusion coefficient ( $D$ ); electrochemical reversibility; and the effects of varying concentration ( $C$ ) and scan rate ( $v$ ).

## Experimental

### Reagents

A 100 mL stock solution of 10 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 1 M  $\text{KNO}_3$  is prepared. Serial dilutions of this solution are performed to give 25 mL solutions of 2, 4, 6 and 8 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 1 M  $\text{KNO}_3$ . A solution of unknown  $\text{K}_3\text{Fe}(\text{CN})_6$  concentration can also be analyzed.

### Apparatus

In this experiment a BAS CV-50W Voltammetric Analyzer running Windows™ software was used, together with a platinum working electrode (MF-2013) (diameter = 1.6 mm), a silver/silver chloride reference electrode (MF-2063) and a platinum wire auxiliary electrode (MW-1032). The platinum working electrode should be lightly polished with alumina and rinsed with water before each experimental run. In addition, the solution should be stirred between experiments in order to restore initial conditions, but it should *not* be stirred during the experiment.

The connections between the potentiostat and the cell are as follows: black=working electrode, white=reference electrode, and red=auxiliary electrode.

## Procedure

### A. Running a CV

1. Add the 2 mM solution of  $\text{K}_3\text{Fe}(\text{CN})_6$  to the cell and connect the electrodes as discussed above.
2. Open the CV-50W software and switch on the potentiostat. Use **Select Mode** in the **Method** menu to select cyclic voltammetry (**CV**) as the technique.
3. Once cyclic voltammetry has been selected, click **OK**. The **General Parameters** dialog box will open automatically. Enter the parameters shown on the top of the next page (the **Sensitivity** is selected from the drop-down list box).

**CV General Parameters**

Initial E : 650 mV  
 High E : 650 mV  
 Low E : 0 mV  
 Scan Rate : 20 mV/s

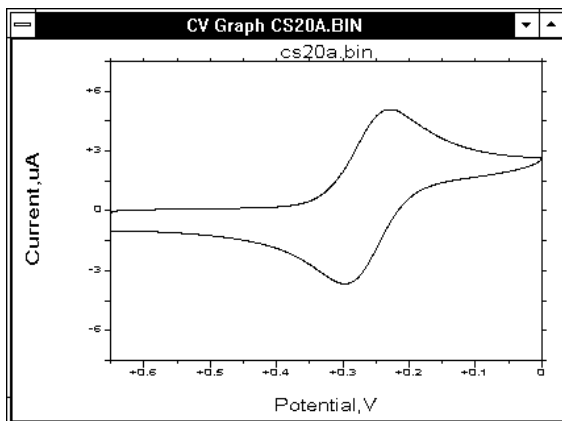
Initial Direction  
 Negative  Positive

Number of Segments : 2

Sensitivity 10 uA/V

Cancel OK Specific >>

4. Select **Start Run** in the **Control** menu to start the experiment (or press F2). The cyclic voltammogram (CV) will appear on screen as it is generated, and it will be rescaled automatically upon conclusion. Below is a cyclic voltammogram of 2 mM  $K_3Fe(CN)_6$  in 1 M  $KNO_3$ . Scan rate = 20 mV/s.



5. Select **Results Options** in the **Analysis** menu and ensure that the **Peak Shape** is **Tailing**, the **Method** is **Auto**, and that **Find peaks after Load data** and **Find peaks after Run** are not checked. Click **OK** to exit the dialog box.

**Results Options**

Peak Shape  
 Symmetrical  Tailing  Sigmoidal

Half peak width : 100 mV

Data Sets : 1 To: 2

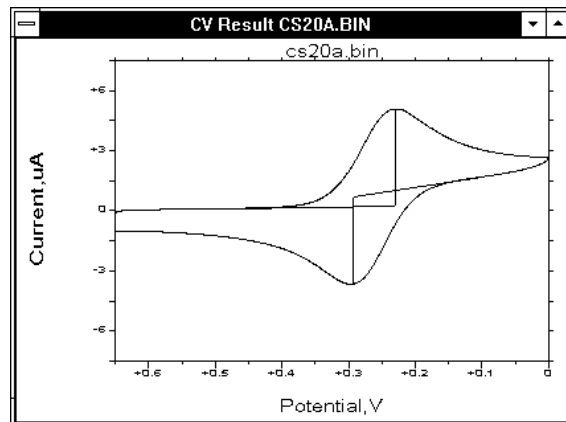
Method  
 Auto  Manual

Sensitivity factor x 1

Find peaks after Load data  
 Find peaks after Run

Cancel OK Find Peaks

6. Select **Results Graph** in the **Analysis** menu to re-display the voltammogram together with the baselines used for the measurement of the peak potentials and peak currents.



The numerical values of these peak parameters are displayed in the **Main** window (below).

**BAS100W CV CS20A.BIN**

File Method Control Math Analysis Graphics Print Help

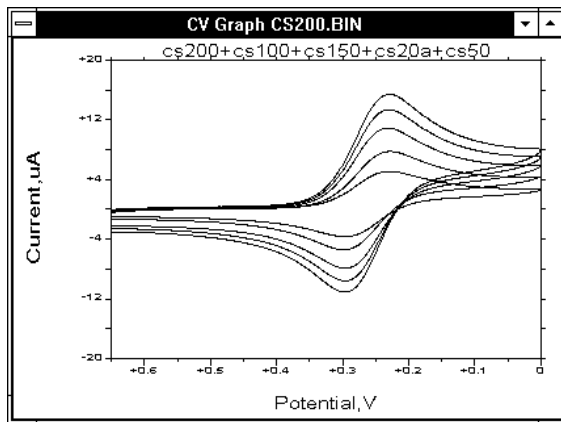
Segment 1:  
 Ep = +230 mV  
 ip = +4.855e-006 A

Segment 2:  
 Ep = +294 mV  
 ip = -4.382e-006 A

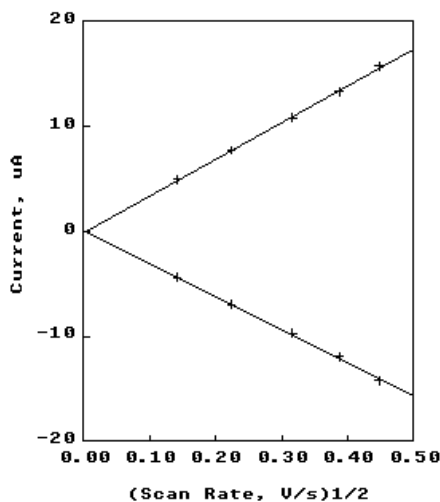
7. Save the experimental data as a binary (**.bin**) file using **Save Data** in the **File** menu. This CV is also retained in the main memory; it is replaced only when another CV is run or another voltammogram is loaded from a disk.

## B. The Effect of Scan Rate

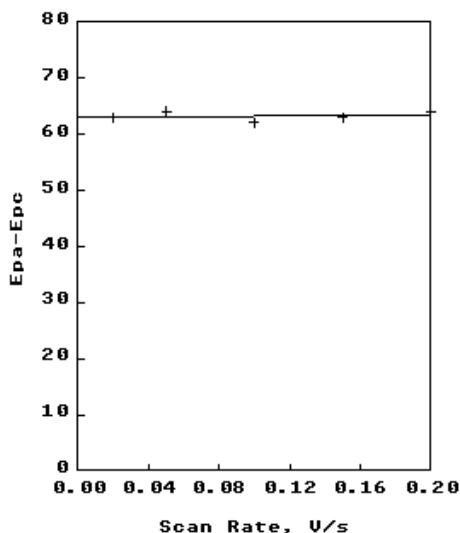
1. Select **General Parameters** in the **Method** menu, and change the scan rate from 20 mV/s to 50 mV/s. Run the experiment again and save the data. Repeat this procedure for scan rates of 100, 150 and 200 mV/s. The CV recorded at 200 mV/s should be retained in the main memory.
2. The CVs for each scan rate can all be displayed on the same graph using **Multi Graph** in the **Graphics** menu. First, open the **Graph Options** dialog box and select **Overlay** as the **Multi-Graph Style**. Then select **Multi-Graph** and click the filenames of the CVs to be plotted from the **File Name** list box. Note that the scale of the axes is determined by the voltammogram in the main memory. Cyclic voltammograms of 2 mM  $K_3Fe(CN)_6$  in 1 M  $KNO_3$  are illustrated on the next page. Scan rates = 20, 50, 100, 150 and 200 mV/s.



3. The scan rate dependence of the peak currents and peak potentials can be shown two ways: by plots of  $i_p$  vs.  $(\text{scan rate})^{1/2}$ ,



and  $\Delta E_p$  vs. scan rate (where  $\Delta E_p$  is the separation of the peak potentials).



### C. The Effect of Concentration

The effect of concentration can be shown by recording the CV at each concentration (2, 4, 6, 8 and 10 mM) and plotting  $i_p$  vs. concentration for either the anodic peak or the cathodic peak. The process can be automated to a certain degree by using the **Calibration** operation under the **Analysis** menu (N.B. this operation can only be used for the peak(s) on the first segment of a cyclic voltammogram).

When activated, the **Calibration** operation will automatically record the voltammograms of a series of solutions under the same conditions (i.e., the same general and specific parameters). Once the voltammogram of a given solution has been recorded, the data will be automatically saved, and then the user is prompted to provide a new solution. The solutions can be of either known or unknown concentration. Once all the solutions have been run, a calibration curve is constructed from the peak currents of the solutions of known concentration (using a least-squares fit), and the unknown concentrations are calculated from this plot. Both the calibration curve and the concentration table are available after the calculation has been completed.

All the concentrations are known in this application, and we are interested only in the linearity of the relationship between the concentration and the peak current.

1. Enter the **General Parameters** shown under A-3. (i.e., use a **Scan Rate** of 20 mV/s). Click **OK** to exit.
2. Select **Calibration** from the **Analysis** menu to see the **Calibration** dialog box illustrated below. Enter the **Number of Samples** (5), the **Concentration Unit** (mM), the **Base Filename** (xxx), and the **Report Name** (the **Report** contains the concentration table). The default file names for the cyclic voltammograms will be **xxx001.bin**, **xxx002.bin**, etc.

The figure is a screenshot of the "Analysis Calibration" dialog box. It contains a table for entering sample data, input fields for "Number of Samples", "Concentration Unit", "Base Filename", and "Report Name", and a "Comments" text area. At the bottom, there are buttons for "New", "Save", "Load", "Samples >>", "Run", "Process", "Plot", and "Close".

#	Filename	#	Filename	#	Filename	#	Filename
1		11		21		31	
2		12		22		32	
3		13		23		33	
4		14		24		34	
5		15		25		35	
6		16		26		36	
7		17		27		37	
8		18		28		38	
9		19		29		39	
10		20		30		40	
						41	
						42	
						43	
						44	
						45	
						46	
						47	
						48	
						49	
						50	

Number of Samples:  Base Filename:

Concentration Unit:  Report Name:

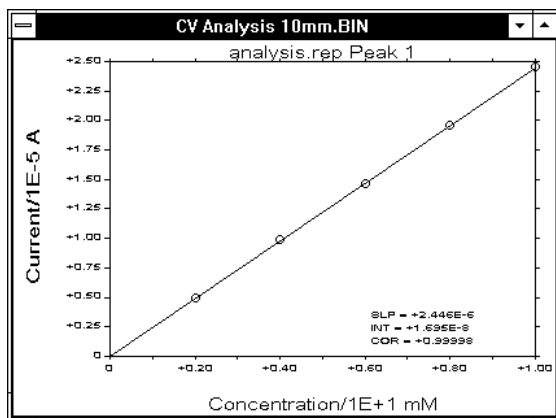
Comments:

Buttons: New, Save, Load, Samples >>, Run, Process, Plot, Close

- The concentration for each of the samples must be entered using the **Samples** dialog box (click **Samples** to view the dialog box illustrated below). For each sample #, click **Standard** and enter the concentration (N.B. the samples should be run in order of increasing concentration). The peak potential for the peak on the first (cathodic) scan must also be entered, together with a tolerance.

	Conc.	Ep(mV)	Tol.	Compound
Peak 1	2.000	230	20	Cathodic
Peak 2	0	0	0	
Peak 3	0	0	0	
Peak 4	0	0	0	
Peak 5	0	0	0	

- Click **Escape** to exit the **Samples** dialog box and then click **Run** to start the experiment. Note that the platinum working electrode should be polished between each run.
- Once all the voltammograms have been recorded, click **Plot** to display the calibration curve for peak 1 (See below).



### Discussion

The asymmetry of a cyclic voltammogram is a frequent source of confusion for students unfamiliar with the technique. The interplay of electron transfer kinetics and diffusional mass transport that determine the shape of a cyclic voltammogram can be readily illustrated using **CV-the Movie™** in the digital simulation software **DigiSim®**. This operation displays the concentration profiles (i.e., the variation of concentration

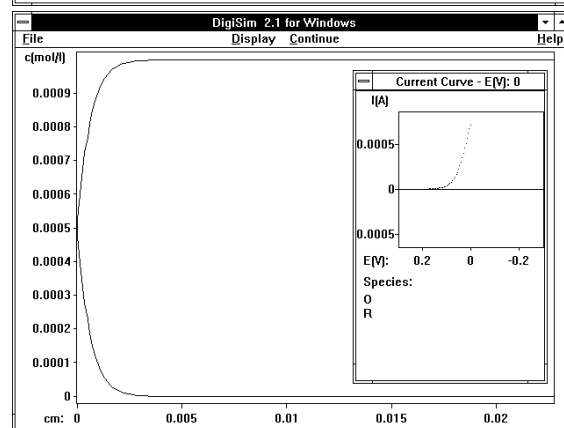
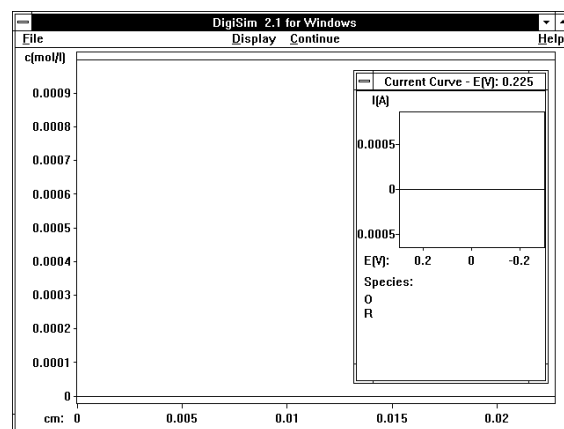
with distance from the electrode surface) as a function of time. Some pertinent sample “frames” are shown below for the redox reaction  $O + e = R$  (concentration of O in the bulk solution is 1 mM).

In this particular example, the electron transfer kinetics are fast, so they are not current-limiting at any potential. Hence, the concentrations of O and R at the electrode surface are determined by the Nernst equation

$$E = E^{0'} + \frac{0.059}{n} \log \frac{C_O^s}{C_R^s} \quad (\text{at } 25^\circ \text{C})$$

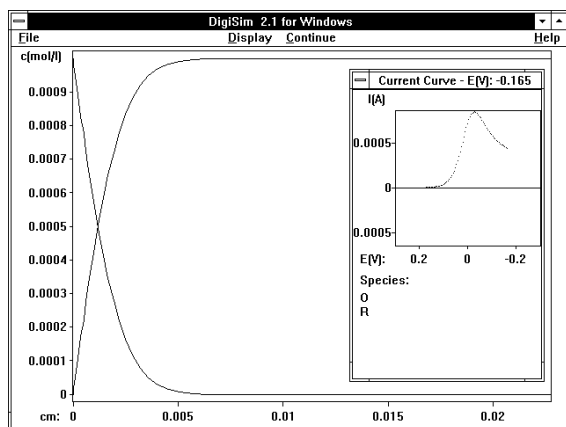
where  $E$  is the applied potential (in V),  $E^{0'}$  is the formal redox potential,  $n$  is the number of electrons transferred, and  $C^s$  is a surface concentration (it is assumed in this equation that the diffusion coefficients of O and R are equal). Such a redox process is frequently referred to as *reversible* or *Nernstian*.

The first of the two frames below shows the concentration profiles at a potential positive of the redox potential. According to the Nernst equation, the concentration of R at the electrode surface is negligible; that is, the concentration of O at the electrode surface is the same as in the bulk solution. As the potential is changed to more negative values, the surface concentration of R is no longer negligible and there is a net conversion of O to R (which generates a net cathodic current). The second frame shows that concentration profiles at  $E = E^{0'}$ . As expected from the Nernst equation, the surface concentrations of O and R are equal.

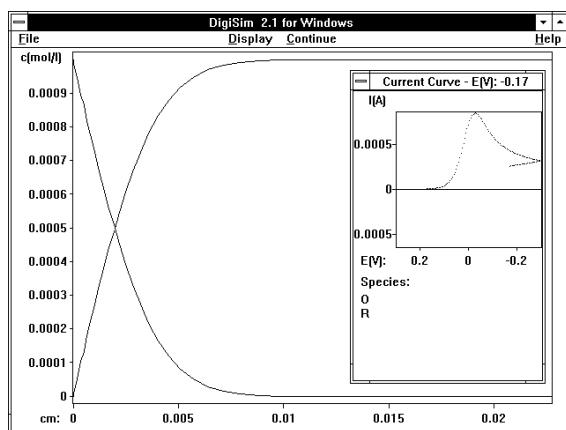


The changes in the surface concentrations of O and R cause concentration gradients for O and R to be set up between the electrode surface and the bulk solution. The motion of molecules down these concentration gradients leads to the diffusion of O *towards* the electrode surface and the diffusion of R *away* from the electrode surface. As can be seen from subsequent frames, the magnitude of the *diffusion layer* (the region in which the concentrations of O and R differ from those in the bulk solution) increases with time.

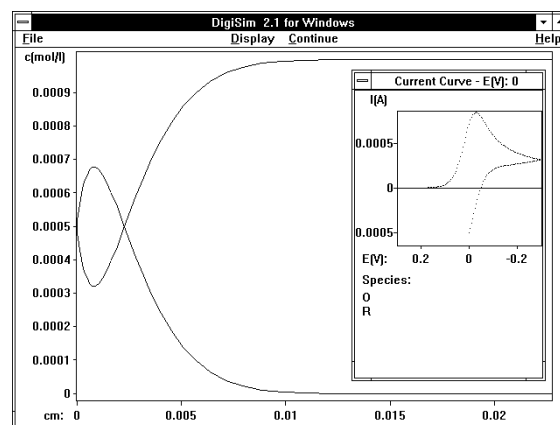
In the third frame (below), the applied potential is sufficiently negative that the molecules of O arriving at the electrode surface are reduced instantaneously. The net cathodic current is therefore determined by the rate at which molecules of O are brought to the surface; that is, the rate of diffusion. Since diffusion is proportional to  $t^{-1/2}$ , the current at this point decays according to  $t^{-1/2}$ .



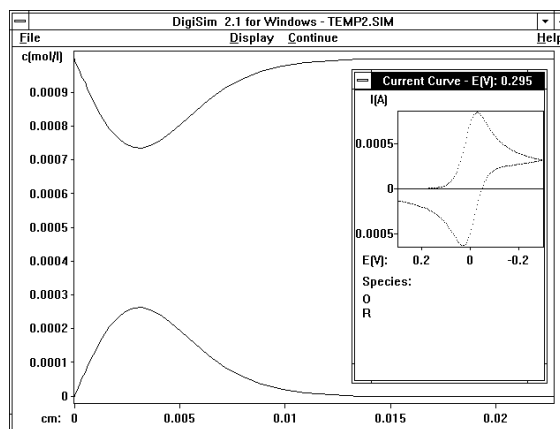
The potential is scanned in a negative direction until the switching potential is attained. At this potential, the direction of the potential scan is reversed. This means that the potential range that has just been traversed is rescanned. Since the potential is still negative relative to the redox potential, the current continues to decay with  $t^{-1/2}$  (frame four). However, as the potential is scanned to more positive values, the surface concentration of O required by the Nernst equation is no longer negligible and there is a net anodic current. Frame five shows the concentration profiles at  $E = E^0$ .



As required by the Nernst equation, the surface concentrations of O and R are again equal.



Frame six shows the concentration profiles at the end potential (which is the same as the starting potential). It should be noted that, although there has been some restoration of the profiles back to their initial levels, there remains a significant concentration of R close to the electrode surface. Not all of the molecules of R, which diffused away from the electrode surface during the first part of the experiment, have been able to diffuse back. As a consequence of this, the current at the end potential does not return to zero. In addition, stirring of the solution is required between experiments in order to restore the true initial conditions.



The important parameters obtained from a cyclic voltammogram are the anodic and cathodic peak currents ( $i_{pa}$  and  $i_{pc}$ ) and the anodic and cathodic peak potentials ( $E_{pa}$  and  $E_{pc}$ ); all of these parameters can be measured automatically by the CV-50W. The peak current for a reversible process is given by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}}$$

where  $A$  is the electrode surface area ( $\text{cm}^2$ ) (obtained using geometric measurement, or more accurately, by

chronocoulometry),  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $C$  is the concentration of the electroactive species in the bulk solution ( $\text{mol}/\text{cm}^3$ ) and  $v$  is the scan rate (V). Therefore,  $i_p$  is proportional to  $C$  and proportional to  $v^{1/2}$ . If  $A$  is known, then  $D$  can be calculated from the slopes of the linear plots described above.

It is often instructive to consider the peak current ratio (peak current on the reverse scan/peak current on the forward scan) rather than the individual peak current values. For a reversible process, this ratio approaches unity; values significantly different from 1 are typically associated with chemical reactions coupled with the electron transfer. For example, the ratio is less than 1 if the electron transfer is followed by a chemical reaction.

The formal redox potential ( $E^0$ ) for a reversible process is given by the mean of the peak potentials. The other characteristic potential parameter is the separation of the peak potentials  $\Delta E_p$ . The theoretical value for  $\Delta E_p$  for a reversible process is  $0.057/n$  V, and it is independent of scan rate. However, the measured value for a reversible process is generally higher due to un-

compensated solution resistance and non-linear diffusion. Larger values of  $\Delta E_p$ , which increase with increasing scan rate, are characteristic of slow electron transfer kinetics.

The successful completion of this experiment will prepare the student to move on to more electrochemistry, such as the study of chemical reactions coupled to electron transfer reactions, the use of non-aqueous solvents, the effects of different electrode materials and the properties of microelectrodes. A number of possible advanced experiments are suggested by the BAS series of "CV Notes" and "Electrochemical Application Capsules".

## References

- 1) P.T. Kissinger and W.R. Heineman, *J. Chem. Ed.* 60 (1983) 702.
- 2) P.T. Kissinger, D.A. Roston, J.J. Van Benschoten, J.Y. Lewis and W.R. Heineman, *J. Chem. Ed.* 60 (1983) 772.

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