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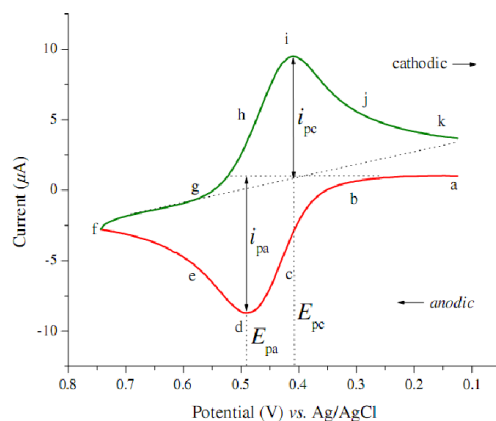
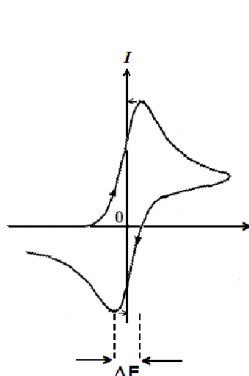
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## STUDY OF ELECTROCHEMICAL PROPERTIES OF FERROCENE USING CYCLIC VOLTAMMETRY

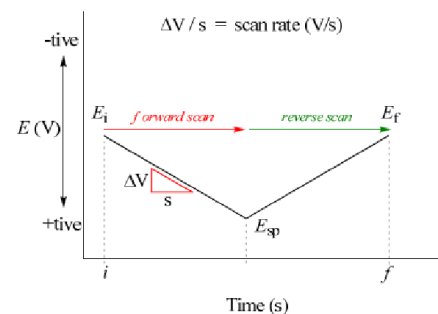
### THEORY

Oxidation and reduction processes are very important in inorganic chemistry. One way in which such processes can be characterized is by cyclic voltammetry. A potential is applied across a solution of the species to be studied and the current measured. The voltage is scanned from a suitable starting point to a predetermined end point and then back again. We will study the redox couple formed by the oxidation of ferrocene to the ferrocenium cation. Both the neutral ferrocene molecule and the cation are stable in solution, and the redox couple is said to be reversible. [Irreversible couples arise when one of the species formed by oxidation (or reduction) undergoes a chemical change. The species that is then re-reduced is chemically different from the species oxidized and reduction takes place at a voltage different from the oxidation voltage].

In principle, the oxidation and reduction of ferrocene take place at the same potential. However, there is typically a finite solution resistance between the working and reference electrodes resulting in a slight difference in potential between the oxidation and reduction steps ( $\Delta E$ ).



A typical CV for ferrocene



The horizontal coordinate of the plot is electrochemical potential presented in units of volts or millivolts. The more negative the reduction potential, the more difficult the species is to reduce, and the higher the energy of the electronic orbital receiving the electron. Species that are reduced at high negative potentials are typically strong reducing agents in their reduced form. Sodium ion is reduced to sodium metal at -2.71 V relative to the reduction potential of hydrogen ion. Species that are easily reduced undergo reduction at a positive potential, relative to hydrogen ion. Fluorine is reduced to fluoride at +2.87 V. Fluorine is a poor reducing agent, but fluorine is a strong oxidizing agent. This behavior is summarized in a standard table of reduction potentials that may be found typically as an appendix in most general chemistry texts.

The vertical coordinate is current in units of microamps. Current is a measure of the number of electrons transferred in the process, and it is typically quite small since the number of electroactive species absorbed on the electrode surface is small. CV plots are conventionally presented with voltage increasing negatively to the right. The current increase above the horizontal is associated with a reduction process as the scan in potential is made in a negative direction and it is said to be cathodic. Once all the species on the electrode has been reduced the scan may be reversed in direction so as to

oxidize the species that was just reduced. The electrons produced by the oxidation step appear as an anodic current below the horizontal. If the couple, consisting of oxidation and reduction steps, is reversible the cathodic and anodic currents will be the same. Further, if the couple is truly reversible the oxidation and reduction steps will occur at nearly the same potential or with a Nernstian  $\Delta E$  no greater than 57 mV. In practice, solution resistance often results in a slightly greater  $\Delta E$ , and the couple is said to be quasireversible.

A third property of the CV is scan rate. A typical value for scan rate is 100 mV/sec. Often, if the reduction (or oxidation) is irreversible due to a chemical transformation, it may become more reversible at a rapid scan rate as oxidation takes place before transformation. The potential at which a reversible redox couple takes place is recorded at the midpoint of  $\Delta E$ .

In all CV methods, the potential (V) of the working electrode is varied continuously with time according to a predetermined potential waveform, while the current (I) is concurrently measured as a function of the potential. The applied potential at the working electrode is measured against a reference electrode of choice, while a counter (auxiliary) electrode is required to balance the I-V applied. Thus, three electrodes are required:

1. WE, Working Electrode (Glassy carbon, Platinum, Silver, Gold)
2. RE, Reference Electrode (Pt wire, Glassy carbon rod)
3. CE, Counter Electrode (Ag/AgCl 3M aq. KCl, Normal Hydrogen Electrode-NHE, Saturated Calomel Electrode, Ag/AgNO<sub>3</sub> 0.01M acetonitrile).

An electrolyte salt must also be dissolved in solution to maintain sufficient conductivity.

As we have discussed already that the potential at the WE is monitored and controlled precisely with respect to the RE via the potentiostat (P). The potentiostat is typically interfaced to a computer which controls the scan in potential at the WE and records current transfer. The counter electrode is used to compensate for the resistance of the solution.

Typically, electrochemical measurements are recorded under N<sub>2</sub> to avoid redox interference from O<sub>2</sub>. Solvents used must be redox inactive over a broad range in potential, and capable of dissolving the compound of interest and a relatively high concentration of electrolyte to reduce solution resistance. Solvents commonly used include acetonitrile, dichloromethane, and sometimes DMSO. The salts commonly used as electrolytes are tetraalkylammonium salts due to their redox inactivity. In our experimental procedure we will use acetonitrile as the solvent, with a solution 0.1 M tetrabutylammonium perchlorate (TBAP), as the electrolyte, and 0.001 M in ferrocene. Prepare enough solution. Once prepared, the solution may be added to the cell for electrochemical characterization.

Comment on Graphs?