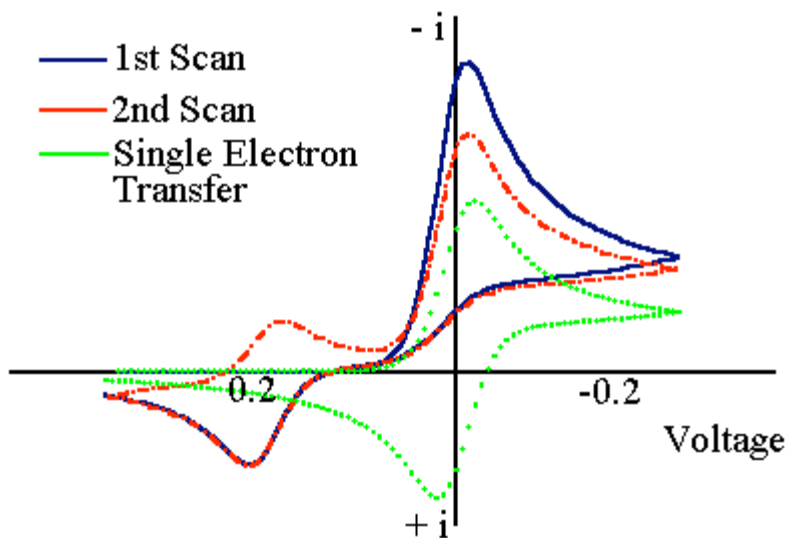


## Assignment: Voltammetry. : Solution Guide

1. (a) For the redox scheme presented below account for the appearance of the cyclic voltammogram.



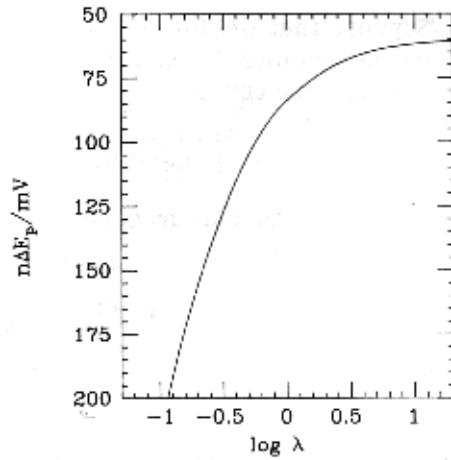
This is an example of an ECE reaction where the product S is beyond its redox potential and is thus in its oxidized form. In the first cathodic scan (voltammetry here is according to the American convention) O is reduced to R (blue line). Note that the current is substantially larger than that for a single electron transfer (green line) in the absence of any chemical step. This is due to the chemical reaction which is occurring rapidly on the time-scale of the cv sweep (see below). As the forward scan proceeds, R is rapidly removed from the diffusion layer. The system responds to this in an attempt to remain in equilibrium (and thus adhere to the Nernst equation)

$$E = E^0 + \frac{RT}{nF} \ln \frac{[O]}{[R]}: \text{ for the process } O = ne + R$$

Since [R] is reduced by the chemical reaction more current flows in order to attempt to maintain the O/R ratio.

In the reverse anodic scan there is little evidence of the re-reduction of R indicating that the chemical reaction is fast on the electrochemical timescale. However we now see a peak due to the oxidation of S to T and the corresponding re-reduction of T to S in the 2<sup>nd</sup> cathodic scan. In the final scan, the oxidation of O to R is again evident, and is still enhanced wrt to the single electron transfer. It is smaller than in the first scan because of the gradual depletion of O from the diffusion layer.

(b) (i) The cyclic voltammogram of ferrocene in DMSO at a platinum microelectrode showed a peak separation of 147mV at a scan rate of 200V/s. If the diffusion coefficient is  $2 \times 10^{-10} \text{ m}^2\text{s}^{-1}$  determine the electron transfer rate constant.



$$\delta = k_0 [RT/(\pi DFc)]^{1/2}$$

From the graph (see slide 22 lecture 5) : we can evaluate  $\delta$  and thus  $k$ .

$$k = 5 \times 10^{-4} \text{ m/s}$$

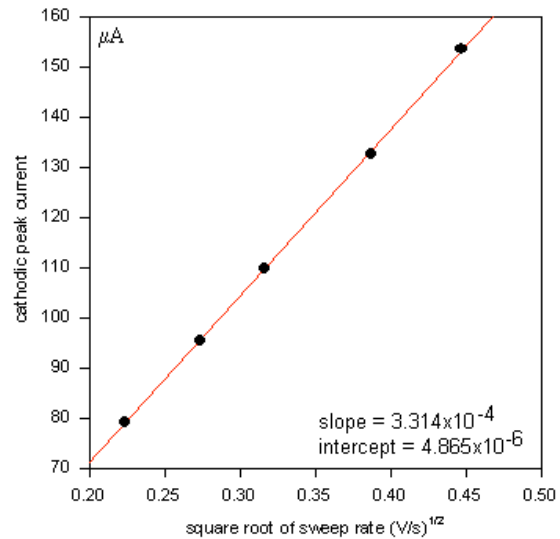
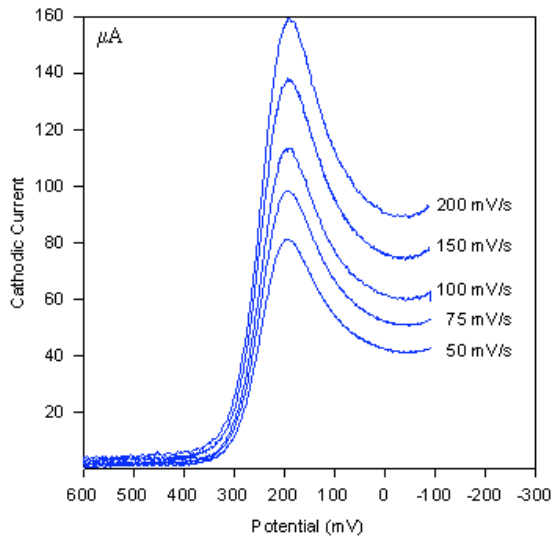
(ii) What assumptions did you make in determining  $k$ ? What are the potential sources of error in such a determination?

The principal assumption here is that the peak shift is not due to ohmic drop as well. Since the voltammetry was recorded at a microelectrode this is probably safe to do. Also one should be very careful in voltammetry. Since the capacitive currents are unknown and uncompensated in LSV there can be some error in peak determinations.

(iii) For the voltammograms below, the electrode area,  $A$ , was  $0.1963 \text{ cm}^2$  and the concentration,  $C$ , was  $2.55 \text{ mM}$ . Determine the diffusion coefficient of the electroactive moiety. Assume a one-electron redox process.

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

the constant has units (i.e.,  $2.687 \times 10^5 \text{ C mol}^{-1} \text{ V}^{-1/2}$ ).



D.  $7 \times 10^{-6} \text{ cm}^2/\text{s}$