1. (20 pts). In a chronoamperometric experiment, the following $i-t$ data were obtained during a potential step experiment to oxidize (1e) ferrocyanide (Fe(CN)$_6^{3-}$) to ferricyanide (Fe(CN)$_6^{4-}$). The measurements were made at a Pt disc electrode.

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Current (μA)</th>
<th>$i^{1/2}$ (s)</th>
<th>$i^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.55</td>
<td>40.2</td>
<td>1.24</td>
<td>49.5</td>
</tr>
<tr>
<td>2.33</td>
<td>32.7</td>
<td>1.53</td>
<td>50.0</td>
</tr>
<tr>
<td>3.11</td>
<td>28.0</td>
<td>1.76</td>
<td>49.3</td>
</tr>
<tr>
<td>3.89</td>
<td>25.0</td>
<td>1.97</td>
<td>49.3</td>
</tr>
<tr>
<td>5.44</td>
<td>21.2</td>
<td>2.33</td>
<td>49.3</td>
</tr>
<tr>
<td>6.98</td>
<td>18.7</td>
<td>2.64</td>
<td>49.4</td>
</tr>
</tbody>
</table>

Is the reaction rate controlled by semi-infinite linear diffusion? If your answer is yes, then provide one or two pieces of evidence in support of your conclusion. Why did they start collecting data at 1.55 s and not before?

- **Constant $i^{1/2}$ product with $t$.**
- $i^{1/2} = \frac{nFAD^{1/2}C}{t^{1/2}}$
- **Started collecting data after 1 s to allow double layer in response to the potential step to fully charge**
- $i^{1/2} = i_{ch} \exp\left(-\frac{E}{kT}\right)$ larger $t$, $i_{ch} \rightarrow 0$

In the same experiment, the following data were obtained from a series of chronoamperometric measurements at boron carbide electrodes. The purpose for these experiments was to determine the electrochemically active area. Explain the data.

**TABLE 3-6**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Geometric area, cm$^2$</th>
<th>Electrochemical area, a cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished</td>
<td>0.36</td>
<td>0.35</td>
</tr>
<tr>
<td>Rough A</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>Rough B</td>
<td>0.44</td>
<td>0.53</td>
</tr>
<tr>
<td>Rough C</td>
<td>0.7</td>
<td>0.94</td>
</tr>
</tbody>
</table>

* Via $i^{1/2}$ curves for ferrocyanide oxidation in 0.5 M KCl.
Researchers used a potential step experiment to study the oxidation of a new drug compound. Assuming there was no adsorption of the drug, calculate the currents at 1, 2, 3, 4 and 5 s during the step. The following parameters are important to know: \( A = 0.1 \ cm^2 \) (disk), \( C = 1 \ mM \), and \( D = 5 \times 10^{-6} \ cm^2/s \). You can put the calculated data in a table. Explain the trend in the current using concentration-distance profiles.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Current (mA)</th>
<th>( t' (\sec) )</th>
<th>( \sqrt{it} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.1</td>
<td>1.00</td>
<td>12.1</td>
</tr>
<tr>
<td>2</td>
<td>8.7</td>
<td>1.41</td>
<td>12.3</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>1.73</td>
<td>12.1</td>
</tr>
<tr>
<td>4</td>
<td>6.1</td>
<td>2.00</td>
<td>12.2</td>
</tr>
<tr>
<td>5</td>
<td>5.4</td>
<td>2.24</td>
<td>12.1</td>
</tr>
</tbody>
</table>

\[
i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}}
\]

\[
k = \frac{nFAD^{1/2}C}{\pi^{1/2}} = \frac{(1)(96,500 \ C/mol)(0.1 \ cm^2)(5 \times 10^{-6} \ cm^2/s)(1.0 \ mM)}{(3.14)^{1/2}}
\]

\[
= 1.21 \times 10^{-5} \ C/s^{1/2}
\]

![Diagram showing the concentration-distance profiles](image)

\[
\left[ \frac{\partial C(0, t)}{\partial x} \right]_{x=0} \quad \text{with } t \rightarrow \text{ within limit}
\]
3 (20 pts.). In the same experiment as described in #2, researchers performed the measurements using a 10 μm diameter disk microelectrode. Assuming spherical diffusion conditions as a possibility, calculate the currents at 1, 2, 3, 4 and 5 s during the step. Using the same parameters as listed in #2. Explain the trend in the current using concentration-distance profiles.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Current (pA, planar)</th>
<th>Current (pA, half-planar)</th>
<th>Current (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.094</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>0.068</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>0.055</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>0.048</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>0.042</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

\[ I(t) = \frac{nFAD_{c_t}}{\pi^{\frac{1}{2}} t^\frac{1}{2}} + \frac{nFAD_{c_0}}{t_0} \]

For this radius, after 1 s, the depletion layer is greater in the concentration than \( t_0 \) to steady state diffusion.

\[ \frac{nFAD_{c_t}}{t_0} = \left( \frac{2 \times 10^{-3} \text{ cm}^3}{5 \times 10^{-7} \text{ cm}^3} \right) \left( \frac{5 \times 10^{-5} \text{ cm}^2}{1.0 \times 10^{-4} \text{ cm}^2} \right) = 0.76 \text{ nA} \]

\[ \frac{nFAD_{c_0}^t}{t_0^{\frac{1}{2}}} = \left( \frac{1.0 \times 10^{-4} \text{ cm}^2}{3.14} \right)^{\frac{1}{2}} = 0.096 \text{ (9.6\times 10^{-5} A)} \]

\[ 4\pi t_0 nFDC = 4\pi \left( 5 \times 10^{-7} \text{ cm}^3 \right) \left( 9.6 \times 10^{-5} \text{ cm}^2 \right) \left( 5 \times 10^{-5} \text{ cm}^2 \right) \left( 1.0 \times 10^{-6} \text{ mol/cm}^3 \right) = 3.0 \text{ nA} \]

\[ \frac{C_R(t)}{C_L} \frac{1.0^4}{\sqrt{1, 2, 3, 4 \pm 5 \text{ s}}} \]

\[ \frac{dC}{dt} \neq 0 \quad \text{No change in flux as time} \]
4 (20 pts). The following cyclic voltammogram was recorded for a reversible redox system. Calculate the number of electrons and the formal potential of the couple.

![Cyclic Voltammogram](image)

**Reversible System**

\[ \Delta E_p = \frac{0.059 \text{V}}{n} \]

\[ n = \frac{0.059}{0.060} = 0.95 \approx 1 \]

\[ E^0 = \frac{E^{\text{ox}}_p + E^{\text{red}}_p}{2} = \frac{0.500 + 0.500}{2} = 0.500 \text{V} \]

Based on your analysis of the voltammetric data presented in the figure below, is the system behaving reversibly (electrochemical reversibility)? What does this mean and what are the characteristic diagnostic voltammetric features of such a system?

**Figure 7.24** Influence of potential scan rate of the cyclic voltammogram; the potential scan rates are (a) 25 (b) 100 and (c) 400 mV s\(^{-1}\). The voltammograms are for the oxidation of R (1 mM); \(D = 10^{-5} \text{cm}^2\text{s}^{-1}\).

![Influence of Potential Scan Rate](image)

A characteristic of a reversible system is a \( \Delta E_p \propto f(\omega) \), \( \Delta E_p \) for these curves is independent of scan rate. \* \( \Delta E_p \propto 0.059/n \text{V} \)

Reversibility means the ET kinetics are such that the cation and redox adjust themselves as rapidly as the potential is being changed according to the Nernst Eq.

\[ \frac{C_{\text{ox}}(t)}{C_{\text{red}}(t)} = f(t) = \exp \left( \frac{nF}{RT} (E_i - \nu t - E^0) \right) \]
5 (20 pts). The total diffusion-limited current in a voltammetric measurement is composed of the planar flux and the radial flux diffusion components, $i_{\text{total}} = i_{\text{planar}} + i_{\text{radial}}$. For a disk microelectrode, the general expression for the radial component is, $i_{\text{radial}} = 4nFDc_0$. The extent to which the planar or radial component dominates depends on the relative dimensions of the electrode and the diffusion layer (i.e., depletion layer thickness). The parameter, $D/vr_0^2$, is useful here. Explain the trends in the voltammetric data shown below.

![Figure 3.20 Cyclic voltammograms for the oxidation of ferrocene at a 6-μm platinum microdisk at different scan rates. (Reproduced with permission [64].)](image)

As the scan rate increases, the diffusion layer thickness decreases (depletion layer) such that its thickness, $\delta$, becomes less than $r_0$, particularly at 10 V/s.

Transition from steady-state to transient diffusion

- At low $\omega$, $Dv/\delta^2 > 1$ (steady-state mass transfer)
- At high $\omega$, $Dv/\delta^2 < 1$ (transient diffusion)
**Key Equations**

\[ \dot{c}(t) = \frac{nFAD^{\frac{1}{2}}C}{(RT)^{\frac{1}{2}}} \]

\[ \dot{i}(t) = \frac{nFAD^{\frac{1}{2}}C}{(RT)^{\frac{1}{2}}} + 4\pi \Gamma_{OnFDC}^+ \]

\[ \frac{dc}{dt} = \frac{C_b - C(t=0)}{\delta} \]

\[ i_e = \frac{nFADC^+}{\delta} \quad \text{(convection)} \]

\[ C_b(t, 0) = \frac{f(t)}{C_{b(0, 0)}} = \exp \left( \frac{nF}{RT} (E_r - E) \right) \]

\[ \dot{E}_{b2} = AC_{dl} J \quad \text{(reaction)} \]

\[ D \left( \frac{\partial^2 c}{\partial r^2} \right)_{r=0} = -D \left( \frac{\partial c}{\partial r} \right)_{r=0} = 0 \]

\[ \zeta = \frac{RTD}{nF^{2}T_c} \]

\[ i_p = 2.69 \times 10^5 \frac{nF^{\frac{1}{2}}AD^{\frac{1}{2}}C^{+}}{D^{\frac{1}{2}}} \]

\[ E_p - E_{b2} = \frac{+1.109 \frac{RT}{nF}}{\frac{28.5 \text{ mV}}{n}} \quad (25^\circ C) \]

\[ (\cdot) \text{ Reduction} \quad (+) \text{ Oxidation} \]

\[ E_{b2} = E_0 + \frac{RT}{nF} \ln \left( \frac{De_0}{D_{o2}} \right) \]

\[ E_{b2} = E_{ph} + \frac{1.09 \frac{RT}{nF}}{\frac{28.0 \text{ mV}}{n}} \quad (25^\circ C) \]

\[ (\cdot) \text{ Reduction} \quad (+) \text{ Oxidation} \]

\[ |E_p - E_{b2}| = \frac{28.5 \text{ mV}}{n} \quad (25^\circ C) \]

\[ i_p = (2.99 \times 10^5) \cdot \frac{1}{2} AC_{dl} D^{\frac{1}{2}} \frac{1}{2} \quad (25^\circ C) \]

\[ \frac{E_p - E_{b2}}{nF} = \frac{477 \text{ mV}}{n} \quad (25^\circ C) \]

\[ (E_p - E_{b2}) = \frac{1.86 \frac{RT}{\alpha F}}{\frac{477 \text{ mV}}{\alpha}} \]