1 (15 pts). In a chronoamperometric experiment, the potential is often stepped from a value where no faradaic current flows to a potential at which the reaction rate is diffusion limited. Draw the potential perturbation, the resulting current-time profile and the concentration-distance profile for a few points along the current-time curve.

2 (10 pts). What are a couple of instrumental and experimental limitations one must be aware of when making i-t curve measurements under "Cottrell conditions"?

1. Response time of the instrument
2. Maximum current reached by potential applied and area of the electrode
3 (15 pts). A disk UME gives a plateau current of 2.32 nA in the steady-state voltammogram for a species known to react with $n = 1$ and to have a concentration of 1 mM and a diffusion coefficient of $10^{-5}$ cm$^2$/s. What is the radius of the electrode?

$$i_{ss} = 4 \pi F D C^* \Gamma_0 = (4)(1)(94,500 \text{ cmol/L})(1 \times 10^{-5} \text{ cm}^2)$$

$$\left(1.0 \times 10^{-4} \text{ mol/cm}^3\right) \Gamma_0$$

$$2.32 \times 10^{-9} \text{ A} = 3.9 \times 10^{-6} \text{ g cm}^{-1} \Gamma_0$$

$$\Gamma_0 = 0.6 \times 10^{-4} \text{ cm or 6.0 \mu m}$$

4 (20 pts). Given $n = 1$, $C^* = 1.00$ mM, $A = 0.02$ cm$^2$ and $D = 10^{-5}$ cm$^2$/s, calculate the current for a diffusion-controlled reaction at (A) a planar electrode and (B) a spherical electrode for $t = 0.5, 1, 2, 3$ and $5$ s.

**Planar**

$$i(t) = \frac{nFADC}{\pi^{1/2}t^{1/2}} = \frac{(1)(94,500 \text{ cmol/L})(0.02 \text{ cm}^2)(1 \times 10^{-5} \text{ cm}^2)(1.0 \times 10^{-4} \text{ mol/cm}^3)}{(3.14)^{1/2} t^{1/2}}$$

$$i(t) = 3.4 \times 10^{-6} \text{ C}^{1/2}/t^{1/2}$$

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.8 \times 10^{-6} A</td>
</tr>
<tr>
<td>1.0</td>
<td>3.4 \times 10^{-6} A</td>
</tr>
<tr>
<td>2.0</td>
<td>2.4 \times 10^{-6} A</td>
</tr>
<tr>
<td>3.0</td>
<td>2.0 \times 10^{-6} A</td>
</tr>
<tr>
<td>5.0</td>
<td>1.5 \times 10^{-6} A</td>
</tr>
</tbody>
</table>

**Nonplanar**

$$A = \frac{a}{2}$$

$$i_a = \frac{nFADC}{\Gamma} = \frac{(1)(94,500 \text{ cmol/L})(0.02 \text{ cm}^2)(1 \times 10^{-5} \text{ cm}^2)(1.0 \times 10^{-4} \text{ mol/cm}^3)}{8.0 \times 10^{-2} \text{ cm}}$$

Calculated for disk geometry $= 2.4 \times 10^{-7}$ A

As that was changed during test. Credit given for spherical calc.
5 (10 pts). Sketch the potential perturbation for cyclic voltammetry, the resulting \( i-E \) curve (for a reversible redox system), and the concentration-distance curves for the reactant and product at both peak potentials.

6 (10 pts). The oxidation of o-dianisidine (o-DIA) occurs by a 2e reaction. For a 2.27 mM solution of o-DIA at a disk electrode of area 2.7 mm\(^2\) with a scan rate of 0.500 V/min, \( i_p = 8.2 \mu A \). Calculate the \( D \) value for o-DIA.

\[
i_p = 2.69 \times 10^5 n^{3/2} A^{-1/2} C^{1/2} D^{1/2} (1)\]

\[
A_{disk} = \pi r^2 = \pi \left( \frac{3.7 \times 10^{-2} \text{ cm}}{2} \right)^2 = 3.7 \times 10^{-2} \text{ cm}^2
\]

\[
U = \left( \frac{0.5 \text{ cm}}{2 \text{ mm}} \right)^2 \left( \frac{1 \text{ mm}}{100 \text{ nm}} \right)^2 = 8.3 \times 10^{-3} \text{ V} \cdot \text{cm}
\]

\[
2.27 \times 10^{-6} \frac{1}{cm^2} = \left( 2.69 \times 10^5 \right) \left( 3.7 \times 10^{-2} \text{ cm}^2 \right)^{1/2} \left( 0.5 \times 10^{-2} \text{ cm} \right)^{1/2} \left( 8.3 \times 10^{-3} \text{ V} \cdot \text{cm} \right)^{1/2}
\]

\[
D^{1/2} = 1.9 \times 10^{-3} \text{ cm}^{1/2}
\]

\[
D = \left( 1.9 \times 10^{-3} \text{ cm}^{1/2} \right)^2 = 3.7 \times 10^{-6} \text{ cm}^2 / \text{s}
\]
7 (10 pts). What does it mean that a redox reaction is kinetically reversible? What are characteristic features of cyclic voltammetric $i-E$ curves for kinetically reversible redox systems at different scan rates?

Concentration ratio \((O^\text{red}/O^\text{ox})\) adjusts according to the Nerster Equation as quickly as potential is changed with time (i.e., scan rate).

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

\[ \Delta E_p = f(u) \]

\[ \frac{i_p}{i_p^{\text{diff}}} = 1 \]

Cot+ ratio adjusts with potential (scan-rate), as dictated by equation.

\[ i(t) = nFADC^* \left( \frac{1}{(1/2)^2} + \frac{1}{r^2} \right) \]

\[ i(t) = \frac{nFAD^{1/2}C^*}{n^{1/2}C^{1/2}} \]

\[ i = (2.68 \times 10^5)n^{3/2}AD^{1/2}C^{1/2} \]

\[ i_{\text{diff}} = 4nFDC^*r_0 \]

\[ i_{\text{ch}} = AC^2 \]