1 (10 pts). For the cyclic voltammetric curves shown, label all key diagnostic features of the curves. Determine \( i_p^{ox} \), \( \Delta E_p \), and \( E^o \). Is the measured \( i_p^{ox} \) value determined from these experimental curves in agreement with what one calculates theoretically? Explain the differences between curves a and b for the redox analyte.

\[ E^\circ_{ox} \approx 25 \text{ mV} \quad \Delta E_p \approx 45 \text{ mV} \quad E_p \approx 70 \text{ mV} \]

\[ E_{p_{1/2}} = E^\circ + \frac{E_{p_{1/2}}}{2} = \frac{25 + (-45)}{2} = 35 \text{ mV} \]

\[ \dot{i}_p^{ox} \approx 7 \text{ mA/cm}^2 \quad \text{assume 1 cm}^2 \quad \Rightarrow \dot{i}_p^{ox} \approx 7 \text{ mA} \]

\[ i_p^{ox} = (2.49 \times 10^{-5}) \pi^{1/2} AD^{1/4} C_{ox}^{1/2} u_1/2 \]

\[ i_p^{ox} = (2.49 \times 10^{-5})(1^{1/2})(1 \text{ cm}^2)(1 \times 10^{-5} \text{ cm}^3/\text{s})^{1/2}(1 \times 10^{-6} \text{ mol/cm}^3)(100 \text{ V/s})^{1/2} \]

\[ \text{Result:} \quad 8.5 \times 10^{-3} \text{ A} \quad \text{or} \quad 8.5 \text{ mA} \]

\[ \text{little larger than estimated values.} \]
In general, cyclic voltammetry is carried out with only an oxidized or reduced species present. In this example, consider only R being present. This means \( R = O + e^- \). For such an experiment with reversible electron transfer,

\[ C_R(x, t) = C^*_R \quad \text{and} \quad C_O(x, t) = 0 \quad \text{at} \quad t=0 \quad \text{(initial condition)}. \]

The boundary condition for this experiment would be at \( x=\infty \): \( C_R(x, t) = C^*_R \) and \( C_O(x, t) = 0 \).

At \( x=0 \),

\[ D \frac{\partial C_R}{\partial x} \bigg|_{x=0} = -D \frac{\partial C_O}{\partial x} \bigg|_{x=0} \]

and:

\[ \frac{C_D(0,t)}{C_R(0,t)} = \exp \left( \frac{nF(E_{i+} + ut - E_{red})}{RT} \right) \]

At the scan rates used in this work, is the redox system behaving reversibly. Provide conclusive proof of this by at least four metrics. Are ohmic effects influencing the curve shapes? Why or why not? Complete the table.

<table>
<thead>
<tr>
<th>Measurable</th>
<th>Reversible Couple</th>
<th>Irreversible Couple</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E_p = E_{p,ox} - E_{p,red} )</td>
<td>59 mV ( \frac{R}{n} )</td>
<td>&gt;59 mV ( \frac{n}{f(t, u)} )</td>
</tr>
<tr>
<td>( E_p - E_{p/2} )</td>
<td>59 mV ( \frac{R}{n} )</td>
<td>48 mV ( \frac{R}{n} )</td>
</tr>
<tr>
<td>( i_{p,ox}/i_{p,red} )</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( i_p )</td>
<td>independent on ( u )</td>
<td>dependent on ( u )</td>
</tr>
</tbody>
</table>

1. \( \Delta E_p \approx 59 \text{ mV} \) and is independent of the scan rate.
2. \( i_{p,ox} \) varies linearly to \( u^{1/2} \).
3. \( E_{p,ox} \) is independent of \( u \).
4. \( \frac{i_{p,ox}}{i_{p,red}} \approx 1.0 \) at all scan rates.

Measuring the forward peak current is usually the most accurate. Measuring the reverse peak current is subject to error. Dependence \( E_{p} \) and \( u \).
3. (10 pts). Cyclic voltammetry is a powerful tool for the study of homogeneous chemical reactions where the reactant is formed by electron transfer. It is possible to investigate the mechanism and kinetics of complex chemistry such as an EC reaction. In such a reaction, a product is generated by a reversible electron transfer reaction, which then undergoes a follow-up chemical reaction that produces a new product, $P'$, that is electrochemically inactive. The shapes of CV curves with scan rate a re diagnostic of different reaction mechanisms.

Explain the trends in the following curves and propose a reaction mechanism. Provide details on why currents increase or decrease with increasing scan rate. Scan rates are a) 10 b) 100 and c) 1000 mV/s.

The form of the voltammogram (shape) will depend on rate constant, $k$, for the following chemical step:

The curve has current homed to $\sqrt{v}$ so you don't see the forward peak current increasing with scan rate. What you do see is the reverse or reduction peak current increase with increasing scan rate. It means more of the oxidized product is available at the electrode surface to be reduced as the speed of the measurement is increased. This is a classical EC behavior.

$$R \rightarrow O \times + e^- \rightarrow O + \rightarrow P'$$

$\frac{1}{2}$-life $d$) $O \left( \frac{1}{2} \right)_{\text{t}} = \frac{\text{log} 2}{k}$

When time scale of measurement is short compared to $t_{1/2}$ (high scan rate) a reversible response is seen, with $i_p \approx i_{pa}$. When time scale of measurement is long compared to $t_{1/2}$ (slow scan rate), then $i_p$ reduced $i_p$ relative to $i_{pa}$ so the rate is less than 1.