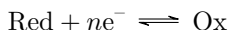
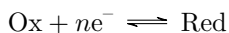


Instructor's Guide for the shinyCV Application

Quick Start

This Shiny app simulates a cyclic voltammetry experiment using the computational method outlined in Gosser, D. K. *Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms*, VCH, New York, 1993 and in Brown, J. H., *J. Chem. Educ.*, **2015**, 92, 1490-1496. Simulations are available for the following mechanisms:

- An E-only mechanism that takes one of the following forms



- An EC mechanism that takes one of the following forms



- A CE mechanism that takes one of the following forms



where Z is a non-electroactive species.

For each mechanism the parameters used to simulate the cyclic voltammetry experiment are divided into five groups:

- **Redox Reaction:** initial direction, number of electrons, and transfer coefficient
- **Redox Species:** formal potential, bulk concentration, and diffusion coefficient
- **Potentials:** starting potential, switching potential, and scan rate
- **Rate Constants:** heterogeneous charge-transfer rate constant, homogeneous first-order rate constants for the forward and the reverse chemical reaction
- **Miscellaneous:** electrode's surface area, temperature, and reset button to reestablish initial conditions

See the *Parameters* tab for more details about these parameters.

The three plots at the top of each mechanism's page show the applied potential as a function of time, the current as a function of applied potential, and the concentrations of Ox, Red, and, where appropriate, Z, as a function of distance from the electrode's surface. The middle plot, which is the cyclic voltammogram, is annotated with its characteristic peak potentials and peak currents, and values for ΔE_p , E_{avg} , and $|i_{p,a}/i_{p,c}|$ or $|i_{p,c}/i_{p,a}|$. Use the sliders included with the plots to select the potential and time, and the concentration limits for the diffusion profiles in the plot on the right.

Computational Details

The simulations here draw on functions in the R-package **eChem**, which is available through [CRAN](#) or through [Github](#). Each simulation uses a separate diffusion grid to calculate and to store the concentrations of Ox and Red—and, for an EC or CE mechanism, the concentrations of Z—as a function of distance from the electrode's surface and as a function of elapsed time as the potential is swept from its starting potential to the switching potential and back to the starting potential. Each diffusion grid is a matrix with n_i rows and n_j columns where a row is a discrete moment in time and a column is a discrete distance from the electrode surface; thus, for example, matrix element $[\text{Ox}]_{i,j}$ stores the concentration of Ox at time i and at distance j .

The mass transfer of Ox, Red, and Z are governed by Fick's Second Law of Diffusion

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2}$$

where C is a species' concentration, D is its diffusion coefficient, and δt and δx are increments in time and distance, respectively. When using the explicit finite difference method, Fick's Second Law is approximated as

$$\frac{C_{i,j} - C_{i-1,j}}{\Delta t} = D \left[\frac{C_{i-1,j-1} - 2C_{i-1,j} + C_{i-1,j+1}}{\Delta x^2} \right]$$

which means that the element $C_{i,j}$ in a diffusion grid is

$$C_{i,j} = C_{i-1,j} + \lambda [C_{i-1,j-1} - 2C_{i-1,j} + C_{i-1,j+1}]$$

where λ is equivalent to $\frac{D\Delta t}{\Delta x^2}$. In essence, this approximation assumes that for each unit of time, diffusion is limited to movement between adjacent locations in the diffusion grid.

Because each element in a diffusion grid is calculated using values from the immediately preceding increment in time and using values from distances that are immediately adjacent, we cannot use this approach to calculate elements in the diffusion grid's first column, its last column, and its first row. The elements in a diffusion grid's last column, which is the distance furthest from the electrode's surface, are filled using that species' initial concentration in bulk solution; that is, the diffusion grid's width, which is defined as $6 \times \sqrt{Dt_{\text{total}}}$, where t_{total} is the time to complete the cyclic voltammetry experiment, is sufficient to ensure that the diffusion layer never extends beyond the diffusion grid's last column. The elements in a diffusion grid's first row, which is for time $t = 0$, also are filled using that species' concentration in bulk solution.

For the E and the EC mechanisms, the concentration of either Ox or Red in bulk solution is greater than zero and the concentration in bulk solution of the other species—and the bulk concentration of Z for the EC mechanism—is zero. For the CE mechanism, the combined concentrations of either Z and Ox, or of Z and Red is greater than zero, with their individual amounts determined by the relative rates of the forward and the reverse chemical reactions; the bulk concentration of the remaining species is zero.

To calculate the concentrations of Ox and of Red at the electrode's surface—that is, to fill the diffusion grid's first column—we first calculate the flux of Ox, J_{Ox} , to the electrode's surface using the concentrations of Ox and of Red in the increment immediately adjacent to the electrode's surface

$$J_{\text{Ox}} = -\frac{k_f[\text{Ox}]_{i,2} - k_b[\text{Red}]_{i,2}}{1 + \frac{k_f\Delta x}{D} + \frac{k_b\Delta x}{D}}$$

The potential-dependent, heterogeneous electron-transfer rate constants, k_f and k_b , are calculated using the Butler-Volmer equation

$$k_f = k^\circ e^{-\alpha n F (E - E^\circ) / RT}$$

$$k_b = k^\circ e^{(1-\alpha) n F (E - E^\circ) / RT}$$

where k° is the potential-independent, heterogeneous electron-transfer rate constant, α is the transfer coefficient, n is the number of electrons in the redox reaction, E is the applied potential, E° is the redox couple's formal potential, F is Faraday's constant, R is the gas constant, and T is the temperature in Kelvin. The concentration of Ox at the electrode's surface, therefore, is

$$[\text{Ox}]_{i,1} = [\text{Ox}]_{i,2} + \frac{J_{\text{Ox}}\Delta x}{D}$$

Because the flux of Red is equal in magnitude but opposite in sign, we also know that

$$J_{\text{Red}} = -J_{\text{Ox}}$$

$$[\text{Red}]_{i,1} = [\text{Red}]_{i,2} + \frac{J_{\text{Red}}\Delta x}{D}$$

By definition, the flux of Z at the electrode surface is zero and

$$[Z]_{i,1} = [Z]_{i,2}$$

Finally, the total current at each increment in time is calculated using the flux for Ox

$$i = -nFAJ_{\text{Ox}}$$

where A is the electrode's surface area.

For a mechanism that includes a chemical reaction, the concentrations of Ox, Red, and Z are modified to include contributions from the chemical reactions. For example, the concentration of Ox in a CE mechanism where it is in equilibrium with Z is

$$C_{i,j} = C_{i-1,j} + \lambda [C_{i-1,j-1} - 2C_{i-1,j} + C_{i-1,j+1}] + k_{\text{chem},f}\Delta t C_{i-1,j} - k_{\text{chem},r}\Delta t C_{i-1,j}$$

where $k_{\text{chem},f}$ and $k_{\text{chem},r}$ are the homogeneous first-order rate constants for the chemical reaction's forward and reverse directions.

Accuracy of the Cyclic Voltammetry Simulations

An important constraint on these simulations is that diffusion is limited to adjacent points on the diffusion grid, which, in turn, requires that

$$\frac{D\Delta t}{\Delta x^2} \leq 0.5$$

As $\Delta t = \frac{t_{\text{total}}}{n_{\Delta t}}$ and $\Delta x = \frac{x_{\text{total}}}{n_{\Delta x}} = \frac{6\sqrt{D \times t_{\text{total}}}}{n_{\Delta x}}$, where $n_{\Delta x}$ is the number of increments in distance and $n_{\Delta t}$ is the number of increments in time, the number of increments in distance and the number of increments in time must satisfy the relationship

$$n_{\Delta x} < \sqrt{18 \times n_{\Delta t}}$$

When this is not the case, the simulation results in oscillations in the calculated current.

The accuracy of a cyclic voltammetry simulation improves if we use more discrete time units and more discrete distance units—subject to the constraint described above—as these determine the increments in time, Δt , and in distance, Δx , both of which affect the calculated values for $C_{i,j}$, for J_{Ox} and for J_{Red} , and for i . In addition, for any scan rate, the number of time units determines the increments in applied potential, ΔE , which affects the calculated values for k_f and k_b , and, therefore, the calculated values for J_{Ox} , J_{Red} , and i .

Although an increase in the number of time units improves accuracy, it does so at the cost of an increase in the time needed to complete the computations and, as a result, the smoothness of the app's response to a change in a parameter's value. For example, using the default conditions for the E mechanism generates these results, where ΔE , which has an expected value of 59 mV, serves as a proxy for accuracy.

Table 1: Effect on Simulations of the Diffusion Grid's Size

number of time units	number of distance units	run-time (s)	ΔE (V)
200	50	0.02	80
1000	100	0.20	60
2000	180	0.60	66
4000	260	1.80	62
10000	420	7.30	61

The simulations in this app use 2000 discrete intervals in time and 180 discrete intervals in distance, which provides a suitable compromise between accuracy and run-time. Note that these options result in individual

diffusion grids with 360,000 individual elements!

For the EC and the CE mechanisms, Gosser suggests that accuracy is reasonable if the number of increments in time satisfies the relationship

$$n_{\Delta t} \geq 4 \times t_{\text{exp}} \times k_{\text{chem}}$$

where t_{exp} is the time to complete the scan and k_{chem} is the homogeneous chemical rate constant. This places constraints on the choices for the scan rate, and the chemical rate constants $k_{\text{chem,f}}$ and $k_{\text{chem,r}}$, which are reflected on the ranges made available in simulations for the EC and CE mechanisms.

Responses to Exercises

The figures included with these answers were created using functions in the R-package **eChem**, which is available through [CRAN](#) or through [Github](#).

Getting Started

1. In his article “Understanding Electrochemistry: Some Distinctive Concepts” (*J. Chem. Educ.* **1983**, *60*(4), 262-264, Larry Faulkner provides a list of five concepts that are important to understanding electrochemistry:

- an electrochemical system is not homogeneous
- many things can happen at once
- current is an expression of rate
- potential is an expression of electron energy
- one cannot control both current and potential simultaneously

Locate a copy of the article and, for each concept, summarize Faulkner’s point and explain why it is crucial to understanding what happens during a cyclic voltammetry experiment.

Sample Response

- An electrochemical system is not homogeneous because the oxidation reaction or the reduction reaction of interest takes place at the interface between the electrode, which usually is a solid—a liquid Hg electrode is an exception—and the solution, or, more specifically, the solution in immediate contact with the electrode surface. As a result, the composition of the solution at the electrode’s surface generally is quite different from the composition of the bulk solution.
- An electrochemical system always includes an oxidation or a reduction reaction that takes place at the electrode’s surface. It may, as well, include chemical reactions that involve the redox reaction’s reactants and/or products. As a result, the rate of the redox reaction is affected both by the rate of electron transfer and by the rates of any chemical reactions.
- When an oxidation reaction takes place, electrons move from the electrode to Ox to effect a reduction to Red, or from Red to the electrode to effect an oxidation to Ox. This movement of electrons is a current and the magnitude of the current, therefore, is directly proportional to the rate of this electron-transfer reaction.
- The more negative the applied potential, the greater the energy of electrons in the electrode. If the electron’s energy is sufficiently large relative to an electroactive species in solution, then the electron can move from the electrode to the solution species, effecting a reduction of Ox to Red. For a sufficiently more positive potential, the electron’s energy in the electrode is less than when it is with the electroactive species; movement of the electron from the solution species to the electrode results in the oxidation of Red to Ox.
- As suggested above, a current flows (or does not flow) in response to the potential applied to the electrode; thus, we can either record how the potential responds to a change in the current, or we can record how the current responds to a change in the potential. The latter is the approach used in cyclic voltammetry.

2. The current in an electrochemical experiment is described as cathodic or anodic. What is the difference between these two types of currents? If a current flows when the potential is scanned from a more positive value to a more negative value, is the current cathodic or anodic?

Sample Response

When oxidation or reduction occurs a current flows through the electrochemical cell. For a reduction reaction, such as $\text{Ox} \rightarrow \text{Red}$, the current is called a cathodic current and it has a positive sign. For an oxidation reaction, such as $\text{Red} \rightarrow \text{Ox}$, the current is called an anodic current and it has a negative sign. Scanning from a more positive potential to a more negative potential leads to reduction and a cathodic current.

3. A redox couple consists of an oxidized species and a reduced species, such as Fe^{3+} and Fe^{2+} , and is characterized by a standard state reduction potential, E° , which for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple is +0.771 V. Write the reaction that corresponds to this potential and the corresponding Nernst equation. What can you say about the relative concentrations of Fe^{3+} and Fe^{2+} when the potential is +0.771 V? +0.551 V? +0.991 V?

Sample Response

The relationship between potential, E , and the concentrations of Fe^{2+} and of Fe^{3+} is given by the Nernst equation, which for the reaction $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ is

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

where E° is the standard state potential for the reduction of Fe^{3+} to Fe^{2+} , R is the gas constant, T is the temperature in Kelvin, n is the number of electrons in the reduction reaction, and F is Faraday's constant. If $E = E^\circ$, then the concentrations of Fe^{3+} and Fe^{2+} are equal and the term $\ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ in the Nernst equation is zero. If E is less positive than E° , as is the case when $E = +0.551$ V, then $\ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ is positive, which means $[\text{Fe}^{2+}] > [\text{Fe}^{3+}]$. If E is more positive than E° , as is the case when $E = +0.991$ V, then $\ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$ is positive, which means $[\text{Fe}^{2+}] < [\text{Fe}^{3+}]$.

4. As indicated on the **Parameters** tab and by the controls for each mechanism, the simulations use the standard state formal reduction potential $E^{\circ'}$, instead of the standard state potential, E° . What is the difference between E° and $E^{\circ'}$, and why is this difference important? In 0.3 M H_3PO_4 , the standard state formal potential for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple is +0.44 V. What does this imply about the ease of reducing Fe^{3+} to Fe^{2+} in H_3PO_4 relative to its reduction in water?

Sample Response

The standard state potential for the reduction of Fe^{3+} to Fe^{2+} is the potential when each is present at unit concentration—or, more correctly, with unit activity—and where there are no additional reactions that might affect the concentrations of one or both of Fe^{3+} or Fe^{2+} . If the solution includes a species, such as H_3PO_4 , that can form a complex with either Fe^{3+} or Fe^{2+} , then the potential that yields unit concentrations (activities) of Fe^{3+} and Fe^{2+} will differ from the standard potential; this is called the formal potential. A formal potential of +0.44 V means that it is easier to reduce Fe^{3+} to Fe^{2+} in the presence of H_3PO_4 .

Mechanism: E

1. Beginning with the default conditions for the reaction $\text{Ox} \rightarrow \text{Red}$, determine the quantitative relationship between the cathodic peak current, $i_{p,c}$, and the bulk concentration of Ox. Repeat for the number of electrons (n), the electrode's surface area (A), the diffusion coefficient (D), and the scan rate (ν). Explain your observations and propose a general equation that relates the cathodic peak current to these parameters.

Sample Response

For the concentration of Ox, the current is 7.98 μA when $[\text{Ox}] = 1.0 \text{ mM}$ and is 79.77 μA when $[\text{Ox}] = 10.0 \text{ mM}$. A 10-fold increase in concentration results in a 10-fold increase in current, which means the current is directly proportional to $[\text{Ox}]$.

For the number of electrons, n , the current is 7.98 μA when $n = 1$, 21.99 μA when $n = 2$, and is 39.62 μA when $n = 3$. The relationship here likely is the most challenging one for students to discover. A 2-fold increase in n from 1 to 2 2.75-fold increase in the current. A 3-fold increase in n from 1 to 3 results in a nearly 5-fold increase in current. Finally, a 1.5-fold increase in n from 2 to 3 results in a 1.8-fold increase in current. With a little exploration of these relationships, it is clear that the current is directly proportional to $n^{3/2}$.

For the diffusion coefficient, D , the current is 7.98 μA when D is $1 \times 10^{-5} \text{ cm}^2/\text{s}$ and is 15.88 μA when D is $4 \times 10^{-5} \text{ cm}^2/\text{s}$. A 4-fold increase in D results in a 2-fold increase in current, which means the current is directly proportional to $\sqrt{D}$.

For the electrode's area, A , the current is 7.98 μA when A is 0.01 cm^2 and is 79.77 μA when A is 10.0 cm^2 . A 10-fold increase in A results in a 10-fold increase in current, which means the current is directly proportional to A .

For the scan rate, ν , the current is 7.98 μA when $\nu = 10^0 = 1 \text{ V/s}$ and is 25.10 μA when $\nu = 10^1 = 10 \text{ V/s}$. A 10-fold increase in ν results in a 3.15-fold increase in current, which means the current is directly proportional to $\sqrt{\nu}$.

Combining all terms suggests the following relationship between the current and the variables

$$i = \text{constant} \times n^{\frac{3}{2}} A D^{\frac{1}{2}} C \nu^{\frac{1}{2}}$$

which is the Randles-Sevcik equation. Substituting in values for $i_{p,c}$ (in amps instead of μA), n , D , C (in mol/cm^3 instead of mol/L), and ν for the default conditions gives the constant as 252,350, which compares favorably with its expected value of 268,600.

- Beginning with the default conditions for the reaction $\text{Ox} \rightarrow \text{Red}$, use the slider below the applied waveform to examine the diffusion profiles for Ox and Red at times of 0, 0.2, 0.5, 0.8, 1.0, 1.3, 1.5, 1.8 and 2.0 seconds. Explain how and why the shape of the diffusion profile for Ox changes as you change the time. What is the relationship between the diffusion profile for Ox and the magnitude and sign of the current?

Sample Response

Figure 1 below shows the diffusion profiles at the specified times. As we change the time, we change the applied potential, which, in turn, determines the concentrations of Ox and Red at the electrode's surface (see Question 3 in the section "Getting Started").

- At $t = 0 \text{ s}$ and $t = 0.2 \text{ sec}$, the potential is sufficiently positive such that only Ox is stable at the electrode's surface. The resulting diffusion profiles are flat and, as the slope of the diffusion profile for Ox is proportional to the current, no current flows.
- At $t = 0.5 \text{ sec}$, the applied potential equals the redox couple's formal potential and the concentrations of Ox and Red at the electrode surface are equal. The diffusion profiles show that Ox is diffusing toward the electrode's surface, which gives rise to a positive current.
- At $t = 0.8 \text{ s}$, $t = 1.0 \text{ s}$, and $t = 1.2 \text{ s}$ only Red is stable at the electrode surface and the concentration of Ox at the electrode surface is 0 mM. The diffusion profile for Ox becomes less steep, and the current decreases, as the diffusion layer grows with time.
- At $t = 1.5 \text{ s}$ the concentrations of Ox and Red at the electrode surface are, again, equal. Because their concentrations at the electrode surface change faster than Ox and Red can diffuse to and from the electrode surface, their diffusion profiles no longer show just a steady increase or decrease with distance from the electrode surface. Instead, the diffusion profiles show a peak or a valley near the electrode surface. The change in slope for the diffusion profile of Ox near the electrode surface gives rise to a change in the sign of the current.

- Finally, at $t = 1.8$ and $t = 2.0$, the concentrations of Ox and Red at the electrode surface return to their original values; the decreasing slope of the diffusion profile for Ox shows that the current is becoming less negative.
3. How does changing the initial direction from Ox $\rightarrow$ Red to Red $\rightarrow$ Ox affect the cyclic voltammogram and the diffusion profiles?

Sample Response

Changing the direction of the initial reaction resets the default conditions so that the starting potential now is more positive than the switching potential (the default conditions are $E_{\text{start}} = +0.50$ V and $E_{\text{switch}} = -0.50$ V for Ox $\rightarrow$ Red and $E_{\text{start}} = -0.50$ V and $E_{\text{switch}} = +0.50$ V for Red $\rightarrow$ Ox). For Ox $\rightarrow$ Red the current is cathodic on the forward scan and anodic on the reverse scan; for Red $\rightarrow$ Ox this is reversed with an anodic current on the forward scan and a cathodic current on the reverse scan. The two peak potentials, $E_{p,c}$ and $E_{p,a}$ remain unchanged, as do the magnitude of the peak currents for the forward and the reverse scan.

4. The cyclic voltammogram is annotated with a set of characteristic values: the cathodic peak current, $i_{p,c}$, and peak potential, $E_{p,c}$, the anodic peak current, $i_{p,a}$, and peak potential, $E_{p,a}$, the difference between the peak potentials, ΔE , the average peak potential, E_{avg} , and the ratio of the peak currents, $|i_{p,a}/i_{p,c}|$ or $|i_{p,c}/i_{p,a}|$. For the default values, the average peak potential is 0.000 V. What does this value represent? Verify your answer by adjusting one or more of the simulation's available parameters.

Sample Response

The average peak potential is just the average of $E_{p,c}$ and $E_{p,a}$. By adjusting the slider for the formal potential, it is easy to demonstrate that E_{avg} is equivalent to the formal potential, E° .

5. When using the default conditions, the theoretical value for $|i_{p,a}/i_{p,c}|$ is 1.00 for Ox $\rightarrow$ Red, and the theoretical value for ΔE is 0.059 V for a one-electron redox reaction. While maintaining the scan rate at 10^0 V/s, determine the values for $|i_{p,a}/i_{p,c}|$ and ΔE for k° values of 10^{-3} , 10^{-2} , 10^{-1} , 10^0 , 10^1 , 10^2 , and 10^3 cm/s. Describe the trends you see in these results and explain why they occur. *Note: Be sure to review the discussion of accuracy for these simulations on the **Computational Details** tab.*

Sample Response

The table that follows summarizes the values for $|i_{p,a}/i_{p,c}|$ and ΔE for the different values of k° .

Table 2: Effect of k° on Peak Current Ratio and ΔE

k° (cm/s)	$ i_{p,a}/i_{p,c} $	ΔE (V)
10^{-3}	0.80	0.343
10^{-2}	0.97	0.137
10^{-1}	0.98	0.073
10^0	0.98	0.066
10^1	0.98	0.064
10^2	0.98	0.064
10^3	0.98	0.064

For small values of k° , ΔE deviates significantly from its theoretical value of 0.059 V, but it more closely approximates the theoretical value as the value of k° increases. With the exception of $k^{\circ} = 10^{-3}$, the peak current ratios are close to the expected value of 1. A small value for k° means that the rate of electron transfer is slow relative to the rate of change in the potential. As a result, the concentrations of Ox and Red are slow to respond to a change in potential, which decreases both the cathodic and the anodic peak currents, and shifts the cathodic peak potential to a more negative value and the anodic peak potential to a more positive value.

6. While maintaining k° at 10^0 cm/s, determine the values for $|i_{p,a}/i_{p,c}|$ and ΔE for scan rates of 10^{-3} ,

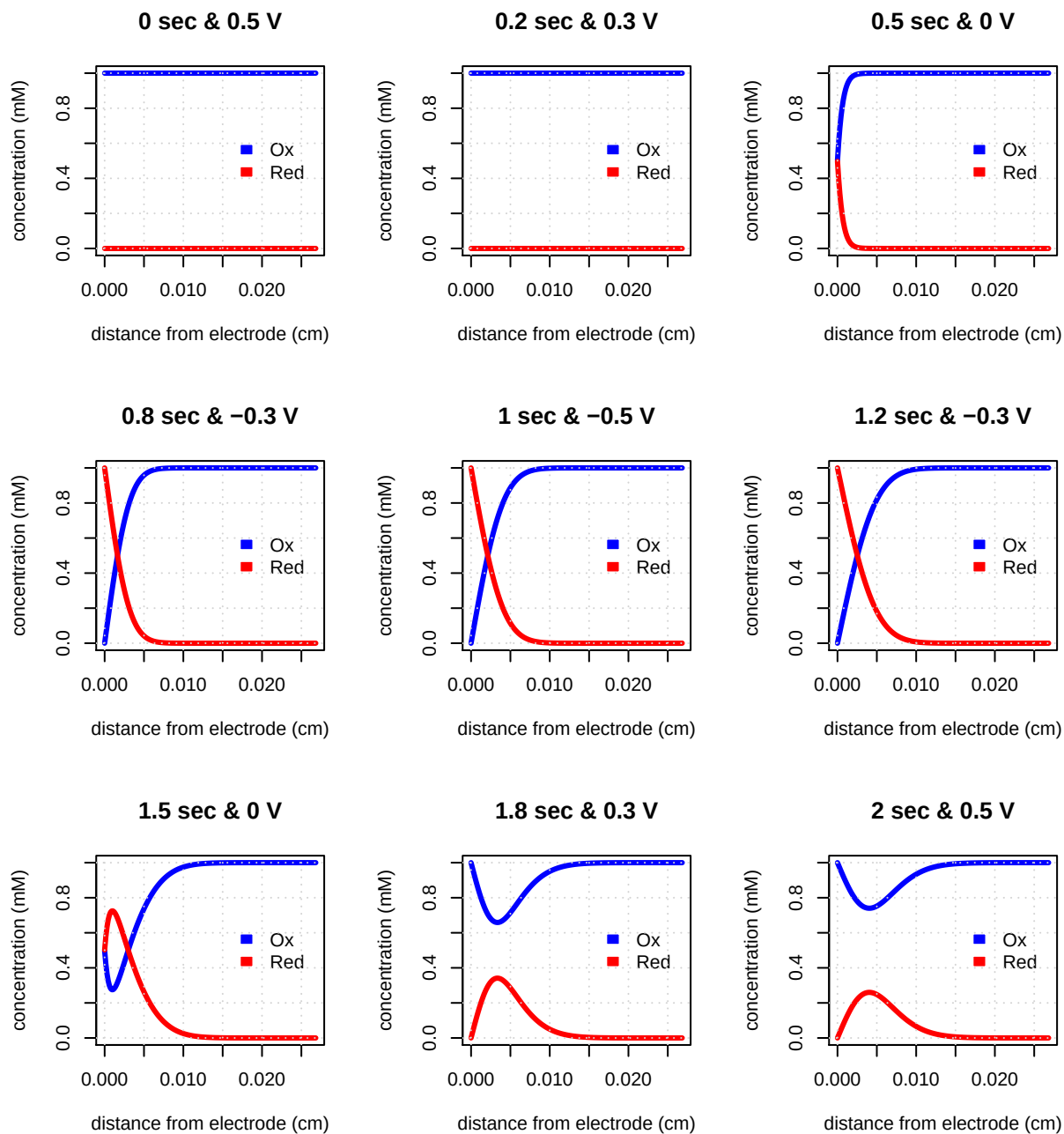


Figure 1: Diffusion Profiles for Mechanism E: Problem 2.

10^{-2} , 10^{-1} , 10^0 , 10^1 , 10^2 , and 10^3 V/s. Describe the trends you see in these results and explain why they occur. *Note: Be sure to review the discussion of accuracy for these simulations on the **Computational Details** tab.*

Sample Response

The following table summarizes the values for $|i_{p,a}/i_{p,c}|$ and ΔE for the different values of ν

Table 3: Effect of ν on Peak Current Ratio and ΔE

ν (V/s)	$ i_{p,a}/i_{p,c} $	ΔE (V)
10^{-3}	0.98	0.064
10^{-2}	0.98	0.064
10^{-1}	0.98	0.065
10^0	0.98	0.066
10^1	0.98	0.068
10^2	0.98	0.073
10^3	0.98	0.090

At all scan rates, $|i_{p,a}/i_{p,c}|$ is close to its theoretical value of 1.0. At slower scan rates ΔE also is close to its theoretical value of 0.059 V; however, as the scan rate increases, ΔE becomes larger than the theoretical value. At higher scan rates the relative rate of electron transfer is sufficiently slow that it takes a more negative potential to achieve reduction on the forward scan and a more positive potential to achieve oxidation on the reverse scan.

- The reaction in a cyclic voltammetry experiment often is described in terms of electrochemical reversibility. In light of your responses to the previous two questions, explain what it means for a reaction to be electrochemically reversible. What criteria can you use to determine if a reaction is electrochemically reversible?

Sample Response

Electrochemical reversibility is the ability to maintain the redox reaction in a state of thermodynamic equilibrium in which the concentrations of Ox and Red are determined by the applied potential as defined by the Nernst equation. To maintain thermodynamic equilibrium, the heterogeneous electron-transfer rate constant, k° , must be sufficiently large relative to the scan rate. If k° is not sufficiently large relative to the scan rate, then ΔE is greater than 0.059 V as it takes a more negative than expected potential to reduce Ox to Red and a more positive than expected potential to oxidize Red to Ox.

- Predict the relative values of $|i_{p,a}/i_{p,c}|$ and for ΔE for a cyclic voltammogram recorded using a scan rate of 10^2 V/s and k° of 10^{-2} cm/s, and a cyclic voltammogram recorded using a scan rate of 10^{-2} V/s and a k° of 10^2 cm/s. Leave all other parameters at their default values. Explain the reasons for your predictions. Run the simulations and evaluate your predictions.

Sample Response

A cyclic voltammogram will show evidence of being more electrochemically reversible when the heterogeneous electron-transfer rate constant, k° , is larger and when the scan rate, ν , is slower; thus, we expect a ΔE closer to its theoretical value of 0.59 V when $k^\circ = 10^2$ cm/s and $\nu = 10^{-2}$ V/s and expect that it will deviate from the theoretical value of 0.59 V when $k^\circ = 10^{-2}$ cm/s and $\nu = 10^2$ V/s. The resulting cyclic voltammograms are displayed in Figure 2 below, with the electrochemically reversible conditions ($k^\circ = 10^2$ cm/s and $\nu = 10^{-2}$ V/s) on the left and the electrochemically irreversible conditions ($k^\circ = 10^{-2}$ cm/s and $\nu = 10^2$ V/s) on the right.

Mechanism: EC

- While maintaining the scan rate at 10^0 V/s, k° , at 10^0 cm/s, and $k_{\text{chem,r}}$, at 10^0 s $^{-1}$, determine $|i_{p,a}/i_{p,c}|$ and ΔE using values of 10^{-2} , 10^{-1} , 10^0 , 10^1 , and 10^2 s $^{-1}$ for $k_{\text{chem,f}}$. Describe the trends you see in

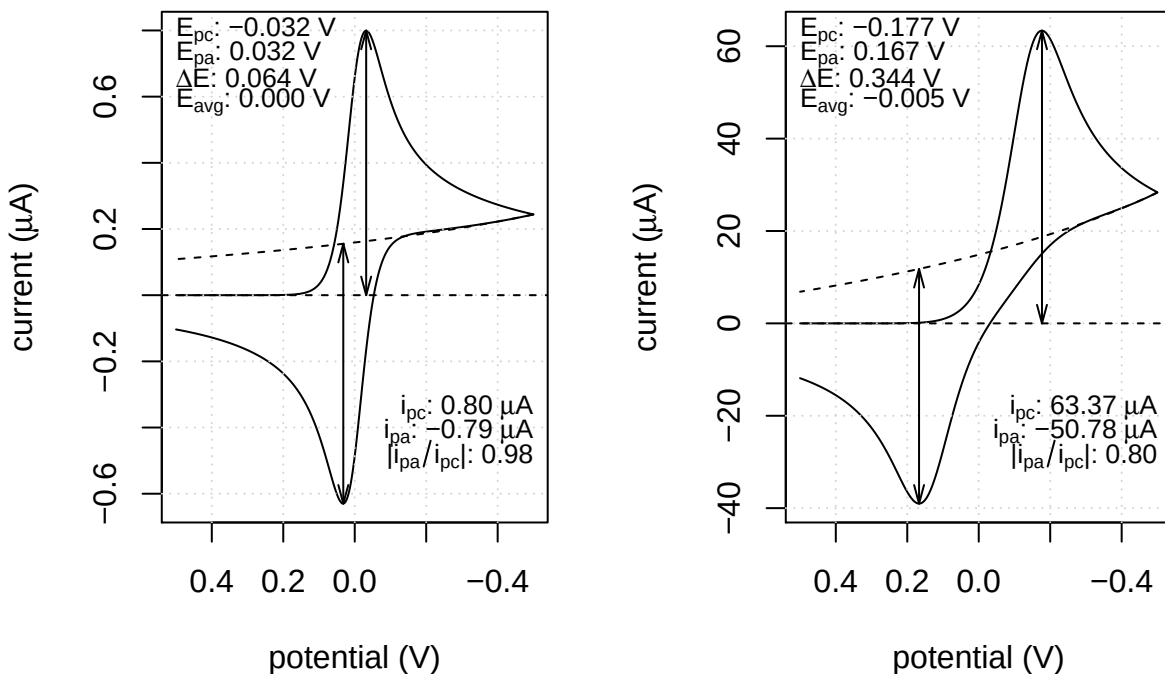


Figure 2: Cyclic Voltammograms for Mechanism E: Problem 8. The CV on the left is for $k^\circ = 10^2$ cm/s and $\nu = 10^{-2}$ V/s and the CV on the right is for $k^\circ = 10^{-2}$ cm/s and $\nu = 10^2$ V/s.

these results and explain why they occur. *Note: Be sure to review the discussion of accuracy of these simulations on the **Computational Details** tab.*

Sample Response

The following table summarizes the values for $|i_{p,a}/i_{p,c}|$ and ΔE for the different values of $k_{chem,f}$.

Table 4: Effect of $k_{chem,f}$ on Peak Current Ratio and ΔE

$k_{chem,f}$ (s^{-1})	$ i_{p,a}/i_{p,c} $	ΔE (V)
10^{-2}	0.98	0.066
10^{-1}	0.95	0.066
10^0	0.73	0.066
10^{+1}	0.30	0.083
10^{+2}	0.18	0.196

When $k_{chem,f}$ is sufficiently small relative to $k_{chem,r}$, the peak current ratio approaches its theoretical value of 1 and ΔE approaches its theoretical value of 0.059 V. As $k_{chem,f}$ increases in value relative to $k_{chem,r}$, however, the peak current ratio becomes significantly smaller than its theoretical value and ΔE becomes greater than its theoretical value. When $k_{chem,f} \ll k_{chem,r}$, the kinetics of the reaction $Z \rightarrow \text{Red}$ is sufficiently fast that Ox and Red remain in thermodynamic equilibrium at the electrode's surface. As $k_{chem,f}$ increases relative to $k_{chem,r}$, the kinetics of the reaction $Z \rightarrow \text{Red}$ become sufficiently slow that some of the Z formed on the forward scan is unable to react back to Red on the reverse scan, which explains the decrease in the peak current ratio.

- While maintaining the scan rate at 10^0 V/s, k° , at 10^0 cm/s, and $k_{\text{chem},f}$, at 10^0 s $^{-1}$, determine $|i_{p,a}/i_{p,c}|$ and ΔE using values of 10^{-2} , 10^{-1} , 10^0 , 10^1 , and 10^2 s $^{-1}$ for $k_{\text{chem},r}$. Describe the trends you see in these results and explain why they occur. *Note: Be sure to review the discussion of accuracy of these simulations on the **Computational Details** tab.*

Sample Response

The following table summarizes the values for $|i_{p,a}/i_{p,c}|$ and ΔE for the different values of $k_{\text{chem},r}$.

Table 5: Effect of $k_{\text{chem},r}$ on Peak Current Ratio and ΔE

$k_{\text{chem},r}$ (s $^{-1}$)	$ i_{p,a}/i_{p,c} $	ΔE (V)
10^{-2}	0.64	0.065
10^{-1}	0.65	0.065
10^0	0.73	0.066
10^{+1}	0.92	0.066
10^{+2}	0.98	0.066

When $k_{\text{chem},r}$ is sufficiently large relative to $k_{\text{chem},f}$, the peak current ratio approaches its theoretical value of 1 and ΔE remains close to its theoretical value of 0.059 V. As $k_{\text{chem},r}$ decreases in value relative to $k_{\text{chem},f}$, however, the peak current ratio becomes significantly smaller than its theoretical value. When $k_{\text{chem},r} \gg k_{\text{chem},f}$, the kinetics of the reaction $Z \rightarrow \text{Red}$ is sufficiently fast that Ox and Red remain in thermodynamic equilibrium at the electrode's surface. As $k_{\text{chem},r}$ decreases relative to $k_{\text{chem},f}$, the kinetics of the reaction $Z \rightarrow \text{Red}$ become sufficiently slow that some of the Z formed on the forward scan is unable to react back to Red on the reverse scan, which explains the decrease in the peak current ratio.

- In addition to electrochemical reversibility, a cyclic voltammogram may show chemically reversible or chemically irreversible behavior. In light of your response to the previous two questions, explain what it means for a reaction to be chemically reversible. What criteria can you use to determine if a reaction is chemically reversible?

Sample Response

Chemical reversibility exists when all Z produced by the reaction $\text{Red} \rightarrow Z$ on the forward scan is able to convert back to Red by the reaction $Z \rightarrow \text{Red}$ on the reverse scan. A peak current ratio that deviates significantly for its theoretical value of 1 provides evidence of chemical irreversibility.

- For scan rates of 10^0 V/s and 10^2 V/s, predict the relative values of $|i_{p,a}/i_{p,c}|$ and for ΔE when $k_{\text{chem},f}$ is set to 10^1 s $^{-1}$ and $k_{\text{chem},r}$ is set to 10^{-1} s $^{-1}$. Leave all other parameters at their default values. Explain the reasons for your predictions. Run the simulations and evaluate your predictions.

Sample Response

A $k_{\text{chem},f}$ greater than $k_{\text{chem},r}$ favors a chemically irreversible redox reaction because the rate at which Z returns to Red is slower than the rate at which Red reacts to form Z. This lack of chemical reversibility likely is greater at a slower scan rate because more Red is converted to Z during the forward scan and remains as Z during the reverse scan. The cyclic voltammograms in Figure 3 show this effect, with an $|i_{p,a}/i_{p,c}|$ of 0.23 when $\nu = 10^0$ V/s and an $|i_{p,a}/i_{p,c}|$ of 0.94 when $\nu = 10^2$ V/s.

Mechanism CE

- While maintaining the scan rate at 10^0 V/s, k° at 10^0 cm/s, and $k_{\text{chem},r}$ at 10^0 s $^{-1}$, determine $|i_{p,a}/i_{p,c}|$ and ΔE using values of 10^{-2} , 10^{-1} , 10^0 , 10^1 , and 10^2 s $^{-1}$ for $k_{\text{chem},f}$. Describe the trends you see in these results and explain why they occur. *Note: Be sure to review the discussion of accuracy of these simulations on the **Computational Details** tab.*

Sample Response

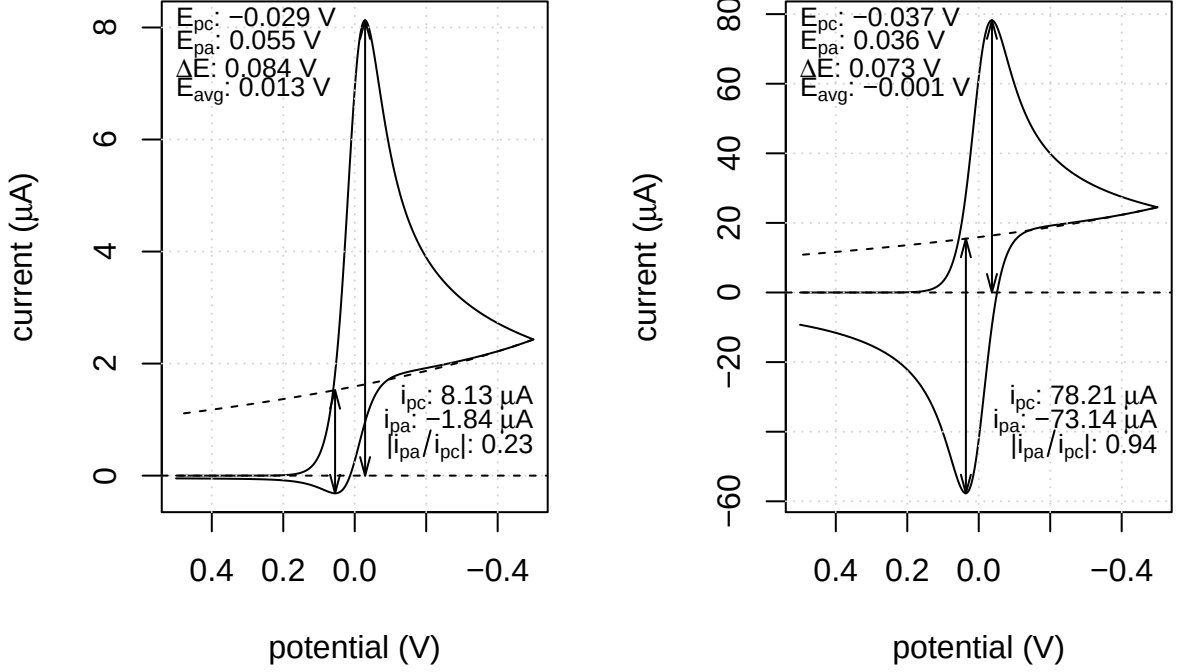


Figure 3: Cyclic Voltammograms for Mechanism EC: Problem 4. The CV on the left is for a scan rate of 10^0 V/s and the CV on the right is for a scan rate of 10^2 V/s.

The following table summarizes the values for $|i_{p,a}/i_{p,c}|$ and ΔE for the different values of $k_{chem,f}$.

Table 6: Effect of $k_{chem,f}$ on Peak Current Ratio and ΔE

$k_{chem,f}$ (s^{-1})	$ i_{p,a}/i_{p,c} $	ΔE (V)
10^{-2}	1.40	0.069
10^{-1}	1.39	0.068
10^0	1.29	0.068
10^{+1}	1.04	0.067
10^{+2}	0.99	0.066

When $k_{chem,f}$ is sufficiently large relative to $k_{chem,r}$, the chemical equilibrium favors Ox over Z such that essentially all Z is present as Ox. The resulting cyclic voltammogram is nearly identical to that obtained with an E-only mechanism with the peak ratio of 1 consistent with electrochemical reversibility. When $k_{chem,f}$ is sufficiently small relative to $k_{chem,r}$, the chemical equilibrium favors Z over Ox such that there is little Ox present and the current during the forward scan is limited by the rate at which Z converts to Ox. The current during the reverse scan is greater than that during the forward scan, which leads to a peak current ratio that is greater than 1; the value for ΔE , however, remains close to its theoretical value of 0.059 V.

- While maintaining the scan rate at 10^0 V/s, k° at 10^0 cm/s, and $k_{\text{chem,f}}$ at 10^0 s $^{-1}$, determine $|i_{p,a}/i_{p,c}|$ and ΔE using values of 10^{-2} , 10^{-1} , 10^0 , 10^1 , and 10^2 s $^{-1}$ for $k_{\text{chem,r}}$. Describe the trends you see in these results and explain why they occur. *Note: Be sure to review the discussion of accuracy of these simulations on the **Computational Details** tab.*

Sample Response

The following table summarizes the values for $|i_{p,a}/i_{p,c}|$ and ΔE for the different values of $k_{\text{chem,r}}$.

Table 7: Effect of $k_{\text{chem,r}}$ on Peak Current Ratio and ΔE

$k_{\text{chem,r}}$ (s $^{-1}$)	$ i_{p,a}/i_{p,c} $	ΔE (V)
10^{-2}	0.99	0.066
10^{-1}	1.02	0.066
10^0	1.29	0.068
10^{+1}	2.51	0.086
10^{+2}	3.15	0.298

When $k_{\text{chem,r}}$ is sufficiently small relative to $k_{\text{chem,f}}$ the chemical equilibrium favors Ox over Z such that essentially all Z is present as Ox. The resulting cyclic voltammogram is nearly identical to that obtained with an E-only mechanism with the peak ratio of 1 consistent with electrochemical reversibility. When $k_{\text{chem,r}}$ is sufficiently large relative to $k_{\text{chem,f}}$, the chemical equilibrium favors Z over Ox such that there is little Ox present and the current during the forward scan is limited by the rate at which Z converts to Ox. The current during the reverse scan is greater than that during the forward scan, which leads to a peak current ratio that is greater than 1; the value for ΔE , however, remains close to its theoretical value of 0.059 V.

- With k° set to 10^0 cm/s, $k_{\text{chem,f}}$ set to 10^{-1} s $^{-1}$, and $k_{\text{chem,r}}$ set to 10^1 s $^{-1}$, predict how increasing the scan rate from 10^0 V/s to 10^2 V/s will affect the shape and the characteristic values of the cyclic voltammogram. Explain the reasons for your predictions. Run the simulations and evaluate your predictions.

Sample Response

A $k_{\text{chem,f}}$ smaller than $k_{\text{chem,r}}$ favors a chemically irreversible redox reaction because the rate at which Z forms Ox is slower than the rate at which Ox reacts to form Z. This lack of chemical reversibility likely is greater at a slower scan rate because Ox is converted to Red during the forward scan at a faster rate faster than it is replaced by the reaction of $Z \rightarrow \text{Ox}$. The cyclic voltammograms in Figure 4 show this effect, with an $|i_{p,a}/i_{p,c}|$ of 2.81 when $\nu = 10^0$ V/s and an $|i_{p,a}/i_{p,c}|$ of 1.03 when $\nu = 10^2$ V/s.

Wrapping Up

- Based on your exploration of these three mechanisms, explain how you can use a set of cyclic voltammetry experiments to deduce whether a system is following an E, an EC, or a CE mechanism. Assume a k° of 10^0 cm/s for all three mechanisms, and assume a $k_{\text{chem,f}}$ of 10^0 s $^{-1}$ and a $k_{\text{chem,r}}$ of 10^0 s $^{-1}$ for the EC and the CE mechanisms.

Sample Response

The simplest approach is to vary the scan rate, ν , and observe its effect on $|i_{p,a}/i_{p,c}|$ and ΔE .

- For an E-only mechanism ΔE is the more important parameter to observe. At slower scan rates the CV will show a ΔE close to its theoretical value of 0.059 V; however, once the scan rate exceeds a reaction-dependent threshold level, ΔE becomes greater than 0.059 V.
- For an EC mechanism $|i_{p,a}/i_{p,c}|$ is the more important parameter to observe. At faster scan rates the CV will show a $|i_{p,a}/i_{p,c}|$ close to its theoretical value of 1; however, once the scan rate falls below a reaction-dependent threshold level, $|i_{p,a}/i_{p,c}|$ becomes smaller than 1.

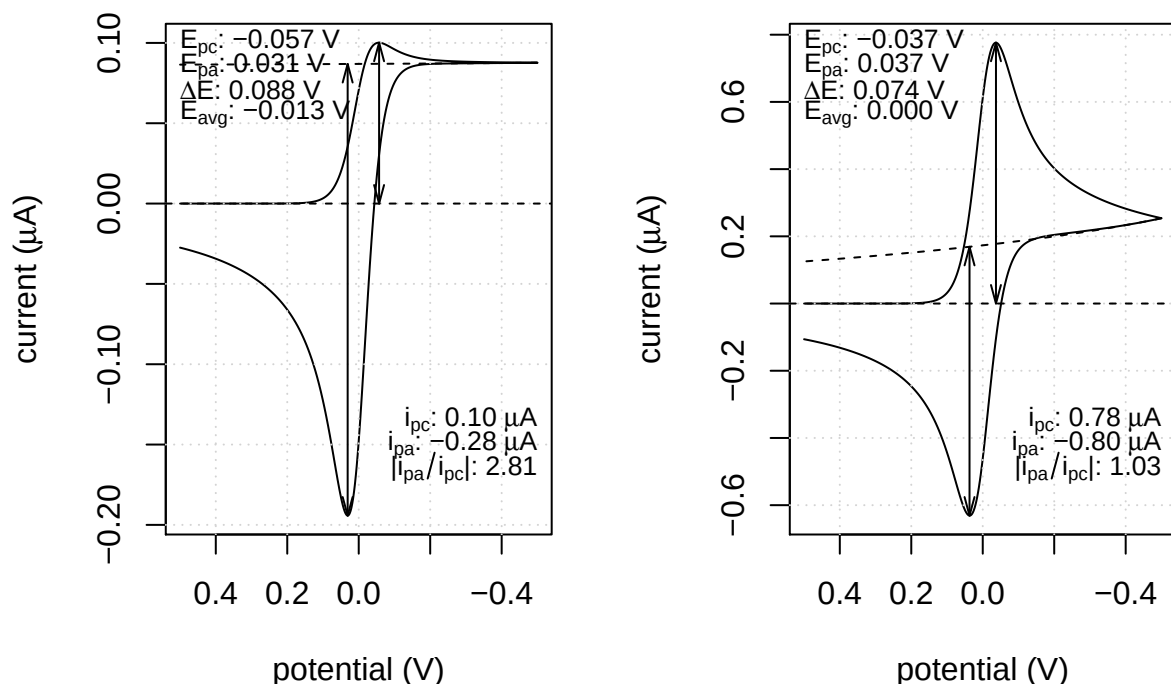


Figure 4: Cyclic Voltammograms for Mechanism CE: Problem 3. The CV on the left is for a scan rate of 10^0 V/s and the CV on the right is for a scan rate of 10^2 V/s.

- For a CE mechanism $|i_{p,a}/i_{p,c}|$ is the more important parameter to observe. At higher scan rates the CV will show a $|i_{p,a}/i_{p,c}|$ close to its theoretical value of 1; however, once the scan rate falls below a reaction-dependent threshold level, $|i_{p,a}/i_{p,c}|$ becomes greater than 1.
2. A cyclic voltammetry analysis of *p*-aminophenol uses an E_{start} of -0.2 V and an E_{switch} of +0.3 V. Cyclic voltammograms collected at scan rates of 0.01, 0.02, 0.03, 0.04, and 0.05 V/s give ΔE values of, respectively, 68, 60, 60, 64, and 64 mV, and $|i_{p,c}/i_{p,a}|$ values of, respectively, 0.96, 0.95, 0.94, 0.94, and 0.93. Is the initial redox reaction an oxidation or a reduction and how many electrons are involved? Does this system show electrochemically reversible behavior? Chemically reversible behavior?

Sample Response

The forward scan is from a more negative potential to a more positive potential, which means the initial reaction is an oxidation of *p*-aminophenol. The ΔE of approximately 0.064 V, suggests a one-electron oxidation as $E = \frac{0.059 \text{ V}}{n}$. Given that both ΔE and $|i_{p,c}/i_{p,a}|$ are relatively independent of the scan rate and close to their expected values, the system is both electrochemically reversible and chemically reversible.

3. When the scan rate for the analysis of *p*-aminophenol is increased to 0.50 V/s, the peak current ratio decreases to 0.79 and ΔE increases to 108 mV. Describe the electrochemical and chemical reversibility at this scan rate.

Sample Response

Under these conditions, the oxidation of *p*-aminophenol no longer is electrochemically reversible or chemically reversible.