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# Chronocoulometry

*Chronocoulometry involves measurement of the charge vs. time response to an applied potential step waveform. The shape of the resulting chronocoulogram can be understood by considering the concentration gradients in the solution adjacent to the electrode surface. Chronocoulometry is useful for measuring electrode surface areas, diffusion coefficients, the time window of an electrochemical cell, adsorption of electroactive species, and the mechanisms and rate constants for chemical reactions coupled to electron transfer reactions.*

Chronocoulometry (CC) is one of the classical electrochemical techniques frequently used in electroanalytical chemistry. As its name implies, CC is the measurement of charge (coulombs) as a function of time (chrono). Applications of this technique include measurement of electrode surface area, diffusion coefficients, concentration, kinetics of both heterogeneous electron transfer reactions and chemical reactions coupled to electron transfer, adsorption, and the effective time window of an electrochemical cell. The aim of this article is to provide an introduction to the basic concepts of CC and some of its applications.

## Applied Potential Waveform

CC is a controlled-potential technique and uses a potential step waveform (**F1a**). The experiment typically starts at a potential (**Initial E**) at which there is no electrolysis. The potential is then changed instantaneously (stepped) to a value that leads to oxidation or reduction of some species in solution (**First Step E**) and is held at that potential for a user-defined time period (**First Step Time**). In a single potential step experiment, the experiment is complete at the end of this **Step Time**. In a double potential step experiment, the potential is then stepped to a third potential (**Second Step E**) at which the species formed on the first step is

reelectrolyzed (in many instances, the **Second Step E** is identical to the **Initial E**). The first and second potential steps are also often referred to as the forward and reverse potential steps, respectively.

The effects of the changes in potential used in the CC experiment can be understood by considering the Nernst equation, which relates the applied potential E (in V), the formal redox potential $E^{o'}$, and the surface concentrations ($C^S$) of the relevant electroactive species (1). For the redox couple $O + ne^- = R$, the Nernst equation is:

$$E = E^{o'} + \frac{0.059}{n} \log \frac{C_O^S}{C_R^S}$$

where n = number of electrons transferred. This shows that changes in the applied potential are accompanied by changes in the ratio of the surface concentrations of O and R. These changes are accomplished by interconversion of O and R *via* electron transfer, which leads to a flow of electrons in the electrical circuit; that is, a current.

**T1** shows the surface concentration ratios required for various potential values relative to $E^{o'}$. Notice that a huge change in the relative surface concentrations (essentially complete interconversion of O and R) can be achieved by changing the applied potential by less than half a volt.

## Concentration-Distance Profiles

The changes in the surface concentrations that accompany a potential step establish concentration gradients in the solution adjacent to the electrode surface. These gradients can be illustrated graphically using concentration-distance profiles, such as those in **F2**, which show the profiles for the redox reaction $O + e^- = R$ starting with a 1 mM solution of O in solution with a suitable electrolyte. The value selected for the **Initial E** is sufficiently positive of the redox potential that no reduction occurs. Profile *a* in **F2a** shows that the concentration of O is 1 mM at the electrode surface and throughout the adjacent solution, whereas profile *a* in **F2b** shows that the concentration of R is 0 mM throughout the solution. The **First Step E** is sufficiently negative of the redox potential that all of O at the electrode surface is instantaneously reduced to R on application of this potential. Profile *b* in **F2a** shows the resulting concentration gradient for O between the electrode surface (0 mM) and the solution at a distance from the electrode (1 mM). This concentration gradient leads to diffusion of O *from* the region of high concentration (the solution at a distance from the electrode) *to* the region of low concentration (the electrode surface), where these O are reduced to R. This leads to the region of

the solution immediately adjacent to the electrode surface becoming depleted in O. The magnitude of this region (the *diffusion layer*) increases with time, as shown by profiles *c* and *d* in *F2a*. There is also a concentration gradient for R between the electrode surface (1 mM) and the solution at a distance from the electrode (0 mM), leading to diffusion of R away from the electrode surface (*F2b*). If the potential is now stepped back to the **Initial E**, all R at the electrode surface is now converted back to O, and additional R is reoxidized as it diffuses back to the electrode surface (*F2c* and *F2d*) (although it should be noted that some R continues to diffuse into solution away from the electrode).

It is important to note that diffusion is the only mode of mass transport used in the CC experiment; that is, the solution must be in a quiescent state. Therefore, all CC experiments are conducted in unstirred solutions.

## Current Response

The response to a potential step is current due to the electrolysis of O or R. Hence, it is instructive to first consider the current vs. time experiment (chronoamperometry [CA]). The electrolysis current i (A) is related to the slope of the concentration-distance profile at the electrode surface, as shown by the following equation for the reduction of O:

$$ i = nFAC_O D_O \left( \frac{\partial C_O}{\partial x} \right)_{x=0,t} $$

where:

n = number of electrons transferred per ion or molecule (eq/mol),
F = Faraday's constant (96,485 C/eq),
A = electrode surface area (cm$^2$),
C$_O$ = concentration of O (mol/cm$^3$),
D$_O$ = diffusion coefficient of O (cm$^2$/s),
t = time (s).

It is important to note that the above equation can be used to predict the shape of the current-time (i vs. t) response simply by measuring the slope of the concentration-distance profile at x = 0 (i.e., at the electrode surface) for the species being electrolyzed. Try to predict the shape of the i vs. t curve for the double potential step CA experiment before reading further.

The i vs. t curve for the double potential step CA experiment is shown in *F1b*. Upon application of each

Relationship between (C$_O^S$/C$_R^S$) and (E - E$^{O'}$) for a reversible system.

| C$_O^S$/C$_R^S$ | E - E$^{O'}$(mV) | |
|---|---|---|
| | n = 1 | n = 2 |
| 10,000/1 | +236 | +118 |
| 1,000/1 | +177 | +88.5 |
| 100/1 | +118 | +59 |
| 10/1 | +59 | +29.5 |
| 1 | 0 | 0 |
| 1/10 | -59 | -29.5 |
| 1/100 | -118 | -59 |
| 1/1,000 | -177 | -88.5 |
| 1/10,000 | -236 | -118 |

Potential wave form of the double potential step technique (a), the current response (b), and the charge response (c).
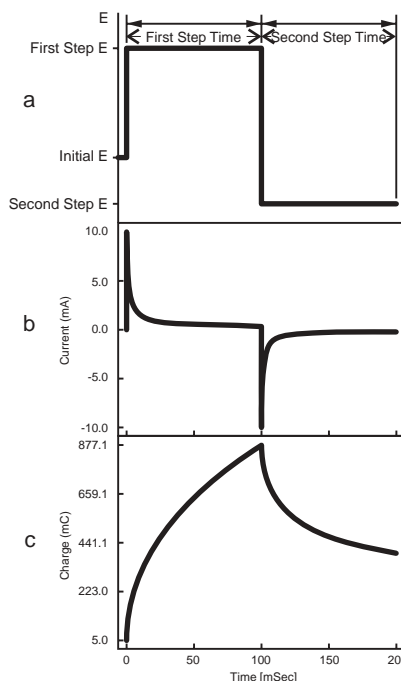
Concentration-distance profiles for the forward potential step for O (a) and R (b), and the reverse potential step for O (c) and R (d).
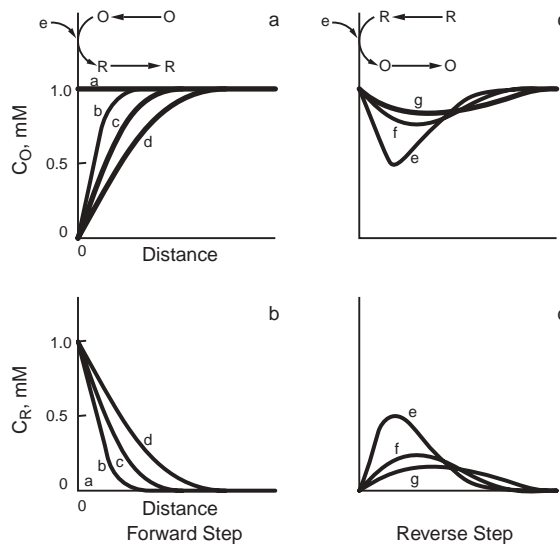
potential step, there is a current "spike" followed by a gradual decay in the current. This response can be rationalized by noting that current is a measure of the rate of electrolysis (2). The current "spike" that follows the application of the potential step is due to electrolysis of the molecules adjacent to the electrode surface. However, once these molecules have been electrolyzed, the rate of electrolysis (and hence the current) is controlled by the rate at which molecules arrive at the electrode surface (O in the forward step and R in the reverse step), which is determined by the rate of diffusion. The decay in the current that follows the current "spike" reflects the decrease in the rate of arrival of relevant molecules at the electrode surface as the region near the electrode becomes depleted. Simply stated, O (or R) have to travel farther to reach the electrode as the experiment proceeds.

The i vs. t plot for CA is described by the Cottrell equation:

$$i = \frac{nFAC_O D_O^{1/2}}{\pi^{1/2}} t^{-1/2}$$

that is, the current decreases as a function of $t^{-1/2}$.

## Charge Response

Since charge is the integral of current with respect to time, response for the CC experiment can be obtained simply by integrating the current response for the CA experiment, and is shown in **F1c**. Similarly, the equation for the Q vs. t curve (the Anson equation) is obtained by integrating the Cottrell equation.

$$Q = \frac{2nFAC_O D_O^{1/2}}{\pi^{1/2}} t^{1/2}$$

The Q vs. t plot for the forward step in **F1c** shows Q as a function of $t^{1/2}$, as expected from the Anson equation. Since the value of Q at any time is a measure of the *total* amount of O that has been reduced up to that point, the charge will decrease following the reverse step due to the reoxidation of R generated by the first potential step. Therefore, the charge due the reoxidation of R on this step ($Q_r$)is the difference between the measured Q and the final value of Q on the forward step ($Q_f$ in **F1c**); that is, $Q_f$ is the baseline for measurement of charge in the reverse step. $Q_r$ is also given by the equation:

$$Q = \frac{2nFAC_O D_O^{1/2}}{\pi^{1/2}} \left[ \tau^{1/2} - (t-\tau)^{1/2} - t^{1/2} \right]$$

where $\tau$ is the **First Step Time**.

## Selection of Potentials

The selection of the **Initial E** and **Step E** values is an important part of the CC experiment. This process requires knowledge of the redox potential, which is most commonly obtained using cyclic voltammetry (1,3). A typical cyclic voltammogram for a reversible system is shown in **F3**. In this
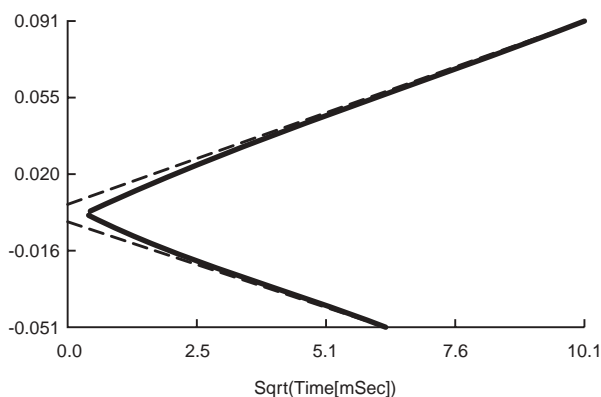
**F3.** Cyclic voltammogram for a reversible system with E$^{o'}$ = 0 V, and n = 1.
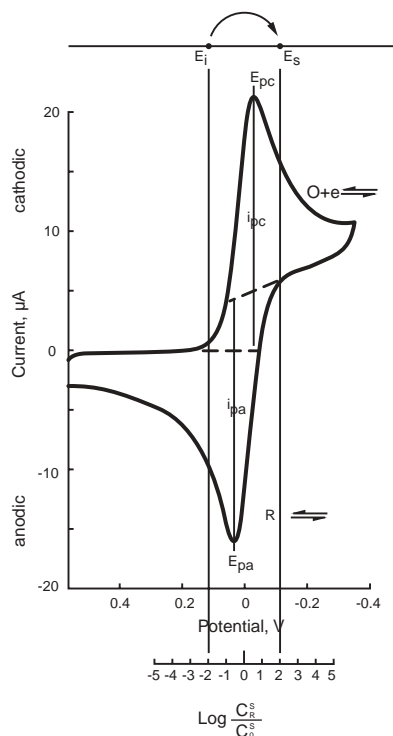


**F4.** Hypothetical plot of Q/t$^{1/2}$ vs. t (axes not to scale).
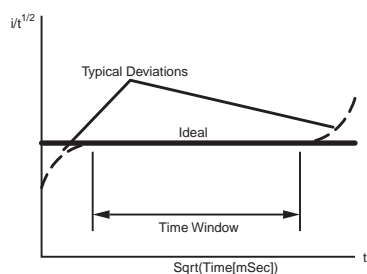


**F5.** Typical Anson plot for a solution species, together with the line used for measuring the slope and intercept.

example, the formal redox potential is at 0V. Therefore, from **T1**, a potential step from +118 mV to -118 mV would cause the surface concentration ratio (O/R) to change from 100/1 to 1/100, which is just sufficient to reduce the surface concentration of O to essentially zero and thereby give results that follow the Cottrell equation. However, a larger step size is typically used, if possible, to ensure that the surface concentration of O is indeed zero. For example, a step from +177 mV to -177 mV would change the ratio from 1000/1 to 1/1000.

## Characterization of the Electrochemical Cell

The Anson equation assumes diffusion to a planar electrode following an instantaneous potential step, and it is instructive to see how accurate this assumption is. This can readily be achieved by a plot of $Q/t^{1/2}$ vs. t, which should be constant if the Anson equation is obeyed. A hypothetical plot of $Q/t^{1/2}$ vs. t is shown in **F4**. The plot is horizontal (i.e., $Q/t^{1/2}$ is constant) over a wide time window, which is the time window in which planar diffusion is maintained in the cell. The positive deviation at long times is due to slight convection in the cell, probably from building vibration. The effect of such slight convection is usually measurable after about one minute for a cell that is reasonably free from vibration. Another source of positive deviation is the onset of spherical diffusion for a mercury drop electrode for which planar diffusion is a valid approximation for up to about a second. The negative deviation at short times is due to the inability of the potentiostat to instantaneously change the applied potential during the potential step. Uncompensated solution resistance causes the actual applied potential to lag behind the excitation signal. Therefore, the ratio of surface concentrations does not change instantaneously, leading to a smaller current (and hence charge) response than predicted until the actual applied potential reaches the required value. The time required to change the cell potential is typically in the microsecond to millisecond time frame. This time can be decreased by minimizing the uncompensated resistance between the working and reference electrodes (4) (by placing

them close together), increasing the concentration of the supporting electrolyte, and decreasing the electrode surface area.

## Measurement of A, D, n, and C from the Anson plot

The Anson equation can be used to calculate A, D, n, and C based on the slope of the Q vs. $t^{1/2}$ plot (the Anson plot). A typical Anson plot for a species in solution measured using the BASi epsilon potentiostat is shown in **F5**, together with the line used to calculate the slope and intercept. The deviation from linearity at short times is again due to inability of the potentiostat to instantaneously change the applied potential. Consequently, data points at short times are not used for calculation of the slope and intercept (e.g., the default setting for the epsilon potentiostat is to discard the first 20% of the data points).

CC is commonly used to calculate electrode surface areas by performing the experiment on a system (such as ferricyanide) for which D, n, and C are known. This is particularly useful for electrodes where the electro-chemically-active surface area is significantly different from the geometric surface area due to the microstructure of the electrode surface. Conversely, diffusion coefficients can be measured by CC using an electrode for which the surface area is known. This includes measurement of $D_e$ values for redox polymer films immobilized on electrode surfaces, where $D_e$ is a measure of the movement of charge through the film by, for example, "electron-hopping" processes (5). Although n can be calculated from CC by assuming a reasonable value for D, n is more commonly calculated by other methods, (e.g., controlled-potential coulometry). Similarly, although the potential step is an integral part of the potential waveform of some electroanalytical techniques commonly used for concentration determination (e.g., pulse and square wave techniques), CC has rarely been used to measure concentration thus far, in part due to poor detection limits. However, it should be noted that the related CA technique has been used successfully for the determination of glucose in blood by commercially available

meters (6). The success of this application is due both to the relatively low sensitivity required for these measurements (concentrations of glucose are on the order of mM) and to the simplicity of the potential step waveform used for CA.

## Adsorption

Chronocoulometry is particularly useful for studying electroactive material that is adsorbed on an electrode surface. Indeed, it was for this purpose that the technique was conceived (7). The key feature is that the charge due to electrolysis of the adsorbed species can be distinguished from the charge that is due to electrolysis of solution species. This distinction is based on the fact that the adsorbed material is on the electrode surface and hence is electrolyzed immediately upon application of the potential step, whereas solution species must diffuse to the electrode surface in order to react.

The total charge ($Q_{total}$) measured in response to the potential step comes from three sources:
a) charging of the double layer ($Q_{dl}$)
b) electrolysis of adsorbed species ($Q_{ads}$)
c) electrolysis of solution (diffusing) species ($Q_{diff}$)

that is:
$Q_{total} = Q_{dl} + Q_{ads} + Q_{diff}$

$$\frac{2nFAC_O D_O^{1/2}}{1/2} t^{1/2} \quad nFA_{\phantom{O}O} \quad Q_{dl}$$

where:
$\Gamma_O$ = amount of adsorbed O, mol/cm$^2$
$Q_{dl}$ = double layer charge, C

The individual contributions of $Q_{diff}$, $Q_{ads}$ and $Q_{dl}$ to $Q_{total}$ in a typical CC experiment are shown in **F6a**. $Q_{diff}$ shows the $t^{1/2}$ dependence discussed above. Since the adsorbed material is electrolyzed instantaneously, $Q_{ads}$ is not time-dependent, as shown by the constant contribution of $Q_{ads}$, in **F6a**. Charging of the double layer is also essentially instantaneous (assuming the time lag shown in **F4** is short), so $Q_{dl}$ is also independent of time and shows a constant contribution in **F6a**. A plot of $Q_{total}$ vs. $t^{1/2}$ is shown in **F6b**. The slope is determined by the Anson plot (i.e., $Q_{diff}$), whereas the intercept is determined by the time-independent

contributions; that is, the sum of $Q_{ads}$ and $Q_{dl}$. Therefore, $Q_{ads}$ can be calculated by subtracting $Q_{dl}$ from the intercept. One approach for calculating $Q_{dl}$ is to perform the experiment on the supporting electrolyte alone. However, this approach assumes that $Q_{dl}$ is the same in the presence and the absence of the adsorbed species, but this assumption is not necessarily valid. An alternative approach is to use 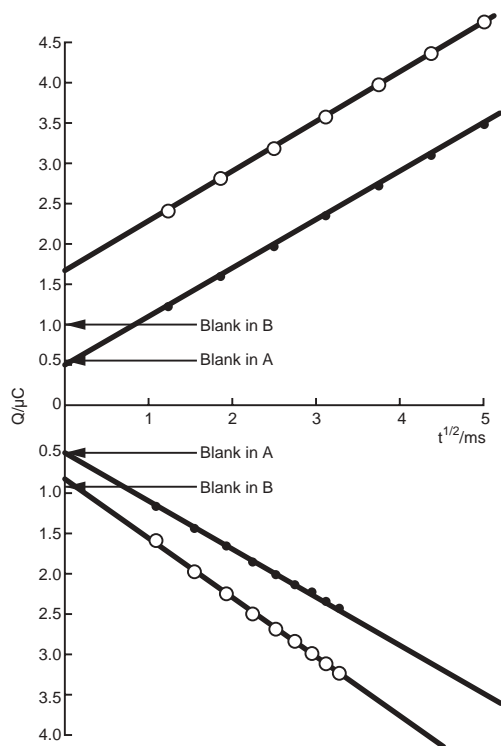double potential step CC. **F7** shows the Anson plots measured in a study of the adsorption of cadmium(II) ions in the presence of thiocyanate ions using the double potential step experiment (8). The first experiment **A** (denoted by dots) was recorded on a solution of cadmium(II) ions in 1 M sodium nitrate, whereas the second experiment **B** (denoted by circles) was recorded on a solution of cadmium(II) ions in 0.2 M sodium thiocyanate and 0.8 M sodium nitrate. The pair of lines for **A** have equal and opposite slopes and equal intercepts, which is consistent with no adsorption by either reactant or product (i.e., the intercept equals $Q_{dl}$). In addition, the intercept is identical to that obtained using a solution of 0.1 M sodium nitrate with no cadmium(II) ions (labeled as **Blank in A**), which is to be expected as this intercept equals $Q_{dl}$. In contrast, the intercepts for the pair of lines **B** are no longer equal. This is consistent with adsorption of the reactant (e.g., cadmium[II] ions), so the intercept for the forward potential step for **B** is the sum of $Q_{ads}$ and $Q_{dl}$ The intercept for the reverse potential step is a measure of $Q_{dl}$ *in the presence of the adsorbed reactant*, and hence $Q_{ads}$ can now be calculated. It should be also noted that this value of $Q_{dl}$ in the presence of the adsorbed reactant is different from $Q_{dl}$ for the 0.2 M sodium thiocyanate and 0.8 M sodium nitrate electrolyte in the absence of cadmium(II) (labeled as **Blank in B**).

## Coupled Chemical Reactions

CC is an effective technique for studying homogeneous chemical reactions that are coupled to the heterogeneous electron transfer reactions. Such coupled chemical reactions often perturb the charge vs. time response in a single- or double-potential step experiment in a predictable way, so information about both the mechanism and the rate of the coupled chemical reaction can be obtained.

One published study that used CC to investigate a coupled chemical reaction involved oxidation of $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-$ (**F8**) (9). The electron-deficient neutral (oxidized) species is more reactive than the monoanion, and readily reacts with phosphines at room temperature to give the monosubstituted phosphine derivatives (the monoanion does not react under these conditions). Therefore, the redox process is an EC mechanism (electron transfer reaction followed by a chemical reaction). Typical charge vs. time responses for a double-potential step CC experiment for an EC process with various values for k (chemical reaction rate) are shown in **F9**. The forward step is unaffected by the chemical reaction, which is to be expected since mass transport to the

**F6.** Charge vs. time (a) and charge vs. (time)$^{1/2}$ (b) responses for system with both solution and adsorbed species. Total charge ($Q_{total}$) shown as well as the individual components.
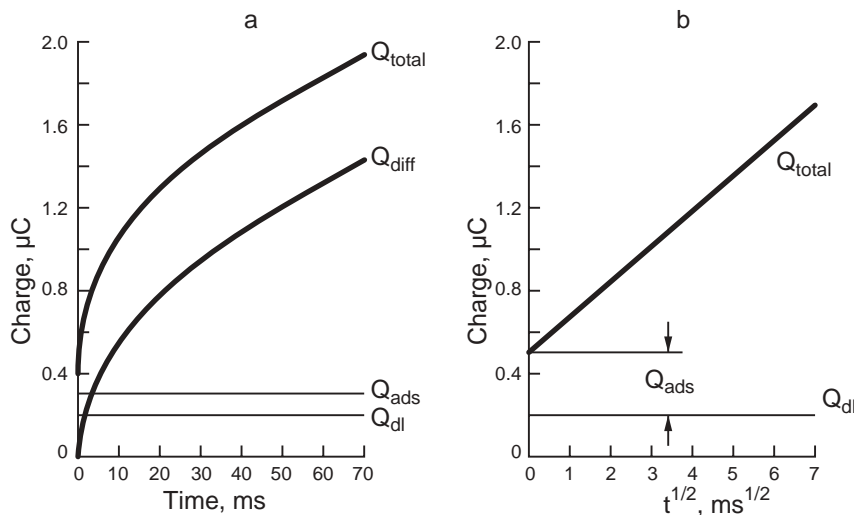


**F7.** Q vs. t$^{1/2}$ and for double potential step from -200 to -900 to -200 mV vs. SCE. A ( ) 1 mM Cd(II) in 1 N NaNO$_3$; B (o) Cd(II) in 0.2 N NaSCN + 0.8 N NaNO$_3$ ( = [ + (t - )$^{1/2}$ - t$^{1/2}$]). Adapted from (9).

electrode surface is dependent on $C_o$ and $D_o$ and is not affected by the fate of the species generated by the forward potential step. However, the charge response of the reverse step is sensitive to k, since the larger the value of k, the smaller the amount of electrogenerated species available for reelectrolysis on the reverse step.

The basis of determination of the value of k is measurement of the ratio of the charge recorded on the reverse step ($Q_r$) to the charge recorded on the forward step ($Q_f$). For a simple electron transfer reaction (i.e., k = 0), the charge ratio $Q_r/Q_f$ is 0.586. (Remember that some of the molecules electrolyzed in the forward step diffuse away from the electrode and so are not reelectrolyzed in the reverse step.) The quantitative effect of the chemical reaction depends upon the rate of the chemical reaction relative to the time scale of the experiment (as defined by the **Step**), so the charge ratio is measured as a function of the **Step Time**. Since the chemical reaction in this example is a substitution reaction, the chemical reaction may be second-order, and hence the charge ratio was also measured as a function of phosphine concentration and for phosphines with different steric and electronic properties. The value of k was then derived from working curves (*F10*) (i.e., by comparison with theoretical results). The variation in the value of k for different phosphines is consistent with an associative substitution reaction.

Although cyclic voltammetry is more often used for mechanistic investigations such as the one described above, one disadvantage of using cyclic voltammetry is that the current response is also sensitive to slow electron transfer kinetics, which can complicate the measurement of quantitative values. However, any effects of slow electron transfer kinetics can typically be eliminated in CC experiments by judicious selection of the step potential; that is, if the potential step is large enough, the electron transfer kinetics will no longer be rate limiting.
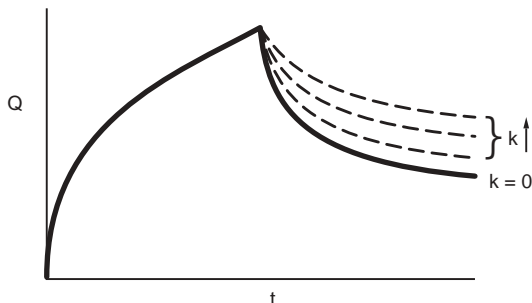
## Conclusion

Although chronocoulometry is a simple electroanalytical technique with many applications, it is not widely used. It is
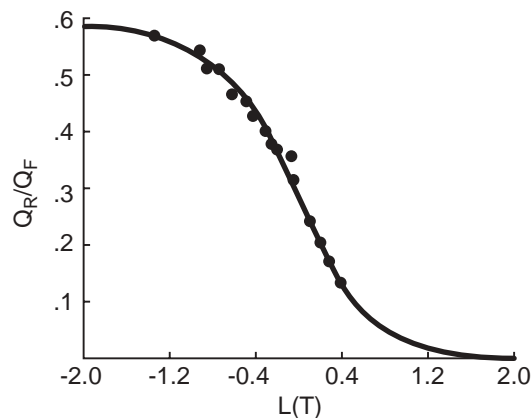
**F8.** Redox interconversion of $[Fe_2(CO)_7(\mu\text{-PPh2})]^n$ (n = 0, -1).
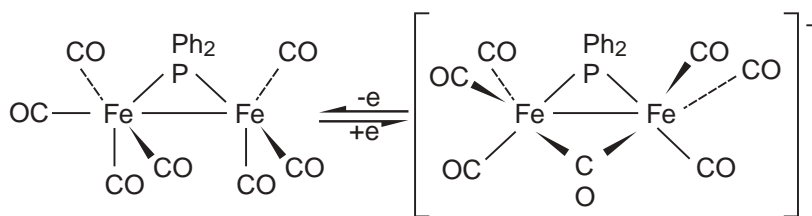


**F9.** Effect of k on the charge vs. time response for an EC mechanism.



**F10.** Variation of $Q_r/Q_f$ with L(T) (L(T) = $\log(k_1[P]$ ) for an electron transfer reaction followed by an irreversible chemical reaction.



our hope that the discussion of the above examples may serve to inform those unfamiliar with this technique about its advantages.

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