

INSTRUCTOR'S MANUAL – ELECTROCHEMICAL METHODS OF ANALYSIS

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INTRODUCTION

The problem sets on electrochemistry can be used in at least two different manners. The primary intent is to use these as a set of in-class, collaborative learning exercises. Groups of 3-4 students work together in discussing and working through the problems. When using the problem sets in this manner, the instructor must actively facilitate and guide students through the material. This manual will guide instructors through each of the problem sets, identifying possible student responses to the questions and the response and activities of the instructor during the progression of the problem.

An alternative to the use of the problems in class is to assign them as out-of-class activities, preferably done as a group activity among students or as a peer-led learning activity. The accompanying text that goes with each problem provides a detailed discussion of each step of the thought process of solving it, such that students could work back and forth between the problem and text on an iterative basis to gain an understanding of the material.

There is no perfect way to assemble groups for such collaborative learning activities. I gather information on the first day of class (year in college, major, prior chemistry courses) and then use this to set groups of 3-4 students that start on the second day of class. I try to make the groups as heterogeneous as possible and they work together for the entire semester. Another strategy is to assign groups for a shorter period of time that might encompass completion of a specific topic or unit, and to then create new groups for the next unit. One other possibility is to have different groups every day of class. Since it is important for groups to work well together, having new groups every day may be less successful than allowing groups to work together for more extended periods of time. I would recommend that the instructor assign groups rather than allowing the students to pick their own. This avoids the potential problem of friends who want to be in the same group but who then do not work well together or stay focused on the assigned task. It also avoids the problem of the student who is left without a group at the end of the selection process, something that can be especially problematic if it is a member of a minority group. When using collaborative groups, it is also important for the instructor to monitor the functioning of the groups and to step in to address either dysfunctional groups or the recalcitrant individual within a group. Peer-evaluation processes are often used by instructors who employ group activities as a way of assessing how well groups are working.

I also expect the groups to meet outside of class for any homework assignments, something that is aided because I am at a residential college. An alternative to this is to schedule a room on the evening before a homework assignment is due and encourage them to come to this place and work in any arrangement they wish on the homework. I have run such sessions for several years now and attend them as a facilitator (one result is that it has cut down considerably the individual traffic to my office seeking help on the homework problems) and it

has been an excellent way to promote collaboration among the students.

The instructor has an especially important role to fulfill during such group activities. I have observed that the more engaged that I am in the process in helping to guide the students through the material, the more effective the learning that occurs. In most instances, it seems that the students are initially stumped by the question, that they begin to explore things that they do know that might apply to answering the question, and that help from the instructor either by letting them know that they are on the right track or by suggesting another direction in which to take their thinking is necessary. As they begin a question, I roam around the room listening in on conversations and looking over their shoulders at what might be written in their notebook. If I hear something interesting, I indicate that to the group. If I see that someone has written something interesting and relevant in their notebook, I tell other group members that they ought to talk with this individual about what they have written, and that the individual should explain to the other group members why they wrote that down. If I hear a group going entirely in the wrong direction, I probe them on why they are heading in that way and then offer suggestions about things to consider that will set them off in the right direction. When all groups have realized an important point, I call time out and summarize the concept at the board. Then I send them back to continue with the next part of the problem. Most of the problems are handled in such an iterative manner where the students work through some important part of the problem, I summarize it at the board when they have developed the concept, and then they return to the next part of the problem. Occasionally a group will just not see something, whereas every other group has gotten the point, and it may require a direct intervention from the instructor with that group to explain the concept. Similarly, there are times when I call their attention to the board to summarize a point when one of the groups still has not gotten the concept but waiting would slow down the remainder of the class to an unacceptable level.

When using these materials, I want the students to discuss and discover the concepts inherent in the problems, so they do not have the text when working on the problems. After they have completed a particular problem, I then put an electronic copy of that portion of the text on the class site. The text thoroughly goes through the thought process for solving each problem and I encourage the students to read it over that evening to reinforce the concepts developed in class that day. I also give homework problems designed to reinforce the concepts developed in class.

ELECTROCHEMISTRY MODULE

I provide a brief introduction to the idea that two electrochemical processes can be used for analytical purposes. One is on the ability of chemical species to transfer electrons. The other is our ability to measure junction potentials. After this, I introduce the first problem set.

Define what is meant by oxidation and reduction.

Define what is meant by an oxidizing and reducing agent. Give a good example of each.

Define what is meant by a half-reaction.

The answers to these three questions have been thoroughly covered in general chemistry and, in the case of the second one they have experience from organic chemistry, and students readily answer all three.

Give an example of a half-reaction and determine whether a half-reaction can be an equilibrium expression. Why or why not?

I prompt the students by providing a particular half reaction (usually the reduction of Cd(II) to cadmium metal) asking them to write the equilibrium constant. Some of them initially want to put the cadmium metal in the expression and it leads to a question about whether the electrons go into the expression. We then discuss how electrons would need to be included to be correct and we can't just weigh out a bunch of electrons to add to a reaction. Then I do talk about how we will often write equilibrium-like expressions for half reactions where we ignore the electrons – pointing out that one half reaction can never occur without the presence of another so there is a source of those electrons.

CHEMICAL ENERGY

I find that it helps to review the concept of chemical energy as a way of relating it to electrochemical potential and deriving the Nernst Equation and do so using the following set of problems. The only information I provide them in advance of this problem set is reminding them that in general chemistry they discussed the importance of something known as the chemical or Gibbs energy.

Now let's think about chemical energy (otherwise known as the Gibbs energy and denoted by G). A bottle of pure A has some amount of chemical energy. A bottle of pure B has some amount of chemical energy. A solution of A in water that is 2 Molar has some amount of chemical energy as does a solution of B in water that is 2 Molar.

Do you think that those four examples have the same or different chemical energy?

Intuition tends to tell the students that these four situations are so different from each other that they likely have different chemical energy.

How would you measure or determine the absolute chemical energy of those four systems?

Students are usually stumped by this question. They often remember something called ΔG or more commonly ΔG° and remember looking up these values in tables. I ask about the meaning of Δ and they realize that this must represent a difference of some sort. I point out that the question is not asking about ΔG but is asking about measuring G. I then indicate that we do not

additional instructions about how to do it. That gets them to realize that without specific instructions different people will choose different concentrations of the chemicals.

What constitutes the standard state?

They usually can answer this, although they may not fully realize that it involves all of the chemical species in the solution starting at a concentration of 1 M. We also discuss how it could be challenging to experimentally set up such a solution since the species involved in the reaction will often immediately react to reach equilibrium. I then point out how electrochemical reactions are rather unique because the two half cells can be set up at standard state conditions but no reaction will take place until the circuitry is completed. I also point out that the difference in chemical energy between the standard state and equilibrium is referred to as ΔG° .

What does it mean for the difference in chemical energy (ΔG) to be positive or negative?

Students usually remember that a negative value of ΔG means that the reaction proceeds toward products and a positive value means it proceeds toward reactants. I like to point out that they should notice that the value of G goes down in both cases, and it is by convention that we assign a negative value to ΔG when the reaction proceeds toward products.

At this point I remind them of two equations they developed in general chemistry.

$$\begin{aligned}\Delta G^\circ &= -RT\ln K \\ \Delta G &= -RT\ln K + RT\ln Q\end{aligned}$$

I point out how $-RT\ln K$ is the difference in chemical energy between the standard state and equilibrium and $RT\ln Q$ is the difference in chemical energy between the non-standard state conditions and the standard state. It is necessary to ask and remind them of what Q is in the second equation.

I also show them using arrows on a diagram (like the one they drew above) representations for the magnitude of ΔG° and several examples of the magnitude of ΔG under different starting conditions (e.g., if the reaction favors products, starting conditions further from equilibrium than the standard state, closer to equilibrium than the standard state, and on the other side of the equilibrium conditions such the reaction would actually proceed in the reverse direction).

I then provide them with two additional equations for electrochemical reactions, indicating that for an electrochemical reaction we can measure something called the electrochemical potential and that this relates to the Gibbs free energy.

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ \\ \Delta G &= -nFE\end{aligned}$$

We then combine the equations relating the Gibbs energy to electrochemical potential to the equations above relating the Gibbs energy to K and Q with the result that we are able to derive

an expression relating E° to K and E to K and Q , the latter of which is the Nernst Equation.

At this point, I introduce the table of standard state potentials. I point out how we can also only measure relative electrochemical potentials and that the reduction of H^+ to hydrogen gas has been arbitrarily assigned a value of 0. I ask them to look at both the magnitude and signs of the E° values for the reduction of Li^+ and fluorine gas. Since they know that lithium prefers to be Li^+ and fluorine prefers to be F^- , they realize that values that are negative (as for the reduction of Li^+) means that the oxidized form is favored and values that are positive (as for the reduction of fluorine gas) means that the reduced form is favored.

Finally, I mention how things like the ionic strength of a solution and acid used in reactions where H^+ is present influence the magnitude of E° and that in some cases it is common to use something known as the formal potential ($E^{\circ'}$).

ELECTROCHEMICAL CELLS

The students are given the following questions on the nature of an electrochemical cell without any preliminary information.

Describe what you know about an electrochemical cell.

The students usually remember aspects of the classic electrochemical cell consisting of a copper and zinc half-cell. They can usually draw a representation of the cell, remember that there is an anode and cathode, and that a wire and salt bridge connect the two half cells.

After they have worked on this for a few minutes, I draw a representation for the copper/zinc electrochemical cell on the board and ask them to look at the table of standard state potentials to identify which half-cell is the cathode and which is the anode.

What processes are responsible for conduction of electricity in an electrochemical cell?

They usually are able to identify that it is electrons in the wire. They may need some prompting to ask what is in solution to realize that it is ions in solution that are able to conduct electricity.

What is the purpose of a salt bridge? What would you put inside a salt bridge?

They often remember what is inside a salt bridge (although they may not have the exact right species) but often don't have a clear recollection of why a cell has a salt bridge other than to complete the circuit. If this is the case, I ask them to consider what happens to the relative concentrations of positive and negative ions as the reaction proceeds. They are able to determine that the copper side will have more negative sulfate ions than positive copper ions as the reaction proceeds and that the zinc side will have more positive zinc ions than negative sulfate ions as the reaction proceeds. Often without prompting, they recognize that the cells won't want to have such a charge buildup. If they don't state this, I prompt them with a question about whether this is a desirable situation to occur.

With that information, they realize that the salt bridge must be a source of ions that can migrate out into the solutions to balance the charge of each half-cell.

I then describe the nature of the junction potential that would build up in the cell without the salt bridge and how a junction potential is inhibitory to the cell proceeding to equilibrium.

When considering what to put in a salt bridge, I provide them with NaCl and KCl as two possibilities and ask if they could see a reason why one would be preferable to the other. Usually one or more students in each group will suggest that KCl might be preferred because of the similar size of the two ions.

I then ask whether you would want a high or low concentration of the salt in the salt bridge and they quickly conclude that a high concentration would be preferable as it could overcome a larger charge buildup or work for a longer time in an electrochemical cell.

Describe two types of situations that would result in the irreversibility of an electrochemical process.

Before considering this problem, I introduce the concept of a voltaic and electrolytic electrochemical cell and the idea that applying a high enough external voltage allows one to drive an electrochemical cell back away from equilibrium as is done when charging a battery.

Students are usually stumped at figuring out a situation when an electrochemical reaction would be reversible. Sometimes one or more groups will propose a situation where the reaction produces a gas and the gas escapes. I discuss with them how if the cell were designed to trap the gases, then the process could be reversed. I then ask them whether they can envision another situation where the produce of the reaction goes away and they usually propose a reaction where the product either further reacts with something or decomposes.

The idea of an overpotential is completely new to them so to get them thinking about this, I ask what needs to happen at each of the electrode surfaces in our example cell, but to especially consider the cathode. They can usually determine that an electron needs to leave the solid electrode to transfer to an ion in solution. I then talk about how the electron must “jump” from the solid to the ion in solution and that there are cases where there is a resistance of the electron to jumping. I then ask them what they might do to make the electron jump and they usually propose to increase the voltage.

Finally, I introduce the shorthand notation that is used to describe an electrochemical cell.

USE OF THE NERNST EQUATION

Since we have derived this, I give them the following set of questions without any significant introduction and allow the groups to think how to go about solving it.

Potassium dichromate reacts with Fe(II) to produce Cr(III) and Fe(III).

A) What is the standard state potential and K for this reaction?

B) What is the cell potential if one half-cell is made up with 1.50 M potassium dichromate and 0.30 M chromium(III)nitrate hexahydrate in 1.00 M nitric acid and

the other half cell is made up with 0.050 M iron(III)chloride hexahydrate and 0.10 M iron(II)chloride tetrahydrate?

C) What is the cell potential if the chromium half-cell were operated at a pH of 7 instead of using 1 M nitric acid?

Working in groups, the students encounter few problems identifying the two appropriate half reactions and writing the complete electrochemical reaction. We have not yet covered the equation for determining the standard state cell potential but usually one or more students remembers it. When we've written the equation on the board, I ask the groups to discuss why you use the numbers directly from the table without needing to change the sign of the oxidation half reaction and why there is no need to account for the stoichiometry in the complete, balanced electrochemical reaction. The second part (why no need to account for stoichiometry) usually gives them a bit more trouble so prompting them think about the meaning of E° is useful to get them on the right track.

After calculating K , I like to have them reflect on the magnitude of the value.

The question in part C gets them to think about the significant effect of pH on the problem. The value of E actually turns out to be negative for the conditions given in the problem, meaning that the reaction goes in the reverse direction from that of standard state conditions.

ELECTROCHEMICAL ANALYTICAL METHODS

Ion-Selective Electrodes

I do a one-day class on ion-selective electrodes in primarily a lecture format. Using the pH electrode as an example, I show pictures from the text material to illustrate how an ion-selective electrode works. I then briefly go over other types of ion-selective electrodes.

Electrodeposition/Electrogravimetry

I first explain the basic concept behind electrogravimetry and then give them the following problem to solve.

Will the presence of Fe(II) at 0.0800 M interfere with the electroplating of 99.9% of the cadmium(II) in a solution in which the cadmium is expected to be present at a concentration of no less than 0.0500 M? Calculate potential values relative to a standard hydrogen electrode.

While doing this problem, they might need help realizing that the final concentration of cadmium will be much lower and that this will change the potential needed for electroplating. They may also need help determining the final concentration after 99.9% has plated, although, one student in each group usually can determine this without any prompting. It is worth developing with them during the problem that the more negative the potential, the less the species wants to be reduced. Once they have completed the calculation for the potential needed to plate out 99.9% of the cadmium, they can see that the iron will interfere.

Suppose the solution had 0.0800 M Cr(III) as a possible interference. Is it possible to plate out 99.9% of the cadmium(II) without any interference from the chromium.

In this case, they see that it should be possible to do the analysis, provide care is taking in setting the plating potential.

Coulometry

Before giving the students the following problem set, I briefly point out how coulometry is similar to electrogravimetry, but instead of weighing a material plated onto an electrode, the current is measured as a function of time.

Draw the plot you would obtain for current (y-axis) versus time (x-axis) if you applied a constant potential high enough to carry the reduction of Cd(II) to cadmium metal. The system has an electrode with a large surface area.

Students in groups usually end up drawing a number of possibilities for this question. Some draw a straight line starting at a high current and going to zero. Others draw the current increasing with time. Others have a fixed current that does not change with time. What I do after seeing the various responses is write the different ideas on the board and then ask groups to see if they can come up with reasons that would rule out any of the possibilities. In that process, the class eventually realizes that the current will diminish with time and then it becomes a matter of determining the shape of the curve. A good question to ask is whether the current would actually ever get to zero, meaning that every ion was reduced. That often sparks the thought that it is likely an exponential decay.

How would you relate the outcome of your plot above to the concentration of Cd(II) in the sample?

Most groups are able to arrive at the conclusion that you need the area under the curve.

What advantages does coulometry have over electrogravimetry?

Some groups realize that coulometry can be used in either an oxidizing or reducing potential. Others may realize that since it doesn't require plating out of a metal, that it can be used for species where both forms in the redox couple are soluble. I usually have to prompt them about the question of sensitivity, asking what the lowest value we can reliably measure by weight and how that might compare to the lowest currents we can measure.

Titrimetric Methods of Analysis

I briefly go over the process of a classical redox titration where the analyte and titrant undergo an electrochemical reaction, the titrant is dispensed from a buret, and a colorimetric indicator is used. Then I point out that there are other ways to conduct and monitor titrations that involve an electrochemical reaction.

Coulometric Titration

I explain the details involved in performing a coulometric titration and then ask the students the following question. During this, I ask what the plot of current versus time would look like when performing a coulometric titration and then after we have this plot on the board, ask them how you would determine the endpoint. Then I give them the following question.

What are some advantages of using a coulometric titration?

They usually can propose some of the advantages (e.g., no buret, no need to prepare solutions with specific concentrations) and I either ask some leading questions to draw out others and then go over any they missed.

Amperometric Titration

I describe the process of performing an amperometric titration and the need for a system in which the products of the titration cannot produce a current. I then give them the following questions.

Draw the plot that would be obtained in an amperometric titration if each of the following occurred (assume that the system is set up with a reducing potential):

- A) Only the analyte undergoes a reduction at the applied potential.**
- B) Only the titrant undergoes a reduction at the applied potential.**
- C) Both the analyte and titrant undergo a reduction at the applied potential.**

Some groups are able to draw the current diagram for (A) whereas others draw an incorrect picture. I draw representations for all of these on the board and then ask them in their groups to either justify what they wrote or point out the problems with others that are on the board. We then have a discussion that usually results in the class agreeing on the correct plot. Having developed the correct answer to (A), most groups are able to readily draw what would be observed in (B) and (C).

Potentiometric Titration

I briefly mention that the titration will be performed by adding the titrant from a burette and a junction potential will be measured using a suitable electrode during the course of the titration. I then give them the following problem set.

Consider a solution of iron(II) that is to be titrated with cerium(IV). The products of the reaction are iron(III) and cerium(III). The course of the titration will be monitored potentiometrically.



If 20 ml of an 0.10 M solution of Fe(II) is to be titrated with 0.10 M Ce(IV), calculate the junction potential that would be measured at a platinum electrode when 5 ml, 10 ml, 20 ml, and 30 ml of titrant have been added.

The following steps will allow you to work through the calculation of the junction potentials.

Write an expression for the total electrochemical potential of this system (this is the Nernst equation for the complete reaction).

The groups are able to write this given our prior work in the class.

What is the total electrochemical potential of the titration reaction at any point during the

titration? Think carefully about this because your first intuition may not be correct.

Groups are often confused by this question. If so, I ask them to consider when the titration reaction is at equilibrium. Some students answer that equilibrium is reached at the equivalence point while others in most groups often realize that equilibrium is reached after each drop of titrant is added. I remind them that useful titration reactions must quickly reach equilibrium.

Which half reaction is easier to use to calculate the junction potential before the equivalence point? Which half reaction is easier to use after the equivalence point?

In answering the previous question, we have discussed that with a total electrochemical potential of zero, it means that the potentials of the cathode and anode are equal ($E_{\text{CAT}} = E_{\text{AN}}$). I then point out that E_{CAT} (or E_{AN}) is equal to the junction potential measured in the system.

I suggest that the groups write out expressions for E_{CAT} and E_{AN} and then construct a chart that shows the amounts of the different species in the reaction for 5 ml, 10, 20, 30 and 40 ml increments of titrant. After making sure they have the chart written correctly, I then ask if they can answer the questions above. During this process, I often need to remind them that K for the reaction is large, and remind them of the use of a back reaction for calculating the concentration of the Ce(IV) before the equivalence point. Groups can then usually see that it is easy to calculate the junction potential using the iron half reaction before the equivalence point and the cerium half reaction after.

I then ask them to calculate the junction potential for each step in their chart. They realize that they don't know how to calculate the potential at the equivalence point, so they complete the rest of the chart. I then give them the equation for calculating the junction potential at the equivalence point and also note what happens with the two half reactions have different numbers of electrons in them.

Voltammetric Methods

After a brief introduction to the general process of voltammetry, I give the students the following two questions to answer.

How can electrostatic migration be eliminated in an electrochemical cell?

After allowing the students to think about this, if they are perplexed or don't have a good answer, I find it helpful to draw a picture on the board of an electrode surface with a negative charge, show a representation of a positive ion in solution but removed from the surface of the electrode, and ask if they can think of something they could do to the system that would eliminate attraction between the negative electrode and positive ion (without changing either the charge on the electrode or ion). Usually the groups are able to think of adding a supporting electrolyte and when asked, reason that a higher concentration would be better.

Samples subjected to voltammetric methods are usually purged with nitrogen or another inert gas before the analysis and maintained under an inert atmosphere during the analysis.

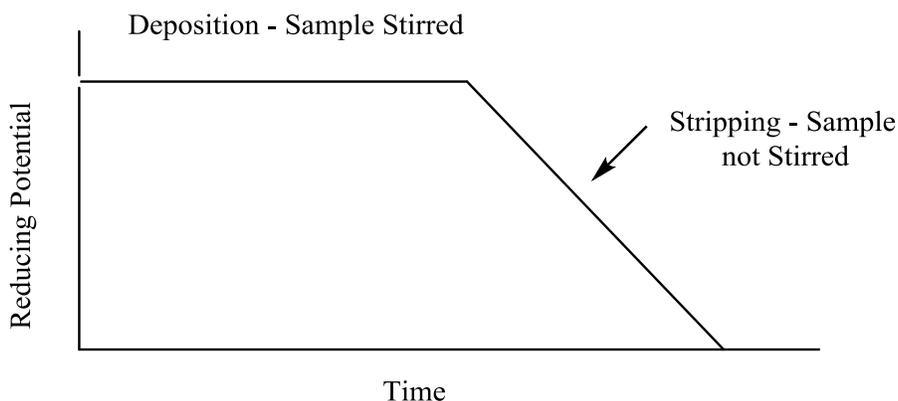
Why is this done?

Most groups can reason out that dissolved oxygen is a problem in electrochemical processes.

Anodic Stripping Voltammetry

I explain the features of the applied potential as a function of time used in ASV. I also explain a bit about the common microelectrodes used in ASV and then give them the following problem.

Suppose you are analyzing a solution that contains Cd(II) and Pb(II) using anodic stripping voltammetry. Considering the voltage profile that is applied as a function in time in anodic stripping voltammetry, draw a plot of the current you would observe in the deposition step (applied voltage is -1.00 V) and in the stripping step. Remember, the procedure uses a microelectrode, which is particularly important to consider in the deposition step.



I try to initially focus the students on the deposition process. They may remember the plot in coulometry (or I may prompt them) and draw something similar for this step. We then discuss that because a microelectrode is used, the solution will never be depleted of the species being analyzed. With the realization that the ions are now plated onto the electrode, they can consider the stripping step. They often realize that the species will strip back off the electrode through an oxidation but may not at first realize that it will produce a sharp peak. As with other portions of this unit, when they are asked to draw a result, I draw their different proposals on the board and ask them to examine all the suggestions and rule out some or select which they think is correct. It may require some questions to get them to realize that the current will have a different sign for the deposition and stripping step.

What feature of the plot can be related to the concentration of the metal?

With a final plot complete, groups realize that the height of the peaks can be related to the concentration of the metal.

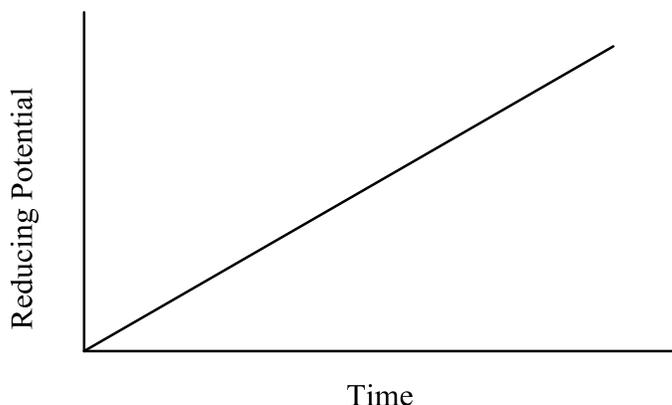
What advantage(s) does anodic stripping voltammetry offer over coulometry or electroplating?

Groups may need some prompting to get to a conclusion that ASV will be more sensitive. If they don't come up with it, I ask whether coulometry could be used to analyze the mixture studied in this problem.

Linear Sweep Voltammetry

I explain the potential versus time profile used in LSV and then give them the following problem set.

Draw the current that would be measured for a solution consisting of Cd(II) and Zn(II) for the voltage profile that is applied in a linear sweep experiment. Assume that the concentration of Cd(II) is about twice as large as that of Zn(II) and that the solution is stirred.



I draw the different responses I see among the groups on the board and ask them to provide reasons why some might be ruled out or another defended. Often they realize at some point that the potential will start to reduce one of the metal ions, but may want to draw a peak instead of realizing that the current will plateau at that point because of the solution being stirred. It is helpful to remind them that it is a microelectrode so there will always be a large excess of ions in solution and the bulk concentration effectively does not change.

What feature of the plot could be related to concentration?

The groups realize that the height of a plateau will relate to concentration.

What feature of the plot can be used for species identification?

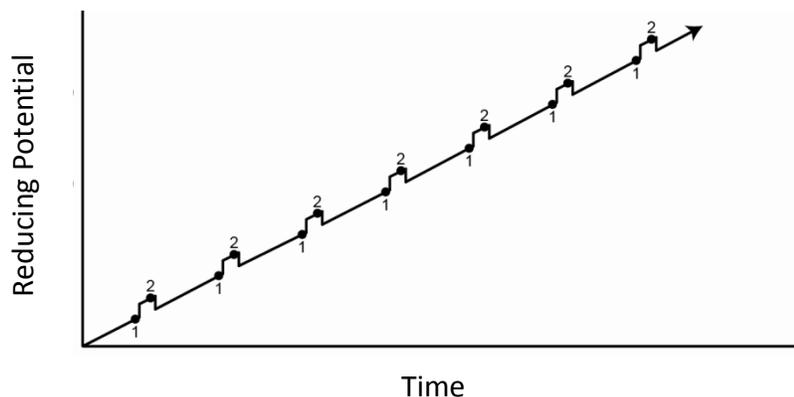
The groups realize that the location of the wave will vary for different species. I then introduce the idea of a half wave potential.

For the exact same solution of Cd(II) and Zn(II), draw the current that would be observed if the solution is not stirred.

We have discussed the concepts of diffusion, electrostatic attraction and physical convection at several places in this unit so the students realize those are the three things to consider.

Assuming a supporting electrolyte has been added to eliminate electrostatic attraction, we can then discuss whether diffusion is fast enough to maintain a plateau for the current. Most of them, when prompted, know that diffusion in solution is fairly slow and are able to reason out that the current will diminish in this case. Sometimes they want to draw a sharp peak instead of a slighter drop.

Consider a voltage profile in a linear sweep experiment where a small, increased voltage pulse is superimposed over a voltage ramp. The current is sampled twice: (1) just before the pulse is applied and (2) just before the pulse ends. The two measurements are subtracted [(2) – (1)] and the difference is plotted. Draw the resulting plot for the sample in question 1. What do you think is the name of this method?



It is important to leave the current versus time drawing on the board from the previous questions and ask them to consider that plot as they think about what will occur here. If they remain stumped, I usually draw some of the points (1) and (2) on the board for places where the current is not changing and for places going through the wave, and then tell them to consider the difference they would get in each case and to plot that. With that prompt, they are able to see that this would lead to a sharp peak for a species. I then point out that the process involves taking the derivative of the curve, hence the name differential pulse linear sweep voltammetry.

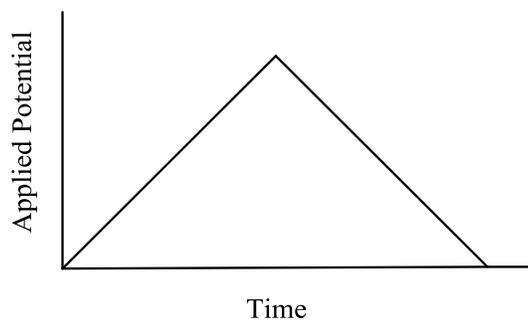
What advantage(s) does the method in the prior question have over regular linear sweep measurements?

Usually the groups are able to propose that the sharp peaks result in a more sensitive method and when prompted, realize that it will be easier to differentiate two species with closer reduction potentials. I draw pictures of these two situations on the board (Figures 27 and 28 in the text) to further illustrate this conclusion.

Cyclic Voltammetry

The prior topics within voltammetry have created the background needed to answer questions on CV, so after a very brief introduction showing the potential versus time profile, I give them the following questions.

Draw a plot of the current (y-axis) versus voltage (x-axis) that you would measure for a solution in which Fe(III) in ferricyanide ($\text{Fe}(\text{CN})_6^{3-}$) is reduced to Fe(II) during the reducing phase of the CV voltage profile shown below. The half reaction is chemically and electrochemically reversible and the solution is not stirred.



Given our discussion of LSV, they can readily draw the forward wave. I remind them that the plot is current (Y-axis) versus potential (X-axis), so that the X-axis is not time. This allows them to realize that there will be a reverse plot of the current and that the sign of the current will change for the reverse process. We can discuss the location of the reverse wave and its magnitude.

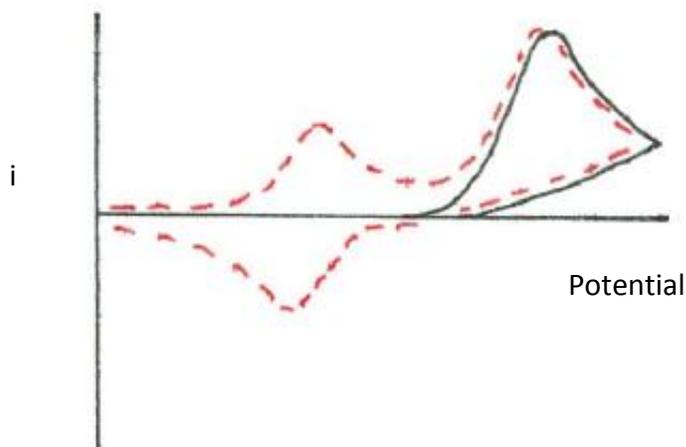
Draw a plot that could be obtained for an electrochemical reaction that is chemically irreversible and forms an electrochemically inactive product.

They usually can draw the resulting CV without any issue.

Draw the plot of current vs. potential that would be obtained for a reversible chemical reaction in which only the reverse reaction has an overpotential, but the potential eventually is sufficient to complete the reverse reaction.

They usually can draw the resulting CV without any issue.

Propose a reaction mechanism that would explain the following cyclic voltammogram. The first voltage cycle is shown as a solid line. The second voltage cycle is shown as a dotted line. A third voltage cycle gives the same output as the dotted line. Assume that a reducing potential is applied.



The groups can usually determine that the first reaction is irreversible and a new species seems to be showing up, indicating that the first product likely decomposed or further reacted. They can also reason out that the new species is a reversible couple.