

# Experiment 13 – Electrochemistry

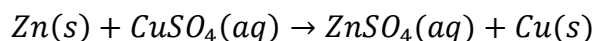
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## Overview

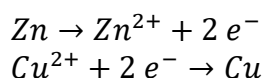
In this experiment, you will have the chance to see how electron transfer processes are important in chemistry. You will work with both electrolytic cells and galvanic (Voltaic) cells, as well as see the effects on electromotive force (EMF), which is measure in Volts, is affected by concentrations of electrolytes in cells.

## Redox Chemistry

Many chemical reactions occur due to a transfer of one or more electrons between species. An example, is the Daniel Cell [1] reaction, which is shown below.

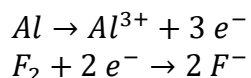


This reaction can be broken down into two **half-reactions**.

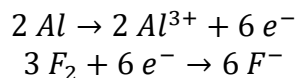


In this pair of reactions, zinc is **oxidizing** (its charge or **oxidation number** is getting larger) and copper is **reducing** (or its charge is getting smaller.) By definition, the half-reaction in which oxidation occurs is called the **anode**, whereas the half-reaction in which reduction occurs is called the **cathode**.

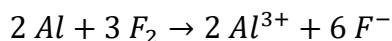
Oxidation and reduction always occur in tandem, since a chemical reaction will neither produce nor consume electrons in net. All of the electrons produced in an oxidation half-reaction must be consumed in the reduction half reaction. Consider the following half-reactions:



In order for these half-reactions to occur as a pair, the fluorine reaction must run three times for each two times the aluminum half-reaction runs. This is necessary in order for the reduction half-reaction to use all of the electrons produced by the oxidation half-reaction.



When added together, (assuming the ions remain separate), the overall reaction is



You'll notice that not only do the types of each element balance across the reaction equation, but also the total charges balance as well (in this case, 0 on both sides.)

But what if the half reactions could be kept separate from one another, forcing the electrons to travel through a wire, or some other electronic device that requires the flow of electrons in order to operate? This is how we create an **electrochemical cell**. (Batteries that you buy are constructed with several of these electrochemical cells connected in series in order to generate the desired voltage.) Combinations of specific half-reactions can be chosen to produce the desired voltage. This will be explored in Part B of this experiment. Part A examines another important application of controlling electron flow: electroplating. Part C will examine the effects of concentration changes on cell voltage. And Part D will explore the relationship between electrochemical measurements and **chemical equilibrium**.

### The Faraday Constant

When performing calculations in chemistry, it is desirable to determine the number of moles of some substance (an element, compound, or ion, for example.) A common way to do this is to convert from mass to moles using the molar mass.

**Example:** An experiment uses 3.52 g of Na (22.99 g/mol). How many mol of sodium are used in the experiment?

**Solution:** The solution requires using the molar mass of sodium. (This found in a periodic table if it was not given in the problem. Well, even though it was given in the problem, it can still be found in the periodic table. It isn't exactly a secret.)

$$3.52 \text{ g} \cdot \frac{\text{mol Na}}{22.99 \text{ g}} = 0.153 \text{ mol Na}$$

It is also possible to calculate the number of moles of electrons using the **Faraday constant** ( $F$ ), which is equivalent to the total charge carried by a mole of electrons. The value of the Faraday constant is

$$F = 96485 \text{ C}$$

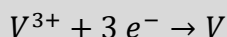
It is also important to note that a coulomb (C) is the amount of charge transferred by a current of 1 ampere flowing for a time of 1 second.

### Part A – Electrolysis

Electroplating is a process by which metal ions in solution are reduced to form metal atoms, which will then adhere to the surface of a metal object such as a spoon or a key.

**Example:** Vanadium is electroplated onto a key from a 1.00 M solution of  $V(NO_3)_3$ . If a current of 3.00 amp is passed for 4.50 min, what mass of vanadium will be plated onto the key? (V: 50.94 g/mol)

**Solution:** In order to solve this problem, we must know the charge on the vanadium ions. Since the charge on nitrate is 1- ( $NO_3^-$ ), and there are three nitrates, the charge on the vanadium ion must be 3+. So the reduction half-reaction is



So the calculation of vanadium that is plated looks as follows:

$$(3.00 \text{ amp}) \left( 4.50 \text{ min} \cdot \frac{60 \text{ sec}}{\text{min}} \right) \cdot \frac{C}{\text{amp} \cdot \text{sec}} \cdot \frac{1 \text{ mol } e^{-}}{96485 C} \cdot \frac{1 \text{ mol } V}{3 \text{ mol } e^{-}} \cdot \frac{50.94 \text{ g}}{\text{mol } V} = 0.1425 \text{ g}$$

The amount of metal deposited is intimately related to the charge on the metal ions in solution.

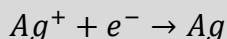
**Example:** It has been found that a current of 1.0 amp passed for 1.0 sec will electroplate a mass of 1.118 mg of silver onto the surface of a key or other object from a solution of an appropriate silver salt. What is the charge on the silver ions in solution?

**Solution:** The ion charge is given by the ratio of the number of moles of electrons to the number of moles of the metal.

$$(1.0 \text{ amp})(1.0 \text{ sec}) \cdot \frac{C}{\text{amp} \cdot \text{sec}} \cdot \frac{\text{mol } e^{-}}{96485 C} = 1.036 \cdot 10^{-5} \text{ mol } e^{-}$$

$$1.118 \text{ mg} \cdot \frac{g}{1000 \text{ mg}} \cdot \frac{\text{mol } Ag}{107.9 g} = 1.036 \cdot 10^{-5} \text{ mol } Ag$$

Clearly, this is a 1:1 ratio, so the charge on the silver ions (which must be an integer) is +1, and the reduction half-reaction is



## Procedure

1. Select the metal to be plated.
2. Enter the current to be used. (Typical values might be on the order of 1.0 to 3.0 amp)

3. Enter the amount of time the current is to be passed through the system. (Typical times might be on the order of 600 seconds.)
4. Calculate the change in the mass of the key by taking the final mass and subtracting the initial mass. From this, determine the number of moles of metal that were plated onto the key.
5. Use the product of time and current to determine the number of moles of electrons passed through the current.
6. The ratio of moles of electrons to moles of metal will be equal to the charge on the metal ions in the solution.

Initial mass of key (g)	
Final mass of key (g)	
Current (amp)	
Time (sec)	
Mass of metal deposited (g)	
Moles of metal	
Moles of electrons	
Charge on metal ions	
Reduction half reaction	

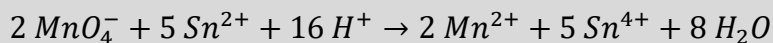
## Part B – Galvanic Cells

The **Nernst equation** is an important tool in determining cell potentials.

$$E_{cell} = E^{\circ} - \frac{RT}{nF} \ln Q$$

where R is the gas law constant (8.314 J/mol K), T is the temperature (in K), n is the number of moles of electrons transferred per reaction equivalent, F is the Faraday constant (96485 C/mol), and Q is the **reaction quotient**. The reaction quotient is the ratio of the concentrations of the products of the overall reaction, each raised to its stoichiometric coefficient to the concentrations of the reactants, again, each raised to its stoichiometric coefficient.

**Example:** Write the form of the reaction quotient (Q) for the reaction



**Solution:** The reaction quotient (Q) is given by

$$Q = \frac{[\text{Mn}^{2+}]^2 [\text{Sn}^{4+}]^5}{[\text{MnO}_4^-]^2 [\text{Sn}^{2+}]^5 [\text{H}^+]^{16}}$$

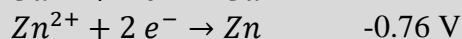
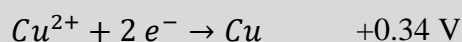
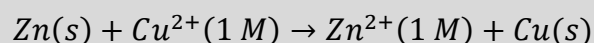
*Note:* pure solids and pure liquids are not included in the expression for  $Q$ . This is why the concentration of  $[H_2O]$  does not appear in the expression above.

Under **standard conditions**, all solutions have unit concentration (1 M). As such, under standard conditions,  $Q$  has a value of unity ( $Q = 1$ ) and so the natural logarithm part of the equation vanishes. This leaves

$$E_{cell} = E^{\circ}$$

The **standard cell potential** can be calculated from the difference in **standard reduction potentials** for the two half-reactions involved in the overall cell.

**Example:** Given the following standard reduction potentials, calculate the standard cell potential for the reaction



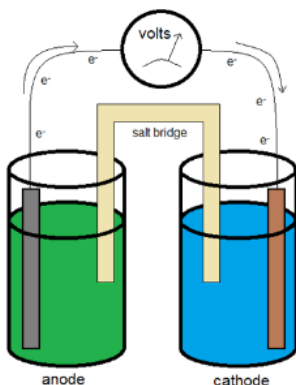
**Solution:** The Standard Cell Potential ( $E^{\circ}$ ) is given by

$$E^{\circ} = E_{red}^{\circ} - E_{ox}^{\circ}$$

In the reaction, copper is clearly reducing and zinc is oxidizing, so

$$E^{\circ} = 0.34 V - (-0.76 V) = +1.10 V$$

## Electrochemical Cells

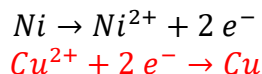


An electrochemical cell can be constructed by connecting two half-reaction cells as shown in the following diagram. In the depicted cell, the half-cell on the left might be constructed with a nickel metal electrode and a solution of nickel (II) nitrate, and the one on the right (the cathode) is constructed using a copper metal electrode in a solution of copper (II) nitrate. The electrodes are connected by wires, forcing the electrons to flow through a volt meter, The two solution must also be connected using a salt bridge in order to complete the circuit.

A shorthand notation to indicate the construction of the cell looks as follows:



The anode is indicated on the left and the cathode on the right. A single vertical line indicates a phase boundary, and a double vertical line indicates a salt bridge separating the two half-cell. The red wire of a volt meter will be connected to the cathode, and the black wire to the anode. So the half reactions for the above cell are



In this portion of the experiment, you will pair several half-cells pairwise in order to determine the relative reduction potentials for the half reactions.

### Procedure

1. Select combinations of the half cells and measure the potential associated with each combination. You will always measure a positive voltage if you attach the red wire to the silver electrode (since silver has the largest reduction potential of the elements used in the experiment, it will be the natural cathode in any pairing.)
  - a. Write the overall reaction for each cell you measure, as well as the standard cell potential.

Red Wire half-reaction (cathode)	Black Wire Half Reaction (anode)	Measured Voltage (V)
$Ag^{+} + e^{-} \rightarrow Ag$		

2. Place the metals in order of decreasing standard reduction potential based on your measurements,
  - a. Assign a standard reduction potential of +0.80 V to the  $Ag^{+} + e^{-} \rightarrow Ag$  half-reaction.
  - b. Based on the above assignment, calculate the standard reduction potentials for the remaining observed half-reactions.

### A few more words about the Nernst Equation

In this part of the experiment, everything is conducted under standard condition and at a temperature of 25 °C (at least nominally.) Because most electrochemical data (such as standard

reduction potential tables) are compiled at 25 °C, it is convenient to simplify the Nernst Equation. Toward this end, two things are typically done.

1. The temperature is assumed to be 25 °C (or 298 K).
2. The natural logarithm is converted to a base-10 logarithm by dividing by 2.303.

When these simplifications are made, the Nernst Equation becomes

$$E_{cell} = E^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$$

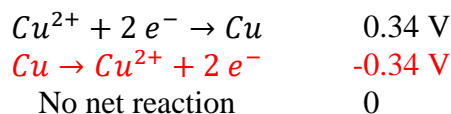
where the value of 0.0592 V is incorporating R, T, F and the factor of 2.303 to convert from ln Q to log Q.

### Part C – Concentration Cells

Consider a cell constructed as follows:



Using the Nernst equation, one can calculate the expected voltage to be produced. In this case, since the anode and cathode half-reactions are the same (but reversed),  $E^{\circ}$  is going to be zero.



And so the Nernst equation (at 25 °C) becomes

$$E_{cell} = -\frac{0.0592 \text{ V}}{n} \log \left( \frac{[anode]}{[cathode]} \right)$$

**Example:** Calculate the expected voltage for the cell



**Solution:** This can be accomplished using the Nernst Equation:

$$E_{cell} = -\frac{0.0592 \text{ V}}{n} \log \left( \frac{[0.002 \text{ M}]}{[2.00 \text{ M}]} \right) = 0.089 \text{ V}$$

In this part of the experiment, you will use the above kind of concentration cell to determine the value of F, the Faraday constant.

**Example:** The voltage for the following cell



is measured (at 25 °C) to be 0.089 V. Based on this, find the value of F, the Faraday constant.

**Solution:** The Nernst equation can be used for this.

$$E_{\text{cell}} = E^{\circ} - \frac{RT}{nF} \ln \left( \frac{[\text{anode}]}{[\text{cathode}]} \right)$$

Clearly,  $E^{\circ} = 0$  (because the cathode half-reaction is the reverse of the anode half-reaction.)  
Plugging in the salient values

$$0.089\text{ V} = 0 - \frac{\left(8.314 \frac{\text{J}}{\text{mol K}}\right) (298\text{ K})}{(2) \cdot F} \ln \left( \frac{[0.002\text{ M}]}{[2.00\text{ M}]} \right)$$

Produces a value for F of

$$F = 96149 \frac{\text{C}}{\text{mol}}$$

*Note:* This value is a little low, but agrees with the literature value to two significant figures.  
What do you think would be needed to get better agreement?

## Procedure

1. Select the concentration of  $[\text{Cu}^{2+}]$  in the anode half-cell.
2. Select the concentration of  $[\text{Cu}^{2+}]$  in the cathode half-cell.
3. Determine the voltage in the concentration cell you have designed.
4. Use the result to determine the value of the Faraday constant based on your results.

## Part D – Relationship to Equilibrium

When a redox system is at equilibrium (when  $Q = K_{\text{eq}}$ ), its overall potential goes to zero. As such, there is an intimate relationship between the standard cell potential (a non-equilibrium condition) and the equilibrium constant.

$$E = 0 = E^{\circ} - \frac{RT}{nF} \ln K_{\text{eq}}$$

Or

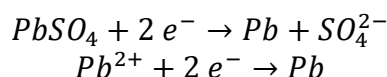


$$E^{\circ} = \frac{RT}{nF} \ln K_{eq}$$

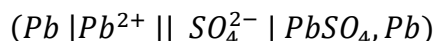
And as before, at 25 °C

$$E^{\circ} = \frac{0.0593 \text{ V}}{n} \log K_{eq}$$

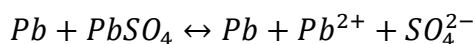
In this part, we will measure the equilibrium constant describing the dissociation of a salt ( $K_{sp}$ ). As an illustration of how this works, consider  $PbSO_4$ , which is considered insoluble because a saturated solution of the salt has such a low concentration. We will use the following half-reactions to determine the value of  $K_{sp}$  for  $PbSO_4$ :



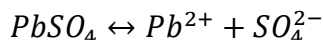
By measuring the standard cell potentials for the cell



One can determine the equilibrium constant for the reaction



Which simplifies to



Note that this reaction was generated by flipping the second half-reaction, so that one half-reaction involves oxidation and the other involves reduction. The equilibrium constant for the dissociation of an ionic compound into its ions in solution is given a special symbol:  $K_{sp}$ . The equilibrium constant for this reaction has the form

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

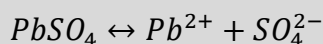
$$E^{\circ} = \frac{0.0592 \text{ V}}{n} \log K_{sp}$$

**Example:** The Standard Cell Potential ( $E^{\circ}$ ) for the cell defined by



is  $E^{\circ} = -0.23 \text{ V}$  at  $25^{\circ}\text{C}$ . From this measurement, determine the value of  $K_{\text{sp}}$  for  $\text{PbSO}_4$ .

**Solution:** As shown above, the overall reaction for the above cell is



We can use the relationship

$$E^{\circ} = \frac{0.0592 \text{ V}}{n} \log K_{\text{sp}}$$

To find the desired value.

$$-0.23 \text{ V} = \frac{0.0592 \text{ V}}{2} \log K_{\text{sp}}$$

Or

$$K_{\text{sp}} = 1.7 \cdot 10^{-8} \text{ M}^2$$

## Procedure

1. Choose an appropriate pair of electrodes to measure the voltage from which you can determine the solubility product ( $K_{\text{sp}}$ ) for the salt you have been assigned. (The filled line is an example.)

Red wire (anode)	Black Wire (cathode)	Voltage (V)
$\text{PbSO}_4 + 2 e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2 e^-$	-0.23 V

## A Few Words about Units

Electrical current, which is related to the number of electrons that pass through a area (such as the cross section of a wire), is measured in **amperes**, abbreviated *amp*. Time, of course, I measured in any convenient units, but for this experiment, the most convenient unit is seconds (sec). The product of current and time is **charge**, and is measured in **Coulombs (C)**. The number of Coulombs of charge is proportional to the number of electrons that pass though a circuit, the constant of proportionality being the charge on one electron (or the **electron charge**,  $e$ ):

$$e = 1.602 \cdot 10^{-19} \frac{\text{C}}{\text{electron}}$$

One way to think of this is to compare electricity flowing through a circuit to water flowing through a pipe. In this analogy, the current is analogous to the rate of flow of the water,

the time is (of course) the time, and the product tell us how full the bucket will be at the end of the pipe.

**Example:** What is the total charge carried by a current of 2.0 amp for a time of 3.0 min?

**Solution:** This is a fairly straightforward calculation!

$$(2.0 \text{ amp}) \left( 3.0 \text{ min} \cdot \frac{60 \text{ sec}}{\text{min}} \right) \cdot \frac{C}{\text{amp} \cdot \text{sec}} = 360 \text{ C}$$

The charge carried by one mole of electrons is called a **Faraday** (F). This can be a useful quantity to know as it shows up in many electrochemical calculations!

**Example:** How many Coulombs are there in one Faraday?

**Solution:** Again, this is a fairly straightforward calculation.

$$1 \text{ F} \cdot \frac{1 \text{ mol } e}{F} \cdot \frac{6.022 \cdot 10^{23}}{\text{mol}} \cdot \frac{1.602 \cdot 10^{-19} \text{ C}}{e} = 96500 \text{ C}$$

*Note:* the value of F is 96485.33212 C, and is a defined value [2].

Another important unit related to electricity is the **Volt** (V). A Volt is a unit of **electromotive force** (emf), and is related to how hard electrons are being pushed (or pulled if you prefer) through a circuit. The product of charge and electromotive force yields **energy**.

$$(1 \text{ C})(1 \text{ V}) = 1 \text{ J}$$

Another commonly used unit of energy is the **electron-Volt** (eV). This is the energy of one electron charge times a potential difference of 1 Volt. This is a convenient unit for describing (among many other things) the energy needed to ionize a single atom. For example, the ionization energy (or ionization potential, IP) of sodium is given by

$$IP(\text{Na}) = 5.1391 \text{ eV}$$

**Example:** How much energy (in kJ/mol) is needed to ionize sodium, given the ionization potential of sodium:  $IP(\text{Na}) = 5.1391 \text{ eV}$ ?

**Solution:** The ionization potential is the energy needed to ionize one atom. So, we can calculate the energy needed for one mol using Avogadro's Number:

$$5.1391 \text{ eV} \cdot \frac{1.60 \cdot 10^{-19} \text{ C}}{e} \cdot \frac{\text{J}}{\text{C} \cdot \text{V}} \cdot \frac{\text{kJ}}{1000 \text{ J}} \cdot \frac{6.022 \cdot 10^{23}}{\text{mol}} = 495 \frac{\text{kJ}}{\text{mol}}$$

Oftentimes, people are concerned with the rate at which energy is delivered in a process. **Power** is what is used to measure this rate. Power is measured in **Watts (W)**. One Watt is equivalent to a rate of energy delivery of one joule per second.

$$1 \text{ W} = 1 \frac{\text{J}}{\text{s}}$$

**Example:** Power is supplied to a system at a level of 10.0 kW. How much energy is delivered in 3.00 min?

**Solution:** This is a straightforward calculation too!

$$(3.00 \text{ min})(10.0 \text{ kW}) \cdot \frac{\left(\frac{1 \text{ J}}{\text{sec}}\right)}{\text{W}} \cdot \frac{60 \text{ sec}}{\text{min}} = 1800 \text{ kJ}$$

Finally, another important concept in electrical measurements is that of **resistance**. Resistance is measured in **Ohms ( $\Omega$ )**. There is a very important relationship between current (*i*), voltage (*V*), and resistance:

$$V = i R$$

**Example:** What is the voltage needed to push a current of 2.0 amp through a circuit with resistance of 13  $\Omega$ ?

**Solution:** This can be calculated using our trusty relationship of  $V = iR$ .

$$V = (2.0 \text{ amp})(13 \text{ ohm}) \cdot \frac{\text{V}}{\text{amp} \cdot \text{ohm}} = 26 \text{ V}$$

## Using a Multimeter

A **multimeter** is a device that can be used to measure a variety of electrical properties, such as voltage, current, and resistance. Most multimeters can also measure for both **alternating current (ac)** and **direct current (dc)** circuits.

## AC vs. DC

## Current, Voltage, Resistance

## Setting the Scale

## Vocabulary and Concepts

alternating current .....	12	half-reaction .....	1
ampere .....	9	Nernst equation .....	4
anode .....	1	Ohm .....	11
cathode .....	1	oxidation number .....	1
charge .....	9	oxidizing .....	1
chemical equilibrium .....	2	power .....	11
Coulomb .....	9	reaction quotient .....	4
direct current .....	12	reducing .....	1
electrochemical cell .....	2	resistance .....	11
electromotive force .....	10	standard cell potential .....	5
electron charge .....	9	standard conditions .....	4
electron-Volt .....	10	standard reduction potential .....	5
energy .....	10	Volt .....	10
Faraday .....	10	Watt .....	11
Faraday constant .....	2		

## References

- [1] K. Schmidt-Rohr, "How Batteries Store and Release Energy: Explaining Basic Electrochemistry," *Journal of Chemical Education*, vol. 95, no. 10, pp. 1801-1810, 2018.
- [2] "The NIST Reference on Constants, Units, and Uncertainty," The National Institutes of Science and Technology (NIST), [Online]. Available: <https://physics.nist.gov/cgi-bin/cuu/Value?f>. [Accessed 23 May 2020].

## Pre-Laboratory Assignment - Electrochemistry

Name \_\_\_\_\_

Section \_\_\_\_\_

## Report Sheet - Electrochemistry

Name \_\_\_\_\_ Date \_\_\_\_\_

Lab Partner(s) \_\_\_\_\_

### Part A - Electrolysis

Fill in the following table for the metal ion and conditions you used

Current (amp)	
Time (sec)	
Mass of metal deposited (g)	
Moles of metal	
Moles of electrons	
Charge on metal ions	
Reduction half reaction	

### Part B - Galvanic Cells

Fill in the following table based on your observations.

Reduction half-reaction	Standard Reduction Potential (V)
$Ag^+ + e^- \rightarrow Ag$	+0.80 V

### Part C - Concentration Cells

Anode [Cu <sup>2+</sup> ] (M)	Cathode [Cu <sup>2+</sup> ] (M)
F =	

### Part D – Connection to Equilibrium

Fill in the following table based on your measurements (the first line is an example):

Red wire (anode)	Black Wire (cathode)	Voltage (V)
$PbSO_4 + 2 e^- \rightarrow Pb + SO_4^{2-}$	$Pb \rightarrow Pb^{2+} + 2 e^-$	-0.22 V

In the space below, show your work for calculating the value of  $K_{sp}$  for your given salt.