# Electrochemical Half Cells and Reactions

**Suggested reading:** *Chang* text – pages 801 – 809

## Cautions

Heavy metals, such as lead, and solutions of heavy metals may be toxic and an irritant.

## Purpose

To determine the cell potential ($E_{cell}$) for various voltaic cells and compare the data with the calculated $E_{cell}$ values.

## Introduction

Electrochemical cells are devices used to convert chemical energy into electrical energy. The most commonly used electrochemical cells are batteries. A battery contains chemical substances waiting to react; the reaction between the substances involves the transfer of electrons from one species to another. When the battery is placed in a device, a complete circuit is made, and the reaction occurs inducing a flow of electrons (current) to run the device. The energy available from a given electrochemical cell is measured as a potential in units of volts.

An electrochemical reaction is composed of two parts: an oxidation half-reaction and a reduction half-reaction. When balancing electrochemical reactions, both mass and charge must be conserved. This means that in addition to making sure the number of each type of atom is equal from reactants to products, the number of electrons being transferred between the species must also be equal. When adding the half-equations to yield the overall equation, the electrons appearing in the two half-reactions must cancel each other. Electrochemical half-reactions are written including the number of electrons needed so the overall charge of the reactants equals the overall charge of the products.

Oxidation and reduction half-reactions each represent half of the overall reaction. An example is the reaction between zinc metal and copper(II) solution:

$$Zn\,(s) + Cu^{2+}\,(aq) \leftrightarrows Zn^{2+}\,(aq) + Cu\,(s) \qquad \text{(Eqn. 1)}$$

This overall reaction has two half-reactions associated with it, the oxidation of the zinc metal:

$$Zn\,(s) \leftrightarrows Zn^{2+}\,(aq) + 2e^{-} \qquad \text{(Eqn. 2)}$$

and the reduction of copper(II) ions:

$$Cu^{2+}\,(aq) + 2e^{-} \leftrightarrows Cu\,(s) \qquad \text{(Eqn. 3)}$$

In this case, both mass balance and charge balance are satisfied in the half-reactions shown for the metals.

Standard *reduction* potentials are used to quantitatively determine the amount of energy available from a given electrochemical reaction. Values of the standard reduction potentials for half-reactions ($E^{0}_{red}$) are provided in tables in nearly every general chemistry text (a selective list is shown in Table 1).

| **Reduction Half Equation** | $E^{o}_{red}$ **, V** |
|---|---|
| $Al^{3+}$ (aq) + 3 $e^{-}$ ⇆ Al (s) | -1.66 |
| $Zn^{2+}$ (aq) + 2 $e^{-}$ ⇆ Zn (s) | -0.76 |
| $Fe^{2+}$ (aq) + 2 $e^{-}$ ⇆ Fe (s) | -0.44 |
| $Sn^{2+}$ (aq) + 2 $e^{-}$ ⇆ Sn (s) | -0.14 |
| $Pb^{2+}$ (aq) + 2 $e^{-}$ ⇆ Pb (s) | -0.13 |
| 2 $H^{+}$ (aq) + 2 $e^{-}$ ⇆ $H_2$ (g) | 0.00 |
| $Cu^{2+}$ (aq) + 2 $e^{-}$ ⇆ Cu (s) | +0.34 |
| $Ag^{+}$ (aq) + 2 $e^{-}$ ⇆ Ag (s) | +0.80 |

*Table 1: Standard Reduction Potentials*

## Electrochemical Half Cells and Reactions

All standard reduction potentials are measured relative to the reduction of $H^+$:

$$2\,H^+(aq) + 2e^- \leftrightarrows H_2(g) \qquad (Eqn.\ 4)$$

which is given a reduction potential of 0.00 V. More positive values of $E^{\mathbf{0}}_{red}$ indicate the species is more easily reduced compared to $H^+$, while more negative values of $E^{\mathbf{0}}_{red}$ indicate the species is more easily oxidized.

Standard reduction potentials can be used to determine the energy available for an overall electrochemical reaction. As in thermodynamics calculations, reversing the direction of the reaction changes the sign of the potential. Thus, the oxidation of copper metal has a $E^{\mathbf{0}}_{ox}$ = -0.34 V associated with it. Once the oxidation and reduction half-reactions are known, $E^{\mathbf{0}}_{red}$ and $E^{\mathbf{0}}_{ox}$ associated with the separate reduction and oxidation processes can be written, and the reactions can be added.

Overall cell voltages ($E^0_{cell}$) can be used to predict the spontaneity of electrochemical reactions. If $E^0_{cell}$ is positive, energy is available from the electrochemical reaction occurring and the reaction is spontaneous as written. On the other hand, if the $E^0_{cell}$ is negative, energy is required to drive the reaction, therefore the reaction is non-spontaneous as written. Galvanic (or voltaic) cells generate an electrical current via spontaneous electrochemical reactions; most batteries fall under this classification. Electrolytic cells require an external current to proceed (non-spontaneous reactions); a commonly used electrolytic process is galvanization of steel to protect it from oxidation (rusting).

Consider the reaction between Zn(s) and copper(II) ions ($Cu^{2+}$) under standard conditions. Since the copper is present as an ion, it will most likely be reduced, while the solid zinc metal will be oxidized. The reduction potentials for the two metals reveal that this is the case; $Cu^{2+}$ has a $E^{\mathbf{0}}_{red}$ of +0.34V, while $Zn^{2+}$ has a $E^{\mathbf{0}}_{red}$ of -0.76V. Since reduction of $Cu^{2+}$ has a more positive potential compared to that of $Zn^{2+}$, $Cu^{2+}$ will be reduced and Zn(s) will be oxidized. These processes are indicated by Equations 5 and 6 below. A net equation and overall standard emf of the reaction ($E^0_{cell}$) are obtained by adding these two half-reactions and canceling the electrons:

$$Zn(s) \leftrightarrows \cancel{2e^-} + Zn^{2+}(aq) \qquad E^o_{ox} = 0.76\ V \qquad (Eqn.\ 5)$$

$$Cu^{2+}(aq) + \cancel{2e^-} \leftrightarrows Cu(s) \qquad E^o_{red} = 0.34\ V \qquad (Eqn.\ 6)$$

$$Cu^{2+}(aq) + Zn(s) \leftrightarrows Cu(s) + Zn^{2+}(aq) \qquad E^o_{cell} = 1.10\ V \qquad (Eqn.\ 7)$$

In this particular example, the overall cell voltage is positive, therefore the reaction is spontaneous as written (energy is available to do work).

In writing a balanced net cell reaction, we may need to multiply the coefficients of the half-cell reactions to properly cancel the electrons. However, *changing the coefficients of a half-cell reaction does not influence the reduction and oxidation potential*. Reduction and oxidation potentials are intensive properties in that they are independent of the stoichiometry of the reaction.

In order to harness the potential from an electrochemical reaction, an electrochemical cell is constructed. A galvanic cell composed of the copper-zinc system mentioned previously is shown in Figure 1. Each half-cell is placed in a separate container. In order to harvest the energy in the overall reaction, a wire and device (in this case a voltmeter) connects the two solid metal pieces, called electrodes. Electrons will flow through this wire from the oxidation half-cell to the reduction half-cell. A salt bridge is used to allow ions to move, balancing the changes in charge due to the flow of electrons.

# Electrochemical Half Cells and Reactions

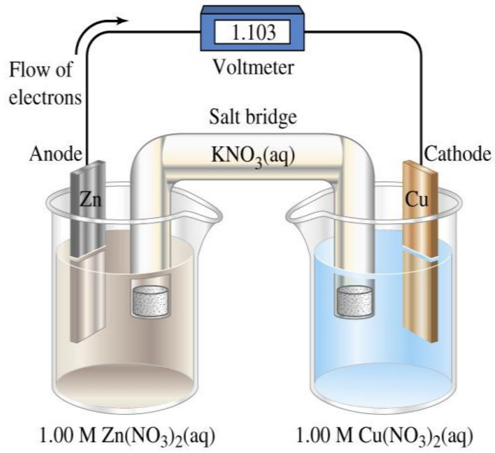


***Figure 1:*** *An electrochemical cell.*
http://cwx.prenhall.com/petrucci/medialib/media_portfolio/text_image

In this experiment various electrochemical reactions and cells will be observed. First, lead and zinc electrodes will be placed directly in copper and lead ion solutions and observed changes will be recorded. Then, electrochemical cells will be constructed using of $Cu/Cu^{2+}$, $Zn/Zn^{2+}$, and $Pb/Pb^{2+}$ half-cells. Based upon the observed voltages and chemical changes, the metals will be ranked in order of their ease of oxidation.

# Electrochemical Half Cells and Reactions

## Procedure

*Note: Metal strips should appear bright and shiny before beginning this experiment. Look carefully for changes either in the appearance of the metal surfaces or the solutions to indicate a reaction.*

### *A. The Zn-Cu Redox System*

A1. Obtain and clean a Zn metal strip with sandpaper. **DO NOT SAND TABLETOPS!**

A2. Obtain a small test tube and fill it with enough 0.1M $CuSO_4$ solution to ensure that the Zn metal strip is half-way submerged.

A3. Place the clean metal in the small test tube containing 0.10 M $CuSO_4$ solution.

A4. After 2.5 minutes, record your observations.

A5. After 5 minutes, record your observations.

A6. Carefully remove the Zn metal strip from the test tube, clean it with sandpaper, and dry using paper towels. Save it to use in Parts C and D.

A7. Retain the $CuSO_4$ solution for use in Part B.

### *B. The Pb-Cu Redox System*

B1. Obtain and clean a Pb metal strip with sandpaper. **DO NOT SAND TABLETOPS!**

B2. Place the clean Pb metal in the small test tube containing 0.10 M $CuSO_4$ solution from Part A.

B3. After 5 minutes, record your observations.

B4. After 10 minutes, record your observations.

B5. Carefully remove the Pb metal strip from the test tube, clean it with sandpaper, and dry using paper towels. Save it to use in Part D.

B6. Pour the $CuSO_4$ solution into the container labeled “Discarded $CuSO_4$ Solution”.

### *C. The Zn-Pb Redox System*

C1. Clean the Zn metal strip with sandpaper. **DO NOT SAND TABLETOPS!**

C2. Obtain a small test tube and fill it with enough 0.1M $Pb(NO_3)_2$ solution to ensure that the Zn metal strip is half-way submerged.

C3. Place the clean Zn metal in the small test tube containing the 0.10 M $Pb(NO_3)_2$ solution.

C4. After 2.5 minutes, record your observations.

C5. After 5 minutes, record your observations.

C6. Carefully remove the Zn metal strip from the test tube, clean it with sandpaper, and dry using paper towels. Save it to use in Part D.

C7. Discard the $Pb(NO_3)_2$ solution into the container labeled “Discarded $Pb(NO_3)_2$ Solution”.

# Electrochemical Half Cells and Reactions

## D. *Electrochemical Cells*

D1. Place about 15 – 20 mL of solutions 0.1 M $Cu(NO_3)_2$, 0.1 M $Zn(NO_3)_2$, 0.1 M $Pb(NO_3)_2$, and 0.1 M $KNO_3$ into small labeled 50-mL beakers.

D2. Clean the copper, zinc, and lead electrodes using steel wool or sandpaper and rinse with deionized water.

D3. Place each metal electrode in its corresponding ionic solution; e.g. copper strip goes into the $Cu(NO_3)_2$ solution. It is important that the correct metal is in the correct solution or your cell will not work properly.

D4. Obtain three small strips of filter paper to be used as salt bridges. Completely wet one strip in the beaker containing 0.1 M $KNO_3$. Carefully remove the completely wet strip and place one end in the $Cu(NO_3)_2$ solution and the other in the $Zn(NO_3)_2$ solution. The salt bridge should not touch the electrodes.

D5. Attach one alligator clip from the voltmeter to the Cu electrode and the second clip to the Zn electrode. If the voltmeter has a negative voltage, reverse the hookup so that each clip is now attached to the other metal in the pair.

D6. Record the voltage of the electrochemical cell.

D7. Repeat steps D4 – D6 for the remaining cells, connecting Cu-Pb and Pb-Zn. Record the positive cell voltages and use a new wet piece of filter paper as a salt bridge for each.

D8. Clean the metal strips with sandpaper or steel wool. Dry each strip using paper towels.

D9. Place each of the metal ion solutions into their respective waste beakers.

## Disposal

Dispose of all solutions into the appropriate waste container.

Return all metal pieces to their original container clean and dry.

## Clean-Up

Clean and dry your work area with water. Wash your hands before leaving the laboratory.

Wash all glassware with soap then rinse 3 times with tap water, and once with deionized water.

## Calculations

*Oxidation Reduction Reactions*

1. Consider the metals and ions involved to write the oxidation and reduction half-reactions; obtain the potentials from Table 1 to calculate $E^0_{cell}$.
2. Predict if each reaction should be spontaneous based upon calculated $E^0_{cell}$.
3. Discuss if your observations are consistent with your prediction of spontaneity.

*Electrochemical Cells*

1. Calculate the net cell voltage by using the tabulated potentials.
2. Calculate the percent error between the experimental and calculated cell potentials using the following equation:

$$\%error = \frac{\left| E_{cell}\,measured - E^0{}_{cell}\,calculated \right|}{E^0{}_{cell}\,calculated} \times 100\%$$

# Electrochemical Half Cells and Reactions

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# Electrochemical Half Cells and Reactions

## Data Sheet

**Name:** ________________________________________ **Lab Partner:** ___________________________

### Oxidation Reduction Reactions

| **A. Zn-Cu System** | | |
|---|---|---|
| **Experimental Observations** | | |
| **Oxidation Half Reaction** | | $E^o_{ox}$ = |
| **Reduction Half Reaction** | | $E^o_{red}$ = |
| **Net Reaction** | | $E^o_{cell}$ = |
| **Predicted Spontaneity** | | |
| **Observed Spontaneity** | | |

| **B. Pb-Cu System** | | |
|---|---|---|
| **Experimental Observations** | | |
| **Oxidation Half Reaction** | | $E^o_{ox}$ = |
| **Reduction Half Reaction** | | $E^o_{red}$ = |
| **Net Reaction** | | $E^o_{cell}$ = |
| **Predicted Spontaneity** | | |
| **Observed Spontaneity** | | |

# Electrochemical Half Cells and Reactions

## Data Sheet

**Name:** ________________________________________

| **C. Zn-Pb System** | | |
|---|---|---|
| **Experimental Observations** | | |
| **Oxidation Half Reaction** | | **$E^o_{ox}$ =** |
| **Reduction Half Reaction** | | **$E^o_{red}$ =** |
| **Net Reaction** | | **$E^o_{cell}$ =** |
| **Predicted Spontaneity** | | |
| **Observed Spontaneity** | | |

***D. Electrochemical Cells***

| **Metals Used** | **$E_{cell}$ Measured** | **$E_{cell}$ Calculated from tabulated potentials** | **% Error** |
|---|---|---|---|
| **Cu-Zn** | | | |
| **Cu-Pb** | | | |
| **Pb-Zn** | | | |

# Electrochemical Half Cells and Reactions

## Calculations:

# Electrochemical Half Cells and Reactions

## Post-lab Assignment

**Name:** ___________________________________

1. Complete the following table with the observed reactions for the electrochemical cells. Write the correct oxidation and reduction half-reaction in the appropriate column for each.

| | **Anode Reaction** | **Cathode Reaction** | **Overall Cell Reaction** |
|---|---|---|---|
| **Cu-Zn** | | | |
| **Cu-Pb** | | | |
| **Pb-Zn** | | | |

2. Compare the measured and calculated potentials of your electrochemical cells. Provide an explanation of the percent errors associated with these values.

3. Based on your reactions for the electrochemical cells, give the order of activity of the metals used in this experiment. List the most active (easiest to oxidize) metal first.

# Electrochemical Half Cells and Reactions

## Pre-lab Assignment

**Name:** ______________________________________

1. Define voltaic cell.

2. Consider the following two reduction reactions and their standard electrode potentials:

$Al^{+3}(aq) + 3e^{-} \leftrightarrows Al(s)$ $E° = -1.66$ V

$Cd^{+2}(aq) + 2e^{-} \leftrightarrows Cd(s)$ $E° = -0.40$ V

   a. Write the *balanced* overall cell reaction for a voltaic cell based on these two half-reactions and calculate the standard cell potential.

   b. Which species is easier to oxidize and why?

   c. Which species is easier to reduce and why?

3. A strip of tin is placed in a $CuSO_4$ solution. Do you expect a spontaneous chemical reaction to occur? If so, write the net cell reaction.