

ELECTROCHEMICAL CELLS

INTRODUCTION

A redox reaction involves the transfer of electrons from one chemical species to another. The energy from a redox reaction can be used to accomplish work by constructing an electrochemical cell. In an electrochemical cell, the oxidation process and the reduction process are separated into two **half-cells** connected by an external wire. The half-cell with the oxidation process is losing negative charge (e-loss) while the half-cell with the reduction process is gaining negative charge (e-gain). To maintain electrical neutrality in both half-cells, a salt bridge (or semipermeable membrane) must connect the two half-cells to permit the transfer of ions between the two solutions. Thus, the salt bridge completes the electrical circuit between the half cells.

The transfer of electrons through the external wire create a current that can do work. The driving force pushing the electrons through the wire is the difference in the attraction for electrons in the two half-cells. This voltage difference is called the **cell potential (E_{cell})** and is measured in volts. The cell potential (E_{cell}) is directly related to the magnitude of the equilibrium constant for the overall oxidation-reduction reaction occurring in the cell. A reaction that more strongly favors product formation (larger K_{eq}) will have a higher cell potential (larger E_{cell}) than a reaction which only moderately favors product formation.

Standard cell potentials (E°_{cell}) can be calculated from potentials (E°) for oxidation and reductions reactions measured under standard conditions (1.00 M solutions, 1.00 atm pressure, 298 K). A positive cell potential means the reaction proceeds spontaneously in the direction the reaction is written; a reaction with a negative cell potential proceeds spontaneously in the reverse direction.

$$(1) \quad E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} + E^{\circ}_{\text{oxidation}}$$

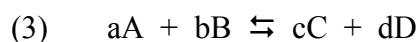
When the concentrations of solutes or partial pressures of gases are **not** at standard conditions, the cell potential (E_{cell}) can be determined with the **Nernst equation** (2):

$$(2) \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.059 / n) \log Q \quad (\text{Nernst equation})$$

Q: reaction quotient

n: moles of e⁻ transferred

For the general cell reaction (3) occurring at 298 K, the Nernst equation can be rewritten as shown in (4):

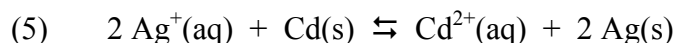


$$(4) \quad (E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.059 / n) \log ([C]^c [D]^d / [A]^a [B]^b)$$

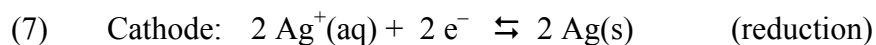
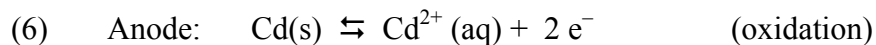
The Standard Potential Table in your textbook lists many half-cell reactions and their voltages. These potentials are measured relative to a selected standard half-reaction (usually the Standard Hydrogen Electrode (SHE): $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$, $E^{\circ} = 0.00 \text{ V}$). Typically, the reactions are listed as reductions. Therefore, the species most easily reduced have large *positive* voltage potentials and the species most easily oxidized have large *negative* potentials.

Cell notations (or cell diagrams) are a shorthand description of galvanic (spontaneous) cells. The reaction at the anode, cathode, reaction conditions (concentration, pressure etc.), and the type of electrode and electrode components are all described. By definition, oxidation takes place at the anode and reduction takes place at the cathode. Electrons flow from the anode to the cathode through the wire connecting the electrodes. (Typically, the anode is designated as the "negative" terminal (since electrons are produced at this terminal) and the cathode is called the "positive" terminal.)

Example: A galvanic cell is constructed from solutions in two beakers connected by a salt bridge and an external wire. One beaker contains 0.15 M $\text{Cd}(\text{NO}_3)_2$ and a Cd metal electrode. The other beaker contains 0.20 M AgNO_3 and Ag metal electrode. The net ionic equation for the cell reaction is:



In the reaction above, cadmium metal is oxidized (loses electrons) and is, therefore, the anode. The silver ion is reduced (gains electrons) to form Ag^0 (the cathode).



Using the rules listed below, cell notation is:



Cell Notation Rules:

1. The anode half-cell is described first; the cathode half-cell follows. Within a given half-cell, the reactants are specified first and products last. As the reader's eye proceeds from left to right s/he is reading a description of the oxidation reaction first and the reduction reaction last (in other words - the direction of electron flow). Spectator ions are not included.
2. A single vertical line indicates that species are in different phases (*e.g.* solid electrode | liquid with electrolyte), but in physical contact with each other. A double vertical line indicates a salt bridge or porous membrane separating the individual half-cells.
3. The phase of the species (s, l, g, aq) is always shown in parentheses. If the electrolytes in the cells are not at standard conditions, concentrations and/or pressure should be included with phase in parentheses as shown in equation (8). If no concentration or pressure is noted, the electrolytes in the cells are assumed at standard conditions (1.00 M or 1.00 atm and 298K).

SAFETY

Safety goggles and aprons must be worn in lab at all times. Solutions containing NH_3 and Na_2S must be prepared in the hoods. 6 M ammonia solutions are caustic and can cause burns and respiratory problems; wash all affected areas thoroughly with cold water. Na_2S can release toxic H_2S gas when mixed with acids (tap water in the sink traps is acidic). The odor of H_2S gas is similar to "rotten eggs". Use a dilute bleach solution to clean any spills containing sulfur. Ventilate the room if the odor is strong and inform the TA so s/he can find the source.

Before starting the experiment, the TA will ask one of you to do a quick demonstration or talk-through one of the following:

- 1) How to clean off the metal electrodes before using
- 2) How to make a salt bridge
- 3) How to clean up the spot plates after you're done with the experiment

PROCEDURES

Work in pairs. The stockroom will provide the following 0.1 M solutions: ZnSO_4 , CuSO_4 , NiSO_4 , MgSO_4 , and their metal electrodes (solid Zn, Cu, Ni, and Mg). (A key to help you identify the metal electrodes should be displayed somewhere in lab.)


Part A: Creating Electrochemical Cells

Obtain a spot plate from the plastic tub in the hood and clean it before use. Use sandpaper to remove any impurities from the metal electrodes - rinse with water and dry after sanding. Put about 25 drops of CuSO_4 and a Cu electrode in one of the wells to create a Cu^{2+}/Cu half cell. Repeat the same procedure with the remaining solutions and electrodes, recording their location on the spot plate in your notebook. As shown below in *Figure 3*, place the wells adjacent to each other, forming a square so they can easily be connected by a salt bridge.



Figure 3. Electrochemical Cell Set Up

Plug the voltage probe into CH1 of the LabQuest2. When the voltage probe leads are touched together, the voltage should display 0.00 V. When the two leads are not in contact with a cell (or each other), a meaningless default voltage may be displayed.

Zeroing the voltage probe: Connect the two ends of the voltage probe together, wait for the voltage reading to stabilize. In the  window, click on the big red box and choose “zero” from the drop-down menu.

Select any two cells and connect them by the salt bridge (*e.g.* place one end of the salt bridge in the Cu cell and the other end in the Zn cell). Determine the potential by touching the voltage probes to the electrodes in the cells. Do this by bringing the black lead of the probe in contact with one metal electrode and red lead in contact with the other electrode. If the voltage reads 0.00 V, then reverse the leads until you have a *positive* voltage. Wait about 5 seconds to take a voltage reading and record the value in your notebook. If the potential fluctuates considerably, sandpaper the electrode gently to remove oxides and impurities.

Determine which cell was the anode and which was the cathode: If the measured voltage is *positive*, the cell connected to the black lead is the anode and the cell connected to the red lead is the cathode. Once you have recorded this information, measure the potentials for the remaining cells, making as many combinations of two cells possible with the solutions provided. Be sure to note the anode and cathode for each combination and use a new salt bridge for each set of cells.

Part B: Measure the effect of concentration on a cell

Measure the voltage again for the Cu/Zn cell. Add 1 drop of 6 M NH₃ solution to the Cu well (stir with toothpick) and record the voltage. Place a piece of white paper under the spot plate to observe the color of the Cu(NH₃)₄²⁺ complex ion that is formed. (This color test is one that is frequently used to determine the presence of copper (II) ion in a solution.) Add one more drop of NH₃ and measure the voltage again. *Did you see any voltage change?* Create a new Cu/Zn cell and repeat the procedure using 2 M Na₂S solution instead of NH₃. Record the voltage after each drop is added and observe the color of the CuS precipitate. (The color of many metal sulfides are often used for identification purposes.)

Make sure to clear your email address and password of the LabQuest2 so others can't access your email account. Shutdown the LabQuest2 and not simply put it to sleep. To shutdown the LabQuest2: press the home key, select System → Shut Down → OK.

Part C: Place solutions in collection bottles

Use a disposable pipet and carefully transfer each solution from its well into the collection bottle in the hood. Place the empty spot plate into the large plastic tub in the hood. Do this carefully as there may be a dilute bleach solution in the tub which can spot clothing. Wash hands thoroughly before leaving lab.

DATA & DISCUSSION

- (1) Summarize Part A with a data table containing the headings: Anode, Cathode, Overall Cell Reaction, and Cell Potential. For each of cell combination, write the anode half reaction, the cathode half-reaction, the overall reaction in cell notation (the concentration of all solutions is 0.1 M), and the potential in volts.

- (2) Create a Reduction Potential Table with the cells containing copper from Part A. Assume the reduction potential for $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ is 0.00 V and calculate the remaining reduction potentials *relative* to $\text{Cu}^{2+} / \text{Cu}$. List the reactions in order of *decreasing* reduction potential.

- (3) Using the Reduction Potential Table from (2),
 - a) Arrange the ions (e.g. Cu^{2+} , Zn^{2+} etc.) *in order of decreasing ability to be reduced*:
 _____ > _____ > etc.
 (most easily reduced)

 - b) Arrange the metals (e.g. Cu, Zn etc.) *in order of decreasing ability to be oxidized*:
 _____ > _____ > etc.
 (most easily oxidized)

- (4) Qualitatively explain the effect of changing concentration of Cu^{2+} on voltage (Part B) using your experimental observations and the K_{eq} values below. (No calculations are required.)
 - (a) $\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$ $K_{\text{eq}} = 1.2 \times 10^{12}$
 - (b) $\text{CuS}(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$ $K_{\text{eq}} = 8.5 \times 10^{-45}$

- (5) What is the color of the 0.1 M CuSO_4 solution? What color changes are observed when ammonia and Na_2S are added to the Cu^{2+} solution?

QUALITATIVE ERROR ANALYSIS

1. What modifications could be made to the procedure to better account for random (indeterminate) errors?
2. List three potential systematic (instrumental, methodological, or personal) errors that could be made in this experiment. (Note: Be specific, systematic errors are in the details. For example, losing your solution because you knocked over the cuvette is not a systematic error – it's a gross one.)
3. Did any gross errors occur? Did you mess up? Did the equipment or instrumentation fail?