Experiment

Electrochemistry and the Nernst Equation

The CCLI Initiative
**Computers in Chemistry Laboratory Instruction**

LEARNING OBJECTIVES
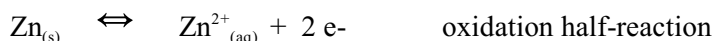
The objectives of this experiment are to . . .

- construct galvanic cells and develop an electrochemical series based on potential differences between half-cells.

- understand the Nernst Equation.

BACKGROUND

Any chemical reaction involving the transfer of electrons from one substance to another is an oxidation-reduction (redox) reaction. The substance losing electrons is **oxidized** and the substance gaining electrons is **reduced**. Let us consider the following redox reaction:

$$Zn_{(s)} + Pb^{2+}_{(aq)} \Longleftrightarrow Zn^{2+}_{(aq)} + Pb_{(s)}$$
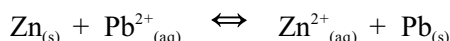
This redox reaction can be divided into an oxidation and a reduction half-reaction:

$$Zn_{(s)} \Longleftrightarrow Zn^{2+}_{(aq)} + 2\ e\text{-} \qquad \text{oxidation half-reaction}$$

And

$$Pb^{2+}_{(aq)} + 2\ e\text{-} \Longleftrightarrow Pb_{(s)} \qquad \text{reduction half-reaction}$$
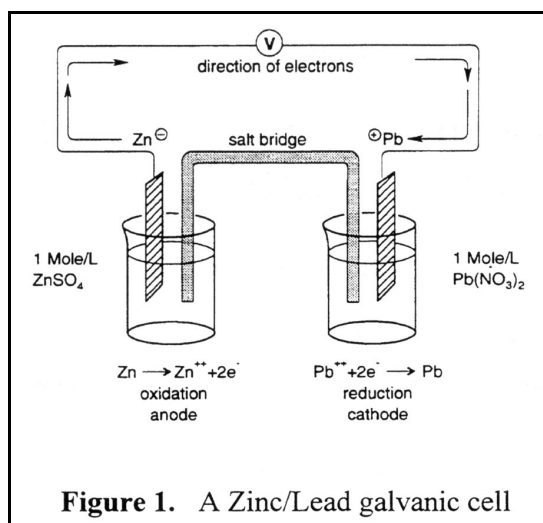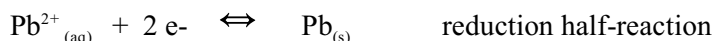

Figure 1. A Zinc/Lead galvanic cell

A **galvanic cell** (Figure 1) is a device used to separate a redox reaction into its two component half-reactions in such a way that the electrons are transferred through an external circuit rather than by direct contact of the oxidizing agent and the reducing agent. This transfer of electrons through an external circuit is electricity.

Each side of the galvanic cell is known as a **half-cell**. For the redox reaction above, each half-cell consists of an electrode (the metal of the half-reaction) and a solution containing the corresponding cation of the half-reaction. The electrodes of the half-cells are connected by a wire along which the electrons flow. In the cell, oxidation takes place at the zinc electrode, liberating electrons to the external circuit. Reduction takes place at the lead

1

electrode, consuming electrons coming from the external circuit.

the electrode at which oxidation occurs is called **anode**.

the electrode at which reduction occurs is called the **cathode**.

Since oxidation releases electrons to the electrode, it is designated the negative electrode in the galvanic cell. Reduction removes the electrons from the cathode; it is the positive electrode. As zinc atoms are oxidized, the excess positive charge (Zn^{2+} ions) accumulates in solution around the zinc anode. Likewise, excess negative charge (NO_3^-) accumulates around the lead cathode as Pb^{2+} ions are removed from solution of $Pb(NO_3)_2$ by reduction to lead metal. These excess charges create an electric field that causes the ions to migrate: positive ions (cations) migrate toward the cathode and negative ions (anions) migrate toward the anode. In order to make this flow of ions between the two half-cells possible, the cells are connected by a porous barrier (or salt bridge) through which the ions flow. The barrier prevents free mixing of the two solutions but permits limited movement of ions so that the electrical neutrality is maintained in each half-cell.

Different metals, such as zinc and lead, have different tendencies to oxidize; similarly their ions have different tendencies to undergo reduction. The cell potential of a galvanic cell is due to the difference in tendencies of the two metals to oxidize (lose electrons) or their ions to reduce (gain electrons). Commonly, a reduction potential, which is a tendency to gain electrons, is used to represent the relative tendency for a given metal ion to undergo reduction.

The voltage measured in the cell is the result of the two half-reactions, and the magnitude of the potential depends on the concentrations of the ions, the temperature, and pressure of gases. When all the concentrations in the zinc/lead system are 1 molar and the temperature is 25 °C, the cell voltage is 0.63 volts. It would be a monumental task to assemble a list of all possible cells and report their voltage. Instead we use the potential of the half-reactions. We cannot measure any half-cell potential directly, so we pick one half reaction, call it the standard, construct a cell, measure the cell voltage and report the potential relative to the standard. The standard that has been chosen by convention is:

$$2\ H^+\ +\ 2\ e^- \quad \Longleftrightarrow \quad H_{2(g)} \qquad\qquad \mathscr{E}° \ = \ 0.00\ V$$

Here the notation $\mathscr{E}°$ is called the standard electrode potential and is the assigned potential of the standard hydrogen electrode when the concentration of H^+ is 1 M and the pressure of the hydrogen gas is one atmosphere. The measured cell voltage using the standard hydrogen electrode is therefore the potential of the other half reaction.
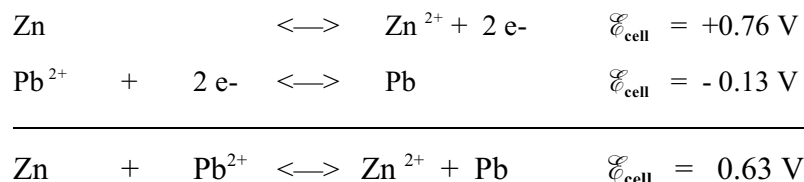
Tables of standard half-reaction potentials have been computed. The reactions by convention are written as reductions and hence the tables are called tables of standard reduction potentials. A brief example follows below in an excerpt from a Standard Reduction Potentials table.

The greater the tendency of the ion to gain electrons and undergo reduction, the less negative (or the more positive) the reduction potential of the ion. In the zinc/lead cell, the lead has a greater tendency to undergo reduction than the zinc.

Some Standard Reduction Potentials at 25 C

Half-reaction					Potential (volts)
Cu^{2+}	+	2 e-	<—>	Cu (s)	+0.34
$2 H^+$	+	2 e-	<—>	H_2 (g)	0.00
Pb^{2+}	+	2 e-	<—>	Pb (s)	- 0.13
Zn^{2+}	+	2 e-	<—>	Zn (s)	- 0.76
Mg^{2+}	+	2 e-	<—>	Mg (s)	- 2.37
Li^+	+	e-	<—>	Li (s)	- 3.05

In the zinc/lead cell the measured potential of 0.63 volts can be deduced from the sum of the potentials of the two half-reactions.

$$Zn \quad\quad\quad\quad\quad <—> \quad Zn^{2+} + 2\ e- \quad\quad \mathscr{E}_{cell} = +0.76\ V$$

$$Pb^{2+} \quad + \quad 2\ e- \quad <—> \quad Pb \quad\quad\quad \mathscr{E}_{cell} = - 0.13\ V$$

$$Zn \quad + \quad Pb^{2+} \quad <—> \quad Zn^{2+} + Pb \quad\quad \mathscr{E}_{cell} = 0.63\ V$$

Note: The sign of the standard reduction potential for the zinc half reaction is reversed to give the potential of the oxidation half reaction.

In Part I of this experiment, other metal/ion half-cell combinations will be tried. From the data, a table will be developed, listing various elements and ions in order of their tendency to gain or lose electrons.

The Nernst Equation

Theoretical predictions of tendency to gain electrons are used to predict the voltage difference between two electrodes. The voltage difference between electrodes, the cell voltage, is also called the **electromotive force, or emf (or $\mathscr{E}_{cell}$)**. Under standard conditions (25 °C, 1 M solution concentration, 1 atm gas pressure), these theoretically predicted voltages are known as **standard emfs (or $\mathscr{E}^{\circ}_{cell}$)**.

In reality, standard conditions are often difficult, if not impossible, to obtain. The **Nernst Equation** allows cell voltages to be predicted when the conditions are not standard. Walter Nernst developed the following equation in the late 1800's while studying the thermodynamics of electrolyte solutions:

$$\mathscr{E}_{cell} = \mathscr{E}^{\circ}_{cell} - (2.303\ RT/n\mathscr{F})\ logQ \quad\quad\quad\quad (1)$$

In equation (1), R is the gas constant (8.314 J mole^{-1} K^{-1}), T is the temperature (Kelvin), $\mathscr{F}$ is Faraday's constant (96,485 coulombs/mole), n is the number or electrons transferred in the balanced oxidation/reduction reaction, and Q is the reaction quotient, or ([products]/[reactants]). If the reactions are carried out at room temperature (25 °C), the Nernst equation becomes

$$\mathscr{E}cell = \mathscr{E}^{\circ}_{cell} - (0.0591/n)\ logQ \quad\quad\quad\quad (2)$$

Note in equations (1) and (2) that if the reaction quotient is equal to 1, then $\mathscr{E}_{cell} = \mathscr{E}°_{cell}$.

In Part II of this experiment, voltages will be measured at various solution concentrations for the copper/zinc galvanic cell and compared with voltages calculated using the Nernst Equation.

SAFETY PRECAUTIONS

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.

BEFORE PERFORMING THIS EXPERIMENT . . .

... you will need a *MicroLAB* program (*electropot.vs.kbd.experiment*) capable of measuring voltages, displaying them on the screen and sending a stable voltage reading and the corresponding concentration value or sample number from the keyboard to the **Spreadsheet** and **Digital Display** views.

EXPERIMENTAL PROCEDURE

Part I: Galvanic cells and the electrochemical series

1. Into a central cup of the 12-well container, carefully pour approximately 5 mL of 0.1 M KNO_3.

2. Into the four wells up (#1), right (#2), bottom (#3) and left (#4) of the central well, pour

about 5 mL of the metallic salt solutions listed below:

> #1   0.1 M $Cu(NO_3)_2$
>
> #2   0.1 M $ZnSO_4$
>
> #3   0.1 M Fe^{2+}/Fe^{3+}
>
> #4   0.1 M $SnCl_2$

3. With clean tweezers (do not use your fingers) take, one by one, four strips of filter paper and dip one end into the central cup (where immersion in the KNO_3 solution will hold one end), the other end into a different one of each of the four outer wells. Any two strips of filter paper from any two of the four outer wells, together with the KNO_3 solution in the central well, make your salt bridge.

4. Hold a copper metal strip with clean tweezers and, on top of a piece of scratch paper, sand the strip to remove any oxide coating. (**DO NOT SAND THE STRIP ON THE LAB BENCH ! !**) One end (2 cm) of the strip should be bent and immersed into the $Cu(NO_3)_2$ solution in its half cell (#1). The rest (3 cm) should extend out to the edge of the cell and should be bent over the rim. There the electrical leads (alligator clips) from the interface will be attached later. Repeat the same procedure with the zinc metal strip and place it in cup #2. Insert an inert electrode (nichrome wire) into the #3 solution, which contains Fe^{2+} and Fe^{3+} at equal concentrations. Insert a strip of tin foil into cell #4.

The pieces of metals and the Fe^{2+}/Fe^{3+} solution will be the electrodes of the galvanic cells. The tin will be the reference electrode; that is, we will measure all cell voltages relative to the reduction of tin:

$$Sn^{2+} + 2\,e- \quad \Longleftrightarrow \quad Sn\,(s) \qquad\qquad \mathscr{E}°_{cell} = 0.00\ V$$

5. Load the cell experiment (***electropot.vs.kbd.experiment***) on your computer in the **Saved Experiments** folder, and read the initial instructions carefully. You will be asked to input your sample number for each measurement.

6. Starting with the Sn/Cu combination, measure the voltage produced from the galvanic cells. Using the red and black lead wires (probes) attached to the red and black posts at V, secure the tin foil and copper metal to the Carrou-Cell™, with the alligator clips. Do not allow the clips to come in contact with the solutions. *Position the probes so that you read a positive voltage for the Sn/Cu system.* Record the voltage (**note: the interface displays voltages in volts when using the voltage leads**). *Leave the probes attached only long enough to get a voltage reading, then disconnect to minimize chemical changes by the current flow.*

The red probe is the positive terminal; the black is the negative terminal. The measured voltage will have a positive sign if the black probe is on the anode and the red probe is on the cathode. Identify and record which metal serves as the anode and which as the cathode.

7. Measure the voltage from the Sn/Zn system and the Sn/Fe system, always having the same probe on the Sn as you did for the Sn/Cu combination.

8. Measure the voltage of the Cu/Zn cell, Cu/Fe and Fe/Zn cells. Be sure to keep the polarities correct as you do this.

Part II: The Nernst Equation

In this part of the experiment, you will examine the effect of solution concentration on the cell voltage for the reaction:

$$Cu^{2+}_{(aq)} + Zn_{(s)} \iff Cu_{(s)} + Zn^{2+}_{(aq)} \qquad (1)$$
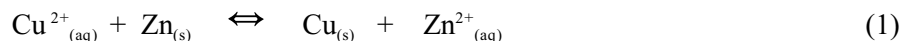
The Nernst Equation allows you to calculate $\mathscr{E}°_{cell}$ as a function of the reactant and product concentrations. For the above reaction at 25 °C, the Nernst Equation becomes:

$$\mathscr{E}_{cell} = \mathscr{E}°_{cell} - (0.0591/2) \log \{[Zn^{2+}] / [Cu^{2+}]\} \qquad (2)$$

Remember, solids and pure liquids are not included in the Q expression. Theoretically, $\mathscr{E}°_{cell}$ for the above reaction is 1.10 V. Thus, the value for $\mathscr{E}_{cell}$ can be calculated, knowing $[Zn^{2+}]$ and $[Cu^{2+}]$.

1. Open the program ***electropot.vs.kbd.experiment*** which your instructor has placed in the **Saved Experiments** folder.

2. Set up five zinc/copper cells using the following Zn^{2+} and Cu^{2+} solution concentrations (in mole per liter). The cells should be assembled in cups 1 through 5, with $Zn/ZnSO_4$ in the central cup.

Cell #	$[Cu^{2+}]$	$[Zn^{2+}]$
1	1.0	1.0
2	0.10	1.0
3	0.010	1.0
4	0.0010	1.0
5	0.00010	1.0

3.   Using the tweezers, dip five filter paper strips in 0.1 M KNO_3 in a small beaker. Use approximately 5 mL of KNO_3. Insert the strips with one end in the center cup, the other end into one of the outer cups just before you are to measure the potential of that combination.

4.   You should now have the five numbered cups each containing a different copper solution with a copper strip attached as in Part I. The central cup contains 1 M zinc solution with a strip of zinc placed in the solution. The filter paper strips, moistened with KNO_3 act as salt bridges for each cell.

5.   *Measure* the voltage ($\mathscr{E}_{cell}$) from each of the above half-cell combinations. Record this voltage in the Data Table in your notebook. The concentrations of the samples will be input from the keyboard when requested, and the corresponding voltages and concentration will be stored in the **Spreadsheet**, **Digital Display** and **Graph** views of the program.

5.   Determine $\mathscr{E}_{cell}$ for an unknown Cu^{2+} concentration.

DATA ANALYSIS

Part I: Galvanic cells and the electrochemical series

1.   Reload your data into the *MicroLAB* program.

2.   Obtain a printout of your data and graph.

3.   Make a table that indicates the relative position of the reduction reactions you observed with respect to the tin half-reaction. Place the reaction for your most positive voltage on top, and your reaction for your least positive (or most negative) voltage on the bottom.

Part II: The Nernst Equation

1.   Load your data into the **Spreadsheet** program.

2.   Use the **Formula** option to calculate $\log([Cu^{2+}])$ for each **sample**, then "Click drag" the formula to column C of the **Spreadsheet**, and the **Y2** axis of the graph.

3.   Assuming $\mathscr{E}^\circ_{cell}$ = 1.10 V and the temperature of the room is 25 °C, *calculate* $\mathscr{E}_{cell}$ for each of the above half-cell combinations. Record this calculated voltage in the **Data Table**.

4.   Print your graph of $\mathscr{E}_{cell}$ (observed) versus $\log [Cu^{2+}]$.

5.   From your plot of $\mathscr{E}_{cell}$ (observed) versus $\log [Cu^{2+}]$, determine the unknown copper ion concentration in the solution.