**purpose**

Measure concentration dependence of voltage output of Ag⁺ concentration cell. Plot $E_{\text{obs}}$ vs. log [Ag⁺], determine the slope, and compare with the Nernst equation.

Determine the solubility product of AgX (X = Cl, Br, and I).

Determine the standard reduction potential of redox couples involving Zn, Cu, and Pb.

**Background Information**

Every oxidation–reduction reaction can be written as a combination of two half-reactions. In one half-reaction, a substance loses electrons (oxidation) and in the other half-reaction, the electrons are gained (reduction). We can assign to each half-reaction an electrical potential that indicates the relative driving force for that half-reaction. For many oxidation–reduction reactions, it is possible to set up an electrochemical cell in which the two half-reactions are placed in separate compartments called half-cells. The two half-cells are connected by a salt bridge, which allows for the movement of ions from one half-cell to another. Each half-cell has an electrode. The two electrodes are connected with a wire through a voltmeter. Electrons flow from the electrode of the half-cell in which oxidation takes place via the wire and through a voltmeter to the half-cell, where reduction takes place. The voltmeter will read the sum of the potentials of the half-cells.
Let $E_A$ be the potential of a half-reaction,

$$A^{m^+} + m \, e^- \rightarrow A$$

and $E_B$ be a potential of a half-reaction (half-cell potentials are tabulated as reduction potentials by convention),

$$B^{n^+} + n \, e^- \rightarrow B$$

Then, the potential of the (overall) reaction,

$$n \, A + m \, B^{n^+} \rightarrow n \, A^{m^+} + m \, B$$

Would be $E_{obs} = E_B - E_A$ (we don't multiply $E$s by $n$ or $m$)

The corresponding conventional notation for the electrochemical cell would be

$$A \mid A^{m^+} \mid \| \mid B^{n^+} \mid B$$

Where $A\mid A^{m^+}$ and $B^{n^+} \mid B$ are the half-cells. If $A$ and $B$ are pure, solid metals, the half-cell potentials at ionic concentrations of $A^{m^+}$ or $B^{n^+}$ other than 1 M are given by the Nernst equation as shown for $A\mid A^{m^+}$ and $B^{n^+} \mid B$ half-cells (as usual, solid electrodes are not shown in the equilibrium quotient),

$$E_A = E_A^0 - \frac{(2.303RT)}{mF} \log[A^{m^+}] \quad (1)$$

$$E_B = E_B^0 - \frac{(2.303RT)}{nF} \log[B^{n^+}] \quad (2)$$

Where $E_A^0$ and $E_B^0$ are the **standard reduction potentials** (the potential corresponding to 1 M concentration species) of this redox pair, the log is base 10, and $[]$ represent molar concentration. The value of $(2.303RT/F)$ is 0.0592 volts at 25°C.

While the magnitude and sign of the potential difference between two half-cells can be measured, the absolute potentials of the individual half-cells cannot. The observed potential difference of an unknown half-cell whose reduction potential is $E_{unk}$ can be measured relative to a reference half-cell ($E_{ref}$). The measured potential would be given by:

$$E_{obs} = E_{unk} - E_{ref} \quad (3)$$

$E_{obs}$ is measured by connecting the two electrodes of the cell through a voltmeter, or more appropriately, a milli-voltmeter. The voltmeter must have high enough impedance to prevent excessive current flow during the measurement. (Current flow indicates that reaction is occurring in the two half-cells, and therefore, their concentrations and potentials are changing.)

A reference electrode could be any that gives a known and reproducible potential. In practice, all electrochemical potentials are quoted relative to the standard hydrogen electrode, the half-cell potential of which is zero by definition. There are many choices
Electrochemistry and the Nernst Equation

of reference electrodes, but one seldom uses the standard hydrogen electrode. In our experiment, we will use as reference an electrode consisting of 0.0100 M Ag+ and Ag for Parts 1 and 2, and 0.0500 M Pb2+/ Pb for Part 3.

The standard reduction potential of the Ag | Ag+ half-cell (relative to the standard hydrogen electrode @ 25°C [SHE]) is

$$\text{Ag}^+ + e^- \rightarrow \text{Ag} \quad E^0 = +0.799 \text{ V (at 25°C)}$$

So, the potential of a half-cell with 0.01 M Ag+ would be

$$E (0.01 \text{ M Ag}^+ / \text{Ag}) = 0.799 - 0.0592 \log(1 / 0.01) = 0.680 \text{ V (at 25°C)}$$

Similarly, for the Pb | Pb2+ half-cell with Pb2+ = 1.0 M, we have

$$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} \quad E^0 = -0.126 \text{ V (at 25°C)}$$

$$E (1.00 \text{ M Pb}^{2+} / \text{Pb}) = -0.126 \text{ V (at 25°C)}$$

Thus, if this Ag+ / Ag electrode were used as reference electrode, $E_{\text{unk}}$ would be $E_{\text{obs}}$ plus 0.680 V (relative to the standard hydrogen electrode). If Pb2+ / Pb were the reference, then $E_{\text{unk}}$ would be $E_{\text{obs}}$ minus 0.126 V (relative to standard hydrogen electrode). You will see below why the departure from an actual molarity of 1.00 in the case of Pb does not affect the measured potential in our case.

Electrochemical cells in which both half-cells involve the same half-reaction, but at different concentrations, are called concentration cells. A concentration cell can be shown schematically as:

$$\text{Ag} | [\text{Ag}^+] = m_1 || [\text{Ag}^+] = m_2 | \text{Ag}$$

half-cell 1 half-cell 2

and an example, from part 1 below, might be

$$\text{Ag (s)} | \text{Ag NO}_3 (1.00 \times 10^{-5} \text{ M}) || \text{AgNO}_3 (1.00 \times 10^{-2} \text{ M}) | \text{Ag (s)}$$

Figure 1 shows the setup of the cell. The potential of this cell will depend on the relative concentrations in both compartments and the Nernst equation for the cell would be:

$$E_{\text{obs}} = 0.0592 \log_{10} ([\text{Ag}]_1 / [\text{Ag}]_2) \quad (4)$$

Note that Eq. 4 is derived by combining Nernst equations of the two half-cells, similar to Eq. 1 and Eq. 2. Subscripts 1 and 2 refers to half-cells 1 and 2, respectively. For this cell, n is 1 and the E’s of the half-reactions cancel because they are the same but of opposite sign. The observed potential of the cell as written will be positive when the concentration of silver is smaller in half-cell 1 and negative if it is larger than the concentration of silver in half-cell 2.
Electrochemistry is a powerful tool for, among other things, observing equilibrium processes and measuring very low ionic concentrations. One can usually come up with a design of an electrochemical cell for whatever processes and chemical systems one is interested in. Studies of such cells, for example, were and are central to our understanding of the complex chains of electron transfer reactions that provide the energy to all living organisms (oxidative metabolism in all cells, photosynthesis in plants). You will see some examples of such connections between processes/systems and electrochemical cells in this experiment.

| CAUTION: A. Ag forms ugly brown spots on contact with skin. B. discard all Pb, Cu, Zn, and Ag wastes in designated containers. |

Part 1

In this part, we will measure $E_{\text{obs}}$ of a series of $\text{Ag}^+$ concentration cells. The cells will be made from a Ag wire inserted in a series of $\text{AgNO}_3$ solutions of different concentrations on one side, and another (fixed) Ag wire placed in a 0.0100 M $\text{AgNO}_3$ solution as a reference. The two half-cells will be connected by a salt bridge made up of a strip of filter paper impregnated with ammonium nitrate solution. As noted above, this constitutes a concentration cell.

According to the Nernst equation, a plot of $E_{\text{obs}}$ against the log of [Ag$^+$] is expected to be a straight line with a slope equal to $-2.303RT/nF$, which is $0.0592/n$ at 25°C. We will determine the slope of such a plot using a least-square fit and compare it with the theoretical value.

Experimental

**SILVER NITRATE SOLUTIONS**
You will be provided with $1.0 \times 10^{-1}$, $1.0 \times 10^{-2}$, $1.0 \times 10^{-3}$, $1.0 \times 10^{-4}$, and $1.0 \times 10^{-5}$ M $\text{AgNO}_3$ solutions in the lab.

**Setup and Calibration of pH/Voltmeter**
Connect two clean, dry silver metal electrodes using marked alligator clips to “INPUT” and “REF” jacks on the back of a pH meter (for some of the meters these go to the center pin and ground connectors, respectively, of a BNC connector; for the others these are the red and black terminals, respectively). Set the pH meter for voltage measurement.

The connections to the pH meter are critical to the determination of the sign of the measured potential of the cell. We must remember that (negatively charged) electrons flow from a lower potential toward a higher potential. If the connections are made as described above, the measured voltage is relative to the reference electrode.
Since our reference half-cell has a silver concentration of $1.0 \times 10^{-2}$ M, the potential of the other half-cell will be negative if the concentration of silver is smaller than that value; i.e., electrons will flow such as to increase the concentration in the other cell. If the concentration in the other half-cell is larger than that in the reference half-cell, the measured potential will be negative; i.e., electrons will flow from the reference half-cell to the other half-cell. In a concentration cell, spontaneous electron flow ($\Delta G < 0$, and therefore $\Delta E > 0$) will always be such as to minimize the concentration difference.

To calibrate the pH meter, take 5 mL of 0.0100 M AgNO₃ in a clean 10 mL beaker. Measure and record the temperature of the solution. Place both Ag electrodes in the beaker and read voltage. If the meter does not read 0 mV, adjust standardize knob until it reads zero. It may take some practice to stabilize the reading.

**Measurement of $E_{obs}$**

Set up the first electrochemical cell as shown in the figure below.

![Figure 1.](https://example.com/figure1.png)

Barely dampen a filter paper strip with NH₄NO₃ solution. Dip one end of the filter paper strip (salt bridge) in 0.0100 M AgNO₃ solution in a 10 mL beaker and the other end in $10^{-5}$ M AgNO₃ solution in another 10 mL beaker. Make sure that both ends of filter paper strip are plastered against the inner walls of the beakers.

Now dip the Ag electrodes in the solutions. Keep the silver wire of the electrode as far away from the filter paper salt bridge as possible. Record the voltage on data sheet.

Proceed to next higher concentration. The reference side remains the same. For each solution rinse the Ag wire with distilled water and dry it with a towel. Use a new salt bridge for each solution.

Collect the data in your notebook. Plot voltage against log of molarity of the AgNO₃ solution on the laboratory computers. Note the slope and goodness of fit. Comment on the slope and compare it with the slope you expect from the Nernst equation (adjusted for the actual temperature). What are the units of the slope?
Part 2. Determination of Solubility Product of a Silver Halide

Electrochemical cells can be used to determine the concentration of an ion in a solution by comparison with a half-cell, where the ion is of known concentration. If the ion is in equilibrium with an insoluble salt containing the ion, the electrochemical concentration cell can be used to measure the solubility product ($K_{sp}$) constant of the insoluble salt.

In this part, you will be provided with an unknown solution of potassium halide (KX; where $X = \text{Cl}, \text{Br}, \text{or I}$) of 0.0500 M concentration, and you will mix it with a known volume of 0.0100 M AgNO$_3$ to produce solid AgX. The procedure is as follows:

To a clean, dry 10 mL beaker, add 5.00 mL of 0.0100 M AgNO$_3$ solution. This will be the reference electrode. To a second clean, dry 10 mL beaker add 5.00 mL of 0.0100 M AgNO$_3$ solution and 5.00 mL of 0.0500 M unknown potassium halide solution. Swirl; a precipitate forms. Connect two solutions by using a newly prepared salt bridge, as in part 1. Dip silver wire electrodes as in part 1 and record the initial voltage ($E_{\text{obs}}$), since it will drop slowly.

**CALCULATIONS**

The solubility product is the equilibrium constant for the reaction:

$$\text{AgX (s)} \rightarrow \text{Ag}^+ + \text{X}^- \quad K_{\text{sp}}$$

To make silver halide as described above, we conduct the reverse of this reaction:

$$\text{Ag}^+ + \text{X}^- \rightarrow \text{AgX (s)}$$

Let us examine the stoichiometry of the reaction as conducted:

Initial Concentration of $\text{Ag}^+$ = 0.0100 M

volume of $\text{Ag}^+$ used = 5.00 mL

mmoles of $\text{Ag}^+$ used = 0.0100 $\times$ 5.00 = 0.0500

initial concentration of $\text{X}^-$ = 0.0500 M

volume of $\text{X}^-$ used = 5.00 mL

mmoles of $\text{X}^-$ used = 0.0500 $\times$ 5.00 = 0.250

Final volume in the reaction cell = 10.00 mL

mmoles of $\text{X}^-$ remaining after = 0.250 – 0.0500 = 0.200

($\text{Ag}^+$ is limiting reagent)

Molarity of $\text{X}^-$ at equilibrium, $[\text{X}^-]$ = 0.200/10.00 = 0.0200M

So, our expression for the solubility product becomes:

$$K_{\text{sp}} = [\text{Ag}^+] [0.0200]$$
The potential measured relative to the reference electrode is:

$$E_{\text{obs}} = 0.0592 \log_{10} (0.0100/m)$$

(Since the silver concentration in equilibrium with the halide, m, is presumably small compared to 0.0100, the measured potential should be positive.)

The above expression simplifies to:

$$E_{\text{obs}} = (-2)(0.0592) - 0.0592 \log_{10} m$$

or,

$$\log_{10} m = -(E_{\text{obs}} + 0.118)/0.0592$$

So,

$$m = 10^{-\frac{E_{\text{obs}} + 0.118}{0.0592}}$$

Finally, we use this value in the expression:

$$K_{\text{sp}} = 0.0200 \text{ m}$$

**Part 3. Standard Redox Potentials for Various Half-Cells**

In this part, you will prepare three half-cells of the form

$$M (s) | M^{2+} (aq) \text{ where } M = \text{Zn, Pb, and Cu}$$

and the anions are the nitrates of these ions, $M (NO_3)_2$ at 0.050 M. Then you will determine the voltage of cells with the permutations Zn/Cu, Zn/Pb, and Pb/Cu. From the knowledge of one half-cell reduction potential and the three measured cell potentials, you will calculate other standard half-cell potentials.

The procedure to set up the Zn/Cu cell is as follows. Clean copper and zinc metal strips with sandpaper or steel wool to remove any oxide layer. Connect the reference lead from the pH meter to the copper strip and the other lead to the zinc strip using alligator clips.

Take 5.00 mL of 0.050 M Cu(NO$_3$)$_2$ solution in a 10 mL beaker and 5.00 mL of 0.050 M Zn(NO$_3$)$_2$ in a second 10 mL beaker. Connect the two half-cells by a salt bridge as explained in part 1. Insert the copper and zinc strips in their respective solutions. Read and record the highest potential observed if the voltmeter drifts. Note carefully the sign of the measured potential. Which electrode is positive? In which half-cell is oxidation taking place?

Similarly, construct Zn/Pb and Cu/Pb cells, each with the reference lead connected to Pb, and measure their voltages. From the measured voltages, calculate the half-cell
reduction potentials for the copper and zinc half-cells, using the known reduction potential for the Pb/Pb^{2+} half cell, \( E^0 = -0.13 \text{ v.} \)

In these calculations, you need to write the balanced equations for each cell and for each half-reaction. For example, in the Cu/Zn case, the overall reaction is

\[
\text{Zn (s) + Cu}^{2+} (0.050 \text{ M}) \rightarrow \text{Cu (s) + Zn}^{2+} (0.050 \text{ M})
\]

The observed voltage is given by

\[
E_{\text{obs}} = E^0_{\text{Cu}} - (2.303 \frac{RT}{2F}) \log_{10} (0.050) - [E^0_{\text{Zn}} - (2.303 \frac{RT}{2F}) \log_{10} (0.050)] = E^0_{\text{Cu}} - E^0_{\text{Zn}}
\]

Note that, since all of the relevant reduction reactions involve two electrons and all the metal ion solution have the same concentration, 0.050 M, only the standard reduction potentials are involved in these calculations.
Part 1. Concentration Cells

<table>
<thead>
<tr>
<th>[Ag⁺]</th>
<th>E&lt;sub&gt;obs&lt;/sub&gt; mV</th>
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Temperature: ______ °K
Slope observed: ________ Slope calculated: ________

Part 2. Solubility Product of Unknown AgX (X = Cl, Br, or I)

Which unknown did you study? ________________

E<sub>obs</sub> of the cell

Ag | AgX(s) | Ag⁺ (m) || Ag⁺(0.010 M) | Ag

Molarity (m) of (Ag⁺) in the above cell

Molarity of X⁻ in the cell

K<sub>sp</sub> of unknown halide (AgX)

Part 3. Standard Reduction Potentials

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<tr>
<th>ELECTROCHEMICAL CELL</th>
<th>E&lt;sub&gt;obs&lt;/sub&gt; (V)</th>
<th>E&lt;sup&gt;0&lt;/sup&gt; OF THE HALF-CELLS (V)</th>
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<td>Cu²⁺/Cu =</td>
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<td>Zn²⁺/Zn and Pb²⁺/Pb</td>
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<td>Cu²⁺/Cu and Zn²⁺/Zn</td>
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Pre-Laboratory Questions

1. Mg (s) dissolves in dilute HCl but Cu (s) does not. What would happen if you dipped Cu (s) into 0.1 M Mg(NO_3)_2 solution?

What would happen if you dipped Mg (s) into 0.1 M Cu(NO_3)_2 solution?

Based on the above, show by an arrow which way the electrons would flow in the cell below:

\[ \text{Mg (s) } | \ 0.1 \text{ M Mg(NO}_3\text{)_2} \ || \ 0.1 \text{ M Cu(NO}_3\text{)_2} \ | \ Cu (s) \]

2. Given that the value of \((2.303RT/nF)\) is 0.0592 at 25°C, what would be the voltage reading for the concentration cell 0.01 M Cu^{2+}/Cu and 1.0 M Cu^{2+}/Cu?

\[ \text{Cu (s) ”input” } | \text{ Cu}^{2+} (1.0 \text{ M}) \ || \text{ Cu}^{2+} (0.01 \text{ M}) \ | \text{ Cu (s) “ref”} \]

Will the voltage be positive or negative?

3. A student followed the procedure of part 3 for an unknown potassium halide and recorded the initial voltage reading as 0.xx Volt (xx is the last two digits of your S.S. #). Calculate \(K_{\text{sp}}\) of the unknown halide.