

Experiment 5: Electrochemical Determination of K_{sp} for Silver Salts

What lab skills will you practice?

- Using a multi-meter
- Serial Dilutions
- Building concentration cells

What chemical concepts will you apply?

- Solubility of salts Silberberg: Chapter 17.3
- Voltaic cells Silberberg: Chapter 19.2
- Cell potentials Silberberg: Chapter 19.3

What report writing skills will you use?

- Writing a worksheet lab report
- Using cell potential to determine concentration
- Analyzing experimental data

Reminders:

- Complete the pre-lab quiz and flowchart at least **one hour before lab**
- Print & bring all Experiment 5 pages to lab
- Some worksheet questions can be completed at home to save time during lab

Objective

In this experiment, you will use measured cell potentials to determine the solubility product (K_{sp}) of silver halides (AgCl, AgBr, and AgI) and describe the trends in their properties.

During this lab period, you will also check out of your equipment drawer and complete a laboratory survey.

Introduction

Concentration Cells

When a metal electrode is immersed in a solution containing its ions (i.e. a **half-cell**), an equilibrium is established, called a **half-reaction**:



If we create two such half-cells, connecting the metal electrodes with a wire and the two solutions with a salt bridge, we will have an electrochemical cell. The salt bridge provides electrical conductivity between the two half-cell solutions, avoiding the buildup of charge (either + or -) on either side, while maintaining separation of the two solutions so that the reaction is forced to pass charge through the wire in order to run.

Electrons flow between the two electrodes due to the difference in potentials between the two half-cells. This potential difference can be measured by a voltmeter inserted into the circuit. An example electrochemical cell (Figure 1) is shown below, constructed using the Fe^{2+}/Fe and Cu^{2+}/Cu half-cells. In this cell, Cu^{2+} is reduced at the cathode, while Fe is oxidized at the anode.

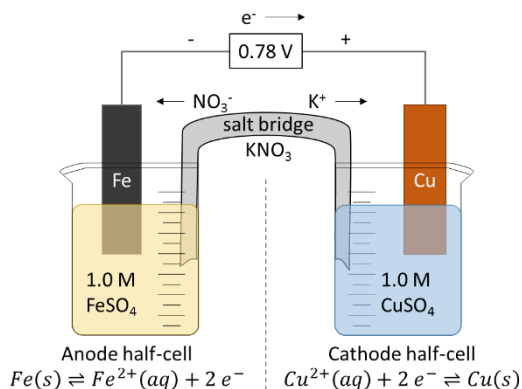


FIGURE 1: EXAMPLE ELECTROCHEMICAL CELL

The reduction potential of a half-cell (E_{red}) will change as concentrations of ions or pressures of gases change. This change is calculated using the **Nernst equation** (Silberberg, section 19.4):

$$E_{red} = E_{red}^0 - \frac{RT}{zF} \ln Q \quad [2]$$

Where: E_{red}^0 is the standard reduction potential for the half-cell
 R is the universal gas constant
 T is the temperature (in K)
 z is the number of moles of electrons transferred in the half-reaction
 F is Faraday's constant
 Q is the reaction quotient

R and F are universal constants.
 T is usually constant (room temperature).
 z depends on the reaction being studied.
 Q changes with reaction conditions.

The reaction quotient is the same as seen in other equilibrium reactions. For a reduction half-cell where the electrode is a solid metal, the reaction quotient would be represented by:

$$Q = \frac{1}{[M^{n+}]} \quad [3]$$

Note that during voltage measurements, very little current flows, so the reaction proceeds very slowly and any concentration changes in each half-cell will be negligible over the measurement time frame.

The overall cell potential, E_{cell} , can be calculated from the **reduction potentials** of the two half-reactions (for a voltaic cell, the reduction potential of the cathode is larger in magnitude than the reduction potential of the anode):

$$E_{cell} = E_{red,cathode} - E_{red,anode} \quad [4]$$

Where: $E_{red,cathode}$ is the reduction potential for the cathode half-cell
 $E_{red,anode}$ is the reduction potential for the anode half-cell

Special cases of electrochemical cells are concentration cells. Each half-cell has identical metal electrodes, but differing concentrations of ions (Silberberg, et al., Section 19.4 pages 840-843). If know the concentration of the electrolyte in one of the half-cells, and measure the cell potential, you can calculate the concentration of the electrolyte in the other half-cell.

By examining the expression for Q and the Nernst equation above, you can determine that as the ion concentration increases, the cell potential will increase. Therefore, in order for the overall reaction to be spontaneous, the cell compartment with the *higher* concentration will act as the cathode. The half-cell reactions will be:



The overall cell equation is the sum of the half-reactions:



And the Nernst equation for the cell becomes:

$$\begin{aligned} E_{cell} &= E_{red,cathode} - E_{red,anode} \\ E_{cell} &= \left(E_{red,M^{n+}}^0 - \frac{RT}{zF} \ln \left(\frac{1}{[M_{higher}^{n+}]} \right) \right) - \left(E_{red,M^{n+}}^0 - \frac{RT}{zF} \ln \left(\frac{1}{[M_{lower}^{n+}]} \right) \right) \\ E_{cell} &= \frac{RT}{zF} \ln \left(\frac{[M_{lower}^{n+}]}{[M_{higher}^{n+}]} \right) \end{aligned} \quad [8]$$

To simplify calculations, Equation [8] can be converted to a base-10 log (rather than ln), and the values of all constants merged into one value (including an assumption that measurements taken at 25°C). Equation [8] then becomes:

$$E_{\text{cell}} = -\frac{0.0592}{n} \log \left(\frac{[M_{\text{lower}}^{n+}]}{[M_{\text{higher}}^{n+}]} \right) \quad [9]$$

Determining K_{sp} Using Concentration Cells

As you observed in the demonstration in class, if you mix a solution containing silver ions with another solution containing halide ion (X^-), AgX(s) will precipitate and will be in equilibrium with its ions:



The equilibrium expression for this system is the **solubility product** (K_{sp}):

$$K_{\text{sp}} = [\text{Ag}^+][\text{X}^-] \quad [11]$$

In order to determine the value of K_{sp} experimentally, you will need to determine the equilibrium concentrations of both the silver and halide ions in the ‘precipitation’ half-cell.

When setting up your concentration cell, one half-cell will contain a known $[\text{Ag}^+]$ concentration, with no added halide. This is your “higher concentration” half-cell.

In the lower concentration “precipitation” half-cell, you will mix a solution of known $[\text{Ag}^+]$ with a solution containing a large excess of $[\text{X}^-]$. Using a large excess of the halide (much more X^- than Ag^+ in solution) serves two purposes. First, even if the initial $[\text{Ag}^+]$ is very low, the amount of *free* Ag^+ in the equilibrium mixture will be reduced to an even smaller value. (In other words, you are ‘pushing’ the equilibrium towards the products.) Second, having a large excess of X^- ensures that the change in $[\text{X}^-]$ after forming the AgX(s) will be negligible. The only significant change in $[\text{X}^-]$ concentration will be the dilution that occurs as you mix the two solutions.

You used a similar strategy to control the $[\text{Fe}(\text{SCN})^{2+}]$ equilibrium in Experiment 3.

By using the observed cell potential and the known (higher) value of $[\text{Ag}^+]$ in the modified Nernst equation (Equation [9]), you can determine the $[\text{Ag}^+]$ in the “precipitation” half-cell (the lower $[\text{Ag}^+]$). Combined with the known halide (X^-) concentration in this half-cell, you will then be able to determine the value of K_{sp} for each silver halide measured.

Serial Dilutions

In order to prepare a series of very low-concentration silver solutions for use in your measurements, you will use a

technique called **serial dilution**. In a serial dilution, you prepare a diluted solution containing Ag^+ , then take an aliquot of the diluted solution to make a more diluted solution, and so on, until the most dilute solution is made. Figure 2 shows a serial dilution schematically.

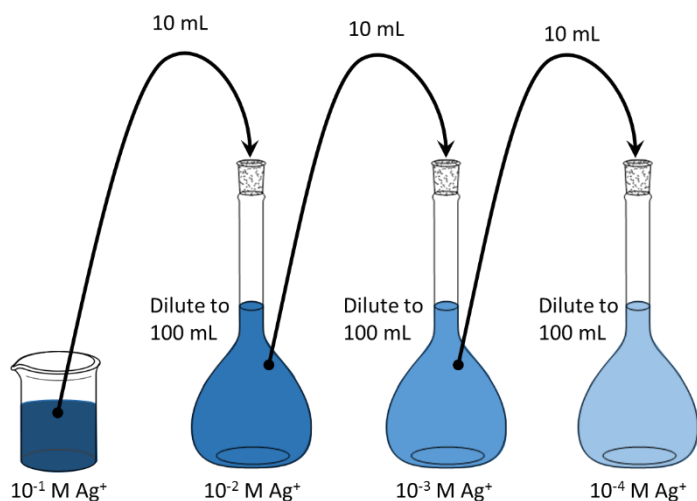


FIGURE 2: SERIAL DILUTIONS

Serial dilution generally produces a more accurate result than one single, large dilution. However, use special care in performing serial dilutions, as an error in making the first solution will carry through into all following solutions.

Preparing for lab

Before coming to lab, make sure you have:

- Read Experiment 5, and printed a copy to bring to lab.
- Completed the online pre-lab quiz – *at least one hour before lab*
- Completed the procedure flow chart on Page 8.
- Prepared yourself by wearing clothing that will completely cover you below the knee, a lab coat and safety goggles. (See the lab manual Introduction and guidelines on D2L)

Experimental Procedure

For this experiment you will work in pairs.

Each partner must submit an individually written lab worksheet before the end of the lab period.

Before beginning, sign out a *Supplementary Equipment Tray* from your TA, containing:

- 1 multimeter
- 2 silver wires
- Sandpaper
- 1 pair of plastic scissor-handled tweezers

By 'signing out' this equipment, you are responsible for it (similar to the equipment in your drawer) until you and your TA sign it back in at the end of lab.

Notes:

Electrochemical reactions are **very sensitive** to contamination. Follow all instructions carefully and make sure that all glassware and metal electrodes are rigorously clean.

Stir solutions with a glass rod, rather than a metal spatula or scoopula to avoid contamination of your solution with metals.

Remember to clean your pipet by rinsing 2-3x with the solution to be pipetted.

Label all of your beakers – the solutions will all look identical!

Rinse out your Ag^+ pipet *immediately* after use; the solution will stain the pipet.

1. **Prepare the dilute Ag^+ solution:** Use serial dilution to create an approximately 10^{-4} M solution of Ag^+ :
 - ↪ Pipet 10.00 mL of **0.10 M** Ag^+ stock solution into a 100.0 mL volumetric flask, dilute to the mark with RO water, and mix well.
 - ↪ Transfer this $\sim 10^{-2}$ M solution into a **clean, dry** beaker, and rinse the volumetric flask several times with RO water.
 - ↪ Pipet 10.00 mL of the $\sim 10^{-2}$ solution into the 100.0 mL volumetric flask, fill to the mark with RO water, and mix well.
 - ↪ Transfer this $\sim 10^{-3}$ M solution into a **clean, dry** beaker, and rinse the volumetric flask several times with RO water.
 - ↪ Pipet 10.00 mL of the $\sim 10^{-3}$ solution into the 100.0 mL volumetric flask, fill to the mark with RO water, and mix well.
 - ↪ Retain the $\sim 10^{-4}$ M Ag^+ solution for use in your electrochemical cell.

2. Prepare the precipitation half-cells.

- ↪ Obtain three **clean, dry** beakers (100 or 150 mL), and label one for Cl^- , one for Br^- , and one for I^- .
- ↪ Into each beaker, pipet 10.00 mL of the dilute Ag^+ solution prepared in Step 1.
- ↪ Into each beaker, add 50.00 mL of the relevant halide solution (e.g. KBr for the Br^- flask).

3. Prepare the electrodes. Your electrodes in each half-cell are Ag wires. Gently sand each wire to remove any oxidation layer, rinse with RO water, and dry.**4. Prepare the reference half-cell and salt bridges.**

- ↪ Put *no more than* 50 mL of KNO_3 from the side bench into a clean beaker. Submerge 6 strips of filter paper and let them soak. These will be your salt bridges.
- ↪ In a **clean, dry** beaker (100 or 150 mL), put *approximately* 50 mL of stock 0.10 M Ag^+ solution.

5. Assemble the cell and measure.

- ↪ Take the half-cell beaker prepared in Step 4 and one of the half-cell beakers from Step 2.
- ↪ Connect the solutions with a salt bridge by draping two of the damp strips of filter paper from Step 4 across the two beakers so that the ends touch each solution.
- ↪ Set your multimeter to measure DC voltage (symbol: $\overline{\overline{V}}$, measures in volts).
- ↪ Using the electrodes prepared in Step 3, complete the circuit by connecting the **red** (+) lead to the reference half-cell (containing 0.1 M Ag^+) and the **black** (-) lead to your silver halide “precipitation” half-cell.
- ↪ Record the measured potential in Table 1 of your worksheet.

Repeat steps 4 and 5 for the remaining two silver halide half-cells. (Prepare a **fresh** reference cell with 0.10 M Ag^+ for each measurement).

Lab Report

Record all observations and work in **non-erasable pen** on the worksheet pages provided as part of this Experiment. Staple together the report pages and the cover page, and submit your completed report to your TA **before leaving lab**.

Cover your solutions with a watch glass while not in use to avoid contamination.

Since $[\text{Ag}]$ is small, the amount of precipitate is also very small, and may not be easily visible.

Be sure the salt bridge is not drippy, as this will affect your measurements.

Do not let the multimeter leads touch the solutions or the salt bridge.

If the leads are reversed (red for black), you will get a negative voltage reading.

Marks Breakdown

The general marking scheme for the lab worksheet is as follows:

Criteria	Marks
Introduction & Procedure	1.5
Data Tables	0.5
Calculations	3.5
Discussion Questions	9
Conclusion & References	1.5
Deductions Up to one mark each could be deducted for: <ul style="list-style-type: none">• Incomplete pre-lab flowchart or calculations• Writing in pencil or erasable ink• Inappropriate significant figures• Missing or inappropriate units in calculations	

CHEMISTRY 209

FALL 2016

WORKSHEET LABORATORY REPORT Experiment 5: Electrochemical Determination of K_{sp} for Silver Salts	
Student Name:	
Date Experiment Performed:	
Lab Section:	Lab Room:
Lab TA Name:	
Lab Partner Name:	

Student Signature:
Date:

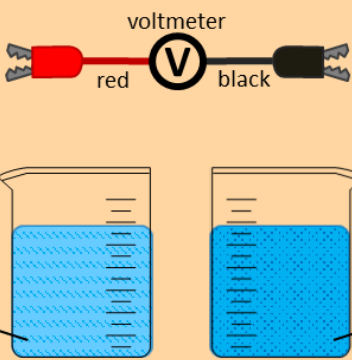
Please staple this cover sheet to the front of your worksheet report (3 pages, including this one).

Submit your completed worksheet to your TA before the end of your lab period.

TA Initials:

Procedure Flow Chart: Pre-lab Assignment

Fill in the blanks in the flowchart below:

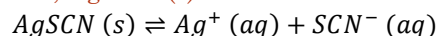
1. Prepare Dilute Ag^+ Solution		2. Prepare precipitation half-cells	
Steps:	Glassware/Equipment:	In each cell:	Glassware/Equipment:
4. Prepare reference half-cell & salt bridges		3. Prepare electrodes	
Steps:	Glassware/Equipment:	Steps:	
3. Assemble Cell and Measure			
Cell schematic:			
			
Cleanup:			
Solution disposal in:			
Items not from equipment drawer:			

Pre-Lab Assignment Part 2: Sample Calculations

To make sure you are ready to complete the necessary calculations during lab time, solve for the three values in the results table below, for a reaction similar to the one you will use in lab. You can check your answers for each calculation with the answers given.

Show all your work for each step so that you can refer to these calculations while you complete your worksheet.

Determine the K_{sp} for silver thiocyanate, $AgSCN(s)$:



Experimental Data:

Volume of 1.00×10^{-4} M Ag^+ solution used in 'precipitation' cell:	10.00 mL
Volume of 1.00 M KSCN added to 'precipitation' cell:	50.00 mL
Measured cell potential vs. a 0.100 M $Ag^+ Ag(s)$ reference cell:	0.645 V

Calculate the $[Ag^+]$ in the 'precipitation' half-cell, based on the cell potential:

This is the lower $[Ag^+]$ value.

$$[Ag^+] = 1.27 \times 10^{-12} M$$

Determine the $[SCN^-]$ in the 'precipitation' half-cell:

(Prepared according to Procedure Step 2, using KSCN instead of KCl, KBr, or KI)

$$[SCN^-] = 0.833 M$$

Determine the K_{sp} for $AgSCN$:

$$K_{sp} = 1.06 \times 10^{-12}$$

Introduction

State the objective: In your own words, briefly state the objective of this laboratory experiment.

Procedure

State the source of the experimental procedure and whether any modifications were made:

Data and Results

Concentration of Ag^+ stock solution (from bottle): _____

TABLE 1: ELECTROCHEMICAL DETERMINATION OF K_{sp}

Silver Salt	Literature K_{sp} (filled out before lab)	Measured Potential (V)	$[\text{Ag}^+]$ (M) in precipitation cell	$[\text{X}^-]$ (M) in precipitation cell	Experimental K_{sp}	% error

Calculations

Show all work (including units) for all calculation steps.

1. Determine the $[\text{Ag}^+]$ in the 'precipitation' half-cell for AgCl (this is the lower $[\text{Ag}^+]$ value):

2. Determine the $[\text{Cl}^-]$ in the 'precipitation' half-cell for AgCl:

3. Calculate the experimentally determined K_{sp} for AgCl:

4. Calculate the % error for your experimentally determined K_{sp} for AgCl:

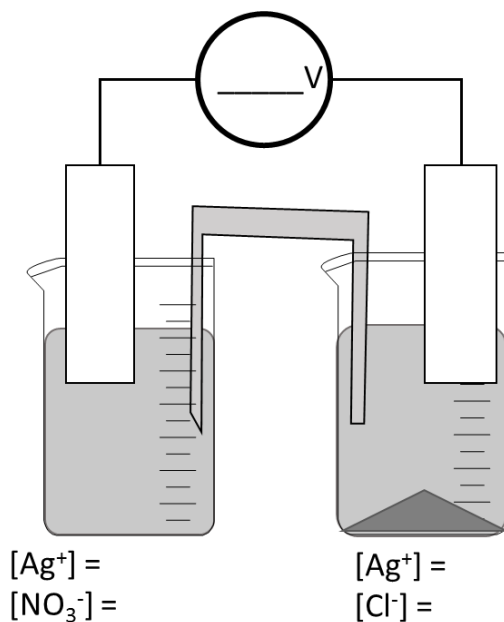
Repeat the above calculations for AgBr and AgI and record the calculated values in Table 1.

Discussion

Answer all questions with a diagram or one-three grammatically correct sentences.

1. *State your major findings:* Write the line notation for the cell used to determine K_{sp} for AgCl, including all relevant concentrations.

2. *State your major findings:* Referring to Figure 1 for content and formatting, label the cell diagram below describing the cell you used to determine K_{sp} for AgCl.



3. *Accuracy of your results:* Comment on the accuracy of your three K_{sp} values, using the values you have calculated to support your claims.
4. *Sources of error/uncertainty:* List two sources of uncertainty in the experimental procedure, and how each would impact your results. (Do not list "human errors" – such as incorrect pipetting technique – unless you know a specific mistake was made).

5. *Significance of your results:* The silver halides have similar chemical properties (e.g. limited solubility) because the halogens are all members of one *period* on the periodic table – Group 17 – that have similar valence electron configuration. What is the common feature of all halogen atom electron configurations?

6. *Significance of your results:* Which is larger, the bromine atom, or the bromide ion?

7. *Significance of your results:* Which is larger the bromide ion, or the chloride ion?

8. *Significance of your results:* Use your knowledge of atomic structure to explain (in 1-2 sentences) your answers to Questions 6 and 7)

Conclusion

Briefly summarize the findings of your experiment:

References

Provide sources for all outside information used in writing your report.