Potentiometry is a powerful analytical technique that relates the cell potential of an electrochemical cell to the activity of one or more species in the cell. The most common potentiometric measurement is pH determination using a hydrogen ion selective electrode. In addition to the hydrogen ion (pH electrode), many other types of ion selective electrodes have been developed (Mg$^{2+}$, Ag$^+$, Na$^+$, Cu$^{2+}$, F$^-$, and many more). In the experiment today you will build your own silver ion selective electrode. You will use the electrode to determine the silver chloride solubility product from a precipitation titration.

A silver ion selective electrode is a very simple device. The electrode consists of a piece of polished silver wire. The silver wire is soldered to a piece of copper wire that is connected to a potentiometer (voltmeter). Figure 1 is a diagram of the system that you will construct.

Figure 1. Diagram of electrochemical cell and silver ion selective electrode.

The cell potential of the electrochemical cell will equal the half cell potential of the Ag$^+$ ion selective electrode minus the reference potential. The equations for the half cell potential of the Ag$^+$ ISE and the net cell potential are written as follows:
\[
Ag^+ + e^- = Ag(s) \quad E^0 = 0.07993 \text{ V}
\]

\[
E_{Ag} = E^0 - \frac{2.303RT}{nF} \log 1/[Ag^+]
\]

\[
E_{cell} = E^0 - \frac{2.303RT}{nF} \log 1/[Ag^+] - E_{ref} - E_j
\]

where \(E_j\) is the reference electrode junction potential.

**Procedure**

1) Construction of Ag\(^+\) ISE. The first step in the construction of the Ag\(^+\) ISE is to prepare the electrode surface. Clean two pieces of silver wire. Solder a wire lead to the top portion of the silver wire. Pass the Ag electrode and the wire lead through a small glass tube which you have fire polished on both ends. Position the Ag electrode so that the polished portion of the electrode protrudes about 1.5 cm out of the end of the glass tube. Glue the electrode and wire in place with two-phase epoxy. Allow the glue to dry completely.

2) Prepare 50 ml of 0.010M AgNO\(_3\) and 0.010 M NaCl standard solutions. From the AgNO\(_3\) stock, prepare three additional 50 ml standards of 1.0 mM, 100 µM, 10 µM silver (I).

3) Using your electrode system titrate 0.100 mMoles of AgNO\(_3\) with 10.0 mM NaCl. Use the Vernier data acquisition system and pumps to perform three replicate titrations. You may choose any convenient volume of analyte, but you must know the initial volume for the analysis step B.

4) Calibrate your electrode response using the four standard solutions.

**Report:** A formal report is not required.

A) Plot your data from step 4 and compute the slope for the electrode. Calculate the detection limit of your electrode based on the slope and uncertainties in the measured electrode potentials.

B) Include a plot of your titration data labeling the relevant parts of the titration curve. Compute the AgCl solubility product by fitting the experimental titration curve to the calculated pAg (based on the Ksp for AgCl). You may use Excel Goal Seek to find the best fit to the data by adjusting an estimate for the log(Ksp) to minimize the residual sum of squares between observed and calculated pAg. The Excel function SUMXMY2(array1,array2) will compute the residual sum of squares between to arrays of data. How well does your data agree with the published value for the Ksp of AgCl?