POTENTIOMETRIC TITRATIONS & SOLUBILITY EQUILIBRIA

Introduction

In this experiment, students will familiarize themselves with potentiometric titration, practice using the first derivative to find the equivalence point, and determine the solubility constant of AgCl using the Nernst equation.

Electrochemical cell

In this experiment, a Cu/CuSO₄ reference electrode will be used in conjunction with a silver wire indicator electrode. The oxidation of copper takes place at the anode while the reduction of silver takes place at the cathode. See Figure 1 for a diagram of an electrochemical cell.

The balanced electrochemical reaction is as follows:

\[
\text{Cu}^0(s) + 2\text{Ag}^+(aq) \rightarrow 2\text{Ag}^0(s) + \text{Cu}^{2+}(aq)
\]  

The line notation for the cell is:

\[
\text{Cu}^0|\text{Cu}^{2+}(0.100 \text{ M})||\text{Ag}^+,\text{AgCl(s)}||\text{Ag}^0
\]

The overall standard electrochemical potential, \(E^\circ_{\text{cell}}\) is:

\[
E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{Ag}^+/\text{Ag}) - E^\circ_{\text{red}}(\text{Cu}^{2+}/\text{Cu})
\]

* Calculate the standard cell potential.
**Titration**

In this experiment, silver ions will be added to a chloride solution (Figure 2). As Ag⁺ is added to the Cl⁻, AgCl will form via the following reaction:

\[
\text{Ag}^+ (aq) + \text{Cl}^- (aq) \rightleftharpoons \text{AgCl(s)}
\]  

(4)

This equation illustrates the solubility equilibrium of silver chloride. A solubility equilibrium exists when a solid compound is in equilibrium with the dissolved ions of that compound in solution. The corresponding solubility constant of AgCl is:

\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}
\]  

(5)

The equilibrium constant, \(K_T\), of the titration is:

\[
K_T = \frac{1}{[\text{Ag}^+][\text{Cl}^-]} = \frac{1}{K_{sp}} = \frac{1}{1.8 \times 10^{-10}} \gg 1
\]  

(6)

As the titration with silver salt proceeds, the number of moles of chloride decreases. At the equivalence point, the number of moles of Ag⁺ added is equal to the number of moles of Cl⁻ present initially. Because of the relatively small \(K_{sp}\), all Ag⁺ and Cl⁻ can be assumed to have combined to form AgCl at the equivalence point. When this information is substituted into the equation for the solubility constant:

\[
K_{sp} = [\text{Ag}^+]^2
\]  

(7)

Beyond the equivalence point, any added Ag⁺ is unreacted, and therefore, in excess. This is illustrated in Figure 3.
Figure 3. Plot depicting the change in moles of Ag\(^+\) and Cl\(^-\) as the titration proceeds.

**The Nernst Equation**

An electrode potential measures the magnitude of the difference between the concentrations of the species in the half-cell and their equilibrium values. The Nernst equation provides a quantitative relationship between the concentration of species and the electrode potential. A reversible half-reaction can be defined as follows:

\[
aA + bB + \ldots + ne^- \rightleftharpoons cC + dD + \ldots \tag{8}
\]

where the capital letters represent atoms, molecules, or ions, e\(^-\) represents electrons, and the lower-case italic letters represent the number of moles of each species. The electrode potential corresponding to equation (8) is given by the following equation:

\[
E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{9}
\]

where,

- \(E^0\) = standard electrode potential
- \(R\) = ideal gas constant, 8.314 J/Kmol
- \(F\) = Faraday's constant, 96,485 C/mol e\(^-\)
- \(T\) = temperature, K
- \(n\) = number of moles of electrons
- ln = natural logarithm

The equation can be rewritten by substituting numerical values for the constants, converting to base 10 logarithms, and defining the temperature as 25°C (roughly room temperature):

\[
E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{10}
\]

The letters in brackets technically represent activities, but usually molar concentrations are substituted into the equation. For example, if species A is a solute, [A] is the concentration of A. If A is a pure liquid, pure solid, or solvent, the activity is one. The Nernst equation describing the electrochemical potential in this experiment is:
In this experiment, the cell potential is proportional to $p\text{Ag}^+$ and will be used to measure the amount of free $\text{Ag}^+$ in solution. At the beginning of the titration, the cell potential will be quite low and will stay almost constant, since almost all of the $\text{Ag}^+$ added will be converted into $\text{AgCl}$ and there will be almost no free $\text{Ag}^+$ in solution. At the equivalence point (represented by the gray line in Figure 3), all of the $\text{Cl}^-$ is consumed to form solid $\text{AgCl}$ and the cell potential spikes as the moles of free $\text{Ag}^+$ drastically increase.

*The titration curve obtained in this experiment is a plot of $E_{\text{cell}}$ (or $p\text{Ag}^+$) on the y-axis and $\text{AgNO}_3$ titrant volume on the x-axis. Using the description above, sketch the titration curve. Hint: Draw a correlation between this titration and a strong acid / strong base titration.*

**Additional background information**

Read the following **before coming to lab** for more details of the experiment. This information will also help you to write a detailed introduction for the lab report.


**Safety**

Safety goggles and aprons must be worn in lab at all times. Silver nitrate solutions are irritating to skin and eyes. It may create black stains on clothes or discoloration of the skin, and is harmful if swallowed. Store all the waste in the correct labeled waste container.

**Procedures**

The stockroom has provided a reference electrode that includes the following:

- A glass reference electrode with the bottom submerged in 0.1 M $\text{CuSO}_4$.
- A 0.1 M $\text{CuSO}_4$ solution.
- Silver and copper wires, both connected to electrical wires at one end.
- An NMR cap to seal the chamber.
Figure 4. Digital image of the Cu and Ag electrode set-ups. The inner (reference) electrode contains a copper wire dipped into 0.1 M CuSO$_4$ solution. The bottom of this reference electrode contains a Vycor frit, which must be in solution at all times. A Vycor frit is a porous piece of glass and is used to allow for ionic conductivity between the filling solution of the reference electrode and the solution in which the electrode is submerged. After putting the reference electrode together, place it back in CuSO$_4$ solution until ready for titration. The silver wire is placed outside as the indicator wire. One electrical wire is connected to the silver wire while the other electrical wire is connected to the copper wire.

Part A. Computer Set Up / Calibrating Voltage Probe

The voltage probe used to measure the voltage change during titration must be calibrated.

1. Prepare the computer for data collection by opening "Exp 28" from the Chemistry with Computers experiment files of Logger Pro.
2. Go to the "Experiment" menu and choose "Calibrate". In the window that appears make sure the "Calibration" tab is chosen. Click on "Calibrate Now".
3. Connect the two ends of the voltage probe together. When the voltage reading in the calibration window stabilizes enter 0.00 in the field beneath "Enter Value".
4. Use a multimeter to measure the potential of a 9V battery. Record the potential.
5. Connect the voltage probe leads to the battery. Make sure the voltage is a positive value.
6. When the voltage reading in the calibration window stabilizes enter the potential you measured with the multimeter in step 4 in the second field beneath "Enter Value". Save this calibration for the rest of the voltage measurements.
Part B: Titration of 150 ppm NaCl

1. Pour 100 mL of 150 ppm NaCl solution into a 250 mL beaker that contains a small magnetic stir bar. Put the beaker on a stir plate.
2. Turn the stir plate on to a medium stirring speed (i.e. 3 – 5).
3. Rinse the reference electrode thoroughly with DI water and position it in the beaker so the stir bar will not hit the electrode. Make sure the silver wire is submerged in solution.
4. Clamp a burette filled with 0.0100 M AgNO₃ above the beaker.

**Figure 5.** Digital image of the titration set-up.

Titration #1: Quick Titration

Perform a quick titration (by adding large increments of titrant) to determine the volume needed to reach the equivalence point.

1. Measure the initial potential of the solution by touching the voltage probes to the electrical wires. One voltage probe is connected to the copper wire in the reference electrode. The other voltage probe is connected to the silver wire, which should be in solution. (See Figure 5.) Bring the black lead of the probe into contact with one of the wires and the red lead into contact with the other. The voltage should be positive, if not, reverse the probe connections. Connect the leads of the voltage probe to get a positive voltage. *Be sure to indicate in your observations which electrode is attached to each color lead.* Click “Record” to record the initial voltage value.
2. Add 2 mL of 0.0100 M AgNO₃ (aq). Wait 20 seconds before recording the voltage to the nearest millivolt.
3. Continue to add 2 mL increments of 0.0100 M AgNO₃ (aq) titrant to the 150 ppm NaCl solution. Wait 20 seconds and record the voltage to the nearest millivolt.

4. To find the equivalence point, prepare a graph of voltage versus volume in Excel. Add the data to Excel as the titration proceeds. The equivalence point is inflection point on the steepest part of the titration curve. Record the equivalence point for further calculation.

5. Continue adding titrant until at least 5 mL past the equivalence point.

6. Remove the beaker from the stir plate and allow its contents to settle undisturbed for the rest of the lab period. Does the solution change by the end of the lab period? Record your observations.

7. Create a first derivative plot in Logger Pro or Excel to get a better estimate of the volume of titrant needed to reach the equivalence point. To do so in Logger Pro:
   a. Under “Data”, select “New Calculated Column…”
   b. Give a name and short name to your calculated column.
   c. Click the “Functions” button, highlight “calculus” and select “derivative”.
   d. Click “Variables”, select your y-variable, and click “Done”. You can then choose to plot your calculated column on the y-axis.

**Titration #2: Careful Titration**

Carry out a more careful titration by adding titrant in small increments as the volume gets close to the equivalence point.

1. Measure 100 mL of 150 ppm NaCl solution into a 250 mL beaker.
2. Before submerging the reference electrode in this new solution, rinse it thoroughly with DI water. Record the initial voltage reading after submerging it in solution.
3. Refill the burette with 0.0100 M AgNO₃(aq) titrant.
4. Add titrant in 5 mL increments until ~5 mL before the equivalence point.
5. Then, slowly add ~0.5 mL increments of titrant until the titration is 5 mL beyond the equivalence point. Record the equivalence point for further calculation.
6. Share results with at least five other students so that a 95% CI can be calculated.

**Part C: Titration of an Unknown**

The stockroom will provide a NaCl solution of unknown concentration. Follow the instructions in Part B, do one quick and one careful titration.

**Part D: Cleaning up**

1. DO NOT throw any solution in the sink. All waste should be placed in the appropriate container in the fume hood.
2. Rinse the reference electrode thoroughly with DI water.
3. Place the reference electrode back into its container making sure the Vycor frit is in solution.
4. Wash and dry the copper wire and silver wire.
5. Return the entire package to the stockroom.