EXPERIMENT 10

The Formal Potential of the Ag^+, Ag and AgCl, Ag Redox Couples in $\mu = 0.1$ M Non-Complexing Media

In this experiment we will determine $E^{o'}$ values, the formal potentials, for the half-reactions:

$Ag^+ + e = Ag$, $\mu = 0.1$ M (1)

$AgCl(s) + e = Ag + Cl^-$, $\mu = 0.1$ M (2)

The values will be obtained from measurements employing solutions which contain known concentrations of $AgNO_3$ (for half-reaction (1)) or known concentrations of KCl (for half-reaction (2)).

The experimental technique to be employed is called **potentiometry**. It involves the measurement of electrical potential (voltage) under conditions of essentially zero current. Because of the i near 0 condition, the concentrations and identities of chemical substances present are essentially unaffected by the experimental procedure. Thus, potentiometry represents a means of monitoring chemical and electrochemical equilibria in an electrochemical cell.

> NOTE: Potentiometric methods are to be contrasted with electrolytic experiments. In the latter an appreciable current passes an electrochemical cell and the concentrations and identities of chemical substances are changed as a result of the process.

In the experiments that follow you will measure the potential of an electrochemical cell using a pH meter (which is a fancy voltmeter) set to read directly in millivolts (mV). (A typical reading might be 27.4 mV. This should be recorded as 0.0274 volts (V.) to avoid later confusion.) The combination of the measuring device and electrochemical cell is called the **measurement circuit**. The electrochemical cell consists of three elements.

1. the cell (or measurement or analyte) solution: This is the solution being measured. You will employ two different types of cell solutions:

(a) a series of solutions containing known concentrations of $AgNO_3$ in KNO_3

medium with ionic strength 0.1 M. Measurements with these solutions will lead to values of the formal potential for the $Ag^+ + e = Ag$, $\mu = 0.1$ M half-reaction.

(b) the series of solutions formed as an $AgNO_3$, KNO_3 mixture is titrated with a KCl solution. The data will lead to a second value of the Ag^+, Ag formal potential and to a value of the AgCl, Ag formal potential.

2. the indicator electrode: In these experiments the indicator electrode is a chunk of pure silver metal which will contact the measurement solution. The electrical potential, E_{ind}, of this electrode depends on the composition of the measurement solution. (The details are described in a later section.) The silver metal indicator electrode is equipped with an electrical wire to connect with one input terminal of the voltmeter.

3. the reference electrode: This is a second electrode which contacts the cell solution and completes the electrical measurement circuit, connecting the solution to the second input terminal of the voltmeter. You will use a "saturated silver-silver chloride" reference electrode (or a modified version of it). The electrode consists of a silver wire dipping in a solution saturated with KCl (about 4 F) and AgCl. One end of the wire will connect with the voltmeter. The wet end of the wire along with the KCl, AgCl mixture is contained in a small tube made with a tiny hole to allow electrical contact to the outside world. The whole wire, solution, tube device contacts a 10% KNO_3 solution (about 1 F KNO_3) held in a second larger tube. The second tube is also built with a tiny contacting hole which will make electrical contact with the measurement solution. This bizarre construction accomplishes two purposes. First, the silver wire within the reference is physically isolated from the measurement solution. It has no clue what or how much of anything is in the measurement solution. Its entire world consists of the KCl, AgCl in the inner compartment and the voltmeter that it connects to. Second, the chloride rich contents of the inner compartment are isolated from (and will not contaminate) the measurement solution. All that the measurement solution sees of the reference electrode is its contact with a 10% KNO_3 solution in the outer reference tube.

> NOTE: The "double junction" construction of this reference electrode is necessary here because even a small amount of chloride leakage from the reference would significantly alter the composition of the dilute Ag^+ cell solution. The 10% KNO_3 barrier ("salt bridge") between the internal reference compartment and the cell solution is unnecessary in most applications. Most

often used is a "single junction" reference. There the KCl, AgCl mixture directly contacts the measurement solution through a small hole or a porous membrane.

Because the silver wire of the inner reference contacts only the KCl, AgCl mixture it represents a fixed source of electrical potential in the measurement circuit. That is, the potential energy of electrons within the silver wire does not depend on the nature or composition of the measurement solution but only on the composition of the KCl, AgCl environment which is constant.

After the measuring device is connected to the electrochemical cell (the two electrodes and cell solution) and after ample time for thermal, chemical and electrochemical equilibration, a reading of the electrical potential will result. How will this be related to the construction and composition of the electrochemical cell?

The electrochemical cell we have described may be represented as:

reference | | measurement solution **|** Ag

"reference" represents the silver wire, saturated KCl, AgCl, 10% KNO_3 device and **|** Ag represents the silver indicator electrode. The **|** symbol represents a boundary where the potential energy of electrons on one side (say in the Ag metal) is different from that on the other side (in the AgCl). The | | symbol represents the boundary between two dissimilar solutions (in this case 10% KNO_3 and the measurement solution).

The electrochemical cell represented as above (consisting of reference, measurement, and silver indicator electrode) has three sources of electrical potential. E_{ref} is the (fixed) potential of the reference electrode; E_{Ag} is the "Nernstian" potential of the silver metal indicator electrode; and E_j is the "liquid junction" potential that appears at the boundary of the 10% KNO_3 salt bridge with the measurement solution.

> NOTE: What is the "Nernstian" potential? It is the electrode potential predicted by the Nernst equation. Suppose that the silver indicator electrode contacts a dilute $AgNO_3$ measurement solution. The potential of the Ag electrode depends on the value of the standard potential for the $Ag^+ + e = Ag$ half-reaction and on the activities of Ag^+ and Ag present.
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> NOTE: What is the liquid junction potential? The subject of the liquid junction potential is a complex one which we will not

discuss in detail. Suffice it to say that its source is related to the way electricity is carried across the boundary between two different electrolyte solutions. Its magnitude depends on the relative concentrations of the various ions at the boundary and on their relative mobilities. What is important here is that movement of charge across the boundary between 10% (about 1 $\underline{F}$) KNO_3 and the cell solution is dominated by the much more concentrated KNO_3 solution. Changes in the composition of the more dilute cell solution have little effect on E_j so that its value may be taken as constant.

The cell potential, E_{cell} , the thing we measure, is:

$$E_{cell} = E_{Ag} - E_{ref} + E_j = E_{ind} - E_{ref}$$

By using a reference (fixed potential) electrode and by controlling the value of the junction potential we have made the measured quantity E_{cell} depend entirely on E_{ind} because E_{ref} and E_j are constants.

What does E_{ind} depend on? In the present case where a silver metal indicator electrode contacts a solution of Ag^+, E_{ind} depends on the activities of Ag^+ and Ag metal. The pure silver metal has activity equal to 1 but the activity of Ag^+ ions depends on all sorts of things including the concentration, ionic activity coefficient, the possible presence of complexing agents, etc., etc., a mess. We would like the potential to depend only on the concentration of $Ag^{+.}$ We can accomplish this by controlling (keeping constant) the values of activity coefficients, etc. in much the same way as we kept E_{ref} and E_j constant. That is, we "swamp" the analyte solution with some added electrolyte called a background electrolyte or supporting electrolyte. In this way the values of activity coefficients, etc. are held constant. NOW, we may relate the potential of the Ag metal electrode to the concentration of Ag^+ ions in the analyte solution by:

$$E_{ind} = E^{o'}_{Ag+,Ag\ ;solution\ conditions} - 0.05916 \log(1/C_{Ag}) + Ej$$

assuming that the major effect is from the ion activity coefficient, we get

$$= E^{o}_{Ag+,Ags} - 0.05916 \log(1/\mathcal{A}_{Ag+}) + Ej$$

If we assume the junction potential, Ej, is small (1-5 mV) than the plot of Ecell vs. $\log(1/\mathcal{A}_{Ag+})$ gives a measure of $E^{o}_{Ag+,Ags}$ from the y-intercept.

The $E^{o'}_{Ag+,Ag\ ;solution\ conditions}$ symbol represents the "formal potential" of the Ag^+, Ag redox couple. The "prime" symbol indicates a "formal potential". The subscript lists the oxidized species (Ag^+) and the reduced species (Ag). (We can immediately write the half-reaction $Ag^+ + e = Ag$.) The subscript "solution conditions" gives pertinent information about the composition of the mixture. For example,

$$E^{o'}_{Ag+,Ag\ ;\ 0.2\ \underline{F}\ KNO3}$$

indicates the formal potential of the Ag^+, Ag redox couple in a medium of 0.2 $\underline{F}$ KNO_3 background electrolyte.

Finally, the symbol C_{Ag} is the concentration in mol/L units of silver ions in the analyte solution.

Before continuing it is important to recognize that the formal potential is in fact a kind of practical standard potential (that you may recall from other courses in Chemistry). The standard potential relates electrode potentials to the activities of solution components. The formal potential relates the electrode potential to the concentrations of materials and includes in its value the various ionic activity coefficients, any complexation reactions and the liquid junction potential. The practical application of the formal potential is illustrated below.

We are going to do an analysis by "direct potentiometry". I have a "saturated calomel reference electrode" (abbreviated S.C.E.) and a silver metal wire that I will use as the indicator electrode. I immerse the electrodes in a solution that contains 1.00×10^{-3} $\underline{F}$ $AgNO_3$ and 0.2 $\underline{F}$ KNO_3 (the background electrolyte). I connect the electrodes to a meter and read a cell potential of +0.373 v. The cell potential is the difference between the potentials of the indicator and reference electrodes:

$E_{ind} - E_{ref}$. This quantity may be thought of as the potential of the indicator, E_{ind} versus the S.C.E. reference. That is E_{cell} is equal to E_{ind} vs. S.C.E.

I now calculate:

$$E_{ind} = E^{o'}_{Ag+,Ag\ ;0.2\ \underline{F}\ KNO3} - 0.05916 \log (1/C_{Ag})$$

$$0.373 = E^{o'}_{Ag+,Ag\ ;0.2\ \underline{F}\ KNO3} - 0.05916 \log (1/1.00 \times 10^{-3})$$

$$E^{o'}_{Ag+,Ag\ ;0.2\ \underline{F}\ KNO3} = 0.550_5 \text{ v. vs S.C.E.}$$

I now do the analysis and use the same silver indicator electrode and reference electrode to measure the potential with a dilute $AgNO_3$ solution with unknown concentration. (I have already added enough KNO_3 so that the mixture contains 0.2 $\underline{F}$ KNO_3.) The cell potential is +0.344 v. As before I interpret this as E_{ind} verses S.C.E. and calculate:

$0.344(\text{v. vs S.C.E.}) = 0.550_5(\text{v. vs S.C.E.}) - 0.05916 \log(1/C_{Ag})$

$C_{Ag} = 3.2_3 \times 10^{-4}\ \underline{F}$

The concentration of Ag^+ in the unknown is $3.2_3 \times 10^{-4}$ $\underline{F}$. This represents a pretty simple and quick analysis.

In an earlier experiment you made essentially the same sort of analysis using a pH meter to determine H^+ concentration in a solution. The glass electrode used in pH measurement is parallel to the silver metal electrode described here. Both electrodes respond to the concentration of a specific ion in the solution: H^+ for the glass electrode and Ag^+ for the silver metal electrode.

Both the glass and Ag metal electrodes are examples of "specific - ion electrodes". Many kinds are available.

IN THE LABORATORY

PART I: $E^{o}_{Ag+,Ag}$

1. Clean a silver metal electrode. This is done by holding the silver metal in 6 F HNO_3 for a few seconds, rinsing with water and then dipping the electrode in 1 F NH_3 for a short time. The electrode is then thoroughly rinsed with water and soaked in a small beaker of fresh water until use. The instructor will demonstrate.

2. Rinse and dry a thermostatted cell. Make certain that the temperature is set at 25°C. Carefully add 100 mL of 0.1 F KNO_3 from a graduated cylinder to the cell along with a stirring bar. Rinse and wipe dry a double junction reference electrode and mount it in the cell. Connect the electrodes to a pH meter and start the stirring motor. The system should be equilibrated for at least 10 minutes.

3. Rinse and fill a 25 mL buret to the zero line with 0.100 F $AgNO_3$ solution and clamp over the cell. (This is not a titration but a buret is a convenient device for preparing $AgNO_3$ solutions directly in the cell). Add 0.50 mL of $AgNO_3$ to the cell. Set the meter to the mV scale and read the cell potential. Wait a minute to make certain that the reading is stable. Record the reading in units of mV (345 mV = 0.345 V.). Add 0.100 F $AgNO_3$ in 0.50 mL increments until you reach exactly 10.00 mL, making a reading of the cell potential upon each addition (20 points). Remove the buret and put it aside. Save the $AgNO_3$ mixture in the cell for the titration that follows.

Part II: Titration of $AgNO_3$ with an unknown KCl solution

1. Rinse and fill a 25 mL buret with the unknown (~ 0.1 F) KCl solution in the lab. Adjust the buret to 0.00 mL before clamping it over the titration cell (that already contains the $AgNO_3$, KNO_3 mixture). Immerse the tip in the cell solution.

2. Record the potential. Add 1 mL of the KCl solution; wait for equilibration and record the potential. Note that the potential has decreased (become less positive) by about 2-3 mV. Continue adding 1 mL portions of the KCl solution until the change in potential between consecutive readings increases to about 6-8 mV. Decrease the size of your additions to 0.5 mL and continue until the potential change reaches 6-8 mV and decrease the additions to 0.2 mL.

When you have passed the endpoint the change in potential with consecutive additions will decrease. When changes reach 3-4 mV per addition you may make 0.5 mL additions, etc. Continue the titration until the entire 25 mL of KCl has been added.

Pour the cell contents into a large beaker. Rescue the stirring magnet and dispose of the titration mixture into the waste bottle. Scrub the inside of the cell with a brush and rinse with several portions of water. Thoroughly rinse the $AgNO_3$ buret with several portions of distilled (not tap) water. Clean up.

THE LABORATORY REPORT

PART I: $E^o_{Ag+,Ag}$

Eq. 1 $$E_{cell}\,(mV, vs. ref)) = E^o_{Ag+,Ag} - 59.16\log(1/\mathcal{A}_{Ag+}) + Ej$$

The formal potential calculated this way is "versus your reference electrode".

1. Use your data of E_{cell} vs. v (mL) of added $AgNO_3$ to prepare a table with columns headed by: "E_{IND} (mV)"; "v 0.100 F $AgNO_3$ (mL)"; "$[Ag^+]$ (M)"; "$\mathcal{A}_{Ag+}$ (M)", , and "$\log(1/\mathcal{A}_{Ag+})$". In calculating the values of $[Ag^+]$ recall that the initial solution volume, V, is 100 mL; the added volume of $AgNO_3$ is v mL and the total volume may be taken as (V + v) mL. For the values of $[Ag^+]$ and $\mathcal{A}_{Ag+}$ retain three significant figures and therefore three figures after the decimal place in $\log(1/\mathcal{A}_{Ag+})$.

NOTE 1: Calculating the activity of Ag^+, $\mathcal{A}_{Ag+}$. You must carefully calculate the ionic strength of the solution initially and at after each addition of $AgNO_3$ and use it to calculate an activity coefficient, γ_{Ag+} by applying the Debey Huckel Eq. .

$$\text{Log}\gamma = -(0.51z^2\mu^{1/2})/(1+(\alpha\mu^{1/2}/305))$$

Part II

1. Plot E_{IND}(mV) vs volume of added KCl (mL). Locate the endpoint on the graph.

2. Accurately locate the endpoint by the "first derivative" method.

3. Calculate the concentration of the KCl titrant. Estimate the error in this measurement from inspection of the first derivative plot (most of the error derives from locating the endpoint).

4. Add the data before the endpoint to the data from Part 1. All of these solutions contain a substantial $[Ag^+]$ that can easily be calculated. For each point calculate the $[K^+]$, $[NO_3^-]$, $[Ag^+]$, ionic strength (μ), γ_{Ag+}, $\mathcal{A}_{Ag+}$, and $\log(1/\mathcal{A}_{Ag+})$.

   NOTE 1: A convenient method for calculating C_{Ag} before the endpoint is to define the "fraction titrated", $f = v/v^*$ where v is the volume of titrant added and v^* is the endpoint volume. At the start of the titration f = 0 and at the endpoint f = 1. The concentration of Ag^+ remaining in the solution before the endpoint is $C_{Ag} = VC_{Ag}^o(1 - f)/(V + v)$. The VC_{Ag}^o term represents the number of millimoles of silver present at the start of the titration. Because your experiment involves a 10.00 mL portion of 0.100 F $AgNO_3$, VC_{Ag}^o has a value of 1.00_0 mmoles.

   NOTE 2: Calculating the activity of Ag^+. You must carefully calculate the ionic strength of the solution at the each of these six points and use it to calculate an activity coefficient, γ_{Ag+}, by applying the Debey Huckel Eq.

$$\mathrm{Log}\gamma = -(0.51z^2\mu^{1/2})/(1+(\alpha\mu^{1/2}/305))$$

5. Plot E_{IND} (y-axis) vs. $\log(1/\mathcal{A}_{Ag+})$ (x-axis) for the combined data collected from Part I and II. Perform a linear regression analysis. The slope should be close to 59.16 mV. Report the slope and the 95 % CL of the slope. Assuming Ejp is negligible, the intercept is a measure of $E^o_{Ag+,Ag}$ (in mV). Report $E^o_{Ag+,Ag}$ and its 95 % CL.

6. There is excess Cl^- for the data after the equivalence point. For each of these points calculate the $[K^+]$, $[NO_3^-]$, $[Ag^+]$, [Cl-], ionic strength (μ), γ_{Cl-}, $\mathcal{A}_{Cl-}$, and $\log(\mathcal{A}_{Cl-})$.

   $E^o_{AgCl,.Ag}$ can be defined by:

   $E_{cell} = E^o_{AgCl,Ag;\mu=0.1} - 0.05916 \log \mathcal{A}_{Cl-}$

7. Plot E_{IND} (y-axis) vs. log $\mathcal{A}_{Cl-}$ (x-axis) for the data collected after the endpoint. Perform a linear regression analysis. The slope should be close to 59.16 mV. Report the slope and the 95 % CL of the slope. Assuming Ejp is negligible, the intercept is a measure of $E^o_{AgCl, Ag}$ (in mV). Report $E^o_{AgCl, Ag}$ and its 95 % CL.

NOTE 1: The chloride concentration in the mixture after the endpoint may also be conveniently calculated in terms of f, the fraction titrated. The definition of f is still $f = v/v^*$ and for $v > v^*$, $f > 1$. The concentration of chloride at $f > 1$ is given by $C_{Cl} = v^*C_{Cl}(f - 1)/(V + v)$. The v^*C_{Cl} term represents the number of millimoles of chloride required to reach the endpoint. This is the same as the number of millimoles of silver present at the start: 1.00_0 mmole in your experiment.

NOTE 2: Calculating the activity of Cl^-. You must carefully calculate the ionic strength of the solution at the each of these six points and use it to calculate an activity coefficient, γ_{Cl-}, by applying the Debey Huckel Eq.

$$\mathrm{Log}\gamma = -(0.51z^2\mu^{1/2})/(1+(\alpha\mu^{1/2}/305))$$

QUESTIONS

1. Does your value for $E^o_{Ag+,Ag}$ agree with the literature value from Appendix H in Harris (799.3 – 197 mV)? Calculate the % error between your experimental value and the literature value?

2. What factors are contributing to differences between the experimental value and the literature value? Hint. Think junction potential! Assuming other errors are negligible, estimate Ej in equation 1.

3. Does your value for $E^o_{Ag/AgCl}$ agree with the literature value from Appendix H in Harris (222 – 197 mV)? Calculate the % error between your experimental value and the literature value?

4. You now have values for E^o for the $Ag^+ + e = Ag$ and $AgCl + e = Ag + Cl^-$ half-reactions and their standard errors. Use these values to calculate $K_{sp} = [Ag^+][Cl^-]$.

$$-\log K_{sp} = (E^o_{Ag+,Ag;\mu=0.1} - E^o_{AgCl,AgCl;\mu=0.1})/59.16$$

Propagate the error to determine the standard error in Ksp. How does it compare with the literature value? Calculate the percent error.

5. Use the concentration of the KCl that you determined from the titration curve and the plot of E_{IND} (y-axis) vs. $\log \mathcal{A}_{Cl-}$ (x-axis) to predict the E_{IND} that would be obtained if a pure sample of the KCl titrant were measured.