Experiment 22

ANALYSIS OF CL^- & I^- IN THE PRESENCE OF EACH OTHER
A POTENTIOMETRIC TITRATION

MATERIALS:

250 mL beaker, 100 mL beaker, 50 mL buret, 100 mL graduated cylinder, 0.020 M $AgNO_3$, silver strip, magnetic stirrer, magnetic stir bar, reference electrode pH meter, 5 mL pipet, sandpaper or steel wool, distilled water wash bottle.

DISCUSSION:

The potential of a metallic conductor immersed in an electrolyte solution may be sensitive to the concentration of one or more of the components of that solution. An obvious analytical application of this phenomenon is its employment in the measurement of concentration. In this experiment the progress of a titration is followed by measurement of the potential of a silver electrode immersed in a solution containing an increasing amount of silver ion. Such a procedure is called a <u>potentiometric titration</u>.

A. Technique:

A typical potentiometric titration involves measuring and recording the cell potential (voltage) after each addition of reagent. Initially, the standard solution is added in large (1-2 mL) increments; as the end point is approached (as indicated by larger potential changes per addition) the increments are reduced in size (0.1 - 0.5 mL). Ordinarily the titration is carried well beyond the end point.

Sufficient time must be allowed for the attainment of equilibrium after each addition of reagent. Precipitation titrations such as the experiment being performed today require several minutes for this, particularly in the vicinity of the equivalence point. A close approach to equilibrium is indicated when the measured potential ceases to drift by more than a few millivolts. Good stirring is frequently effective in hastening this process.

B. Titration Curves for a Halide Mixture of Chloride and Iodide

In this experiment, the potential of a silver electrode, immersed in a solution containing silver ions is measured. Since an electrochemical cell must have two electrodes or half-cells, the variable potential of the silver electrode is measured with respect to a reference electrode, the potential of which is invariant in this experiment. The potential of the silver electrode depends upon the concentration of Ag^+ ion in accordance with the Nernst Equation.

$$\mathscr{E} = 0.80 + 0.059 \log [Ag^+]$$

If iodide or chloride are present in solution, the maximum concentration of silver ion may be found through the K_{sp} relationships for silver iodide and silver chloride, respectively.

$$\left[Ag^+\right] = \frac{K_{sp}}{\left[I^-\right]} \quad \text{and} \quad \left[Ag^+\right] = \frac{K_{sp}}{\left[Cl^-\right]}$$

Since the K_{sp} (AgI) = 8 x 10^{-17} and the K_{sp} (AgCl) = 2 x 10^{-10}, it is clear that as long as substantial amounts of iodide ion remain in solution, the addition of silver ions will precipitate only silver iodide and the concentration of silver ion will be limited by the K_{sp} of AgI and the remaining iodide. Once the iodide is "removed" as silver iodide, the concentration of silver ions may increase until precipitation of silver chloride commences. The concentration of silver ions will then depend upon the K_{sp} of silver chloride and the amount of chloride remaining

in solution.

Since the silver ion concentration increases most rapidly when the iodide and the chloride equivalence points are reached, the potential of the silver electrode will also change most rapidly at these points. A plot of cell potential vs. volume of silver nitrate added will show steep potential changes at the volumes of silver nitrate corresponding to the equivalence points. Figure 1 illustrates the shape of the potential - volume plot which will be obtained.

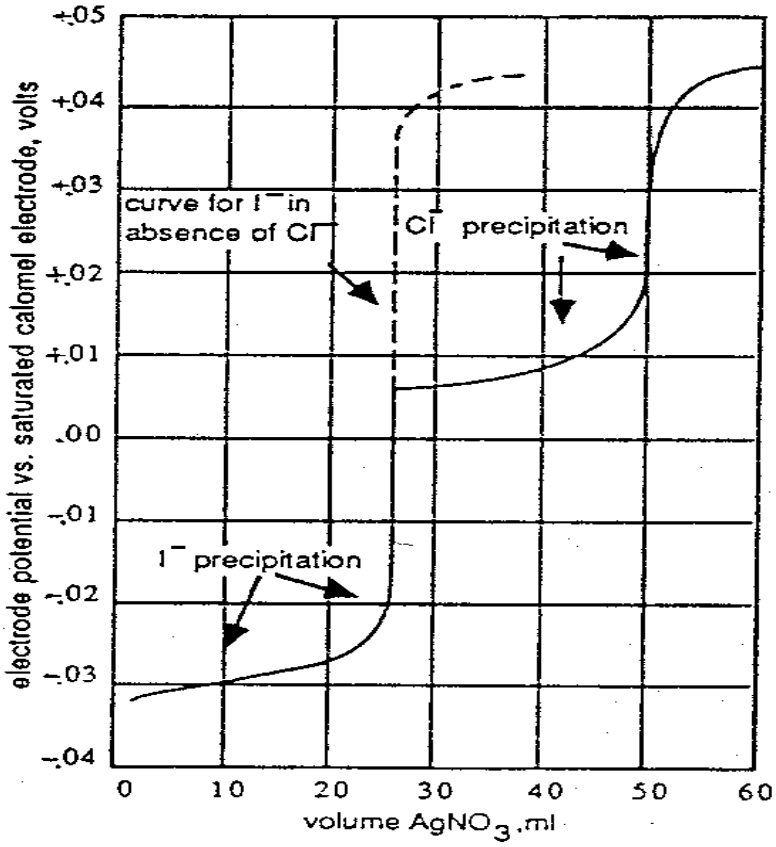

Figure 1 Potentiometric Titration of Halide Mixtures

Procedure: (work in pairs)

Fill the 50 mL buret with standardized (0.020M) $AgN0_3$ solution, to be used as titrant.

Assemble the apparatus as indicated in Figure 2. Use the 250 mL beaker for the unknown solution. Do not put in the magnetic stir bar yet. If the silver strip is not shiny, a few strokes with the steel wool will remove any corrosion products from the surface.

Carefully measure out 75 mL of distilled water and pour it into the 250 mL beaker. Add the stir bar. Using the 5 mL pipet, add 5 mL of your unknown to the beaker.

Switch the dial on the pH meter into the "-MV" position and record the potential. As you run your titrations, plot the results on a piece of graph paper. Include this graph along with your analysis of the unknown

when you submit your lab report. Data manipulation and graphing can be easily accomplished using a computer spreadsheet such as QUATTRO.

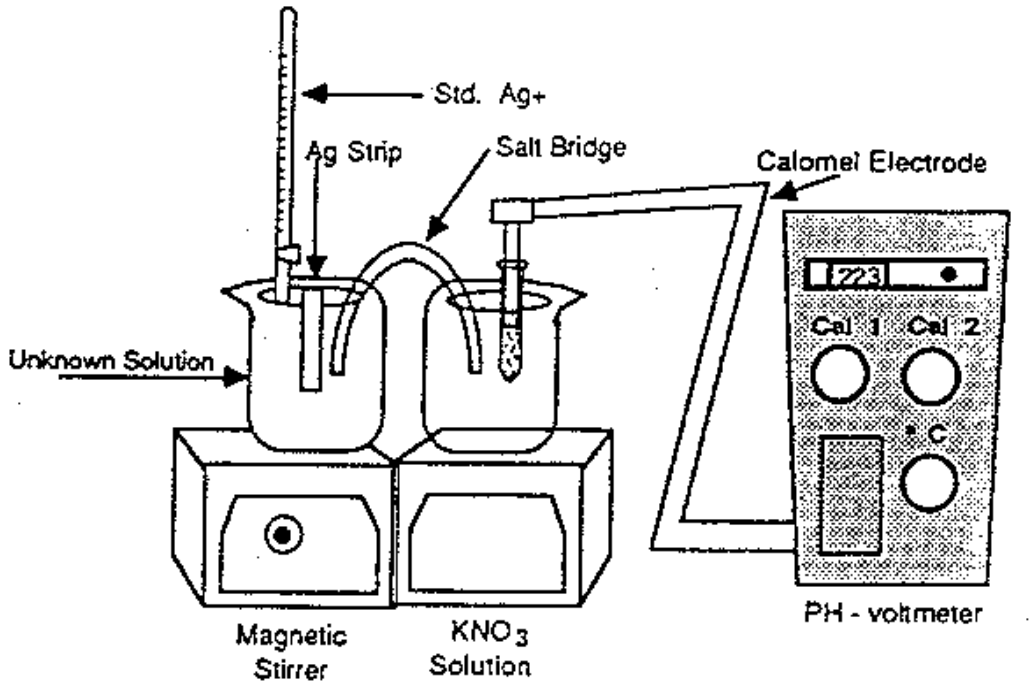

Figure 2

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 22

mL $AgN0_3$	relative potential	mL $AgN0_3$	relative potential	mL $AgN0_3$	relative potential

Unknown number: _____

Concentration of standard $AgNO_3$ solution: _____

volume of $AgNO_3$ added to reach I^- equivalence point: _____

Concentration of I^- in 5.00 mL sample of unknown: _____

volume of $AgNO_3$ added from I^- equivalence point to the Cl^- equivalence point: _____

Concentration of Cl^- in 5.00 mL sample of unknown: _____

Questions:

The cell used in the titration consists of the following half-reactions:

$$Ag^+ + e^- \rightarrow Ag \qquad \mathscr{E}^o = +0.80 \text{ V}$$

$$2\ Hg + 2\ Cl^- \text{ (satd. KCl)} \rightarrow Hg_2Cl_2 + 2e^- \qquad \mathscr{E}^o = -0.24 \text{ V}$$

(constant throughout titration)

The second half-reaction represents the mercury electrode whose voltage is constant throughout the titration. Since the concentration of silver ion varies during the procedure, the reduction potential is determined by the Nernst equation which for this half-reaction has the form:

$$\mathscr{E} = \left[+0.80 - 0.059\log\left(\frac{1}{\left[Ag^+\right]}\right)\right] \text{V}$$

Thus the cell may be represented as follows:

$2(Ag^+ + e^- \rightarrow Ag)$	$\mathscr{E} = [0.80 + 0.059 \log [Ag^+]]$ V
$2\ Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e$	$\mathscr{E} = -0.24$ V
$2\ Ag^+ + 2\ Hg + 2\ Cl^- \rightarrow Hg_2Cl_2 + 2\ Ag$	$\mathscr{E}_{cell} = 0.80 + 0.059 \log [Ag+] - 0.24$V

1.a. If the unknown solution originally contains 2.1×10^{-2} M I^-, what must be the concentration of Ag^+ to initiate the precipitation of the AgI? (For AgI: $K_{sp} = 8.0 \times 10^{-17}$)

b. If the unknown solution originally contains 2.1×10^{-2} M Cl^-, what must be the concentration of Ag^+ to initiate the precipitation of the AgCl? (For AgCl: $K_{sp} = 2.0 \times 10^{-10}$)

<u>Note</u>: Since a higher Ag^+ concentration is required to precipitate the AgCl than is required to precipitate the AgI, the AgI will precipitate first, and its precipitation will control the Ag^+ concentration until the AgCl begins to precipitate.

c. When the AgI begins to precipitate what is the potential of the silver electrode? What is the cell potential?

potential of silver electrode: _____

cell potential: _____

d. When the $[I^-]$ drops to 1.2×10^{-3} M, what is the $[Ag^+]$?

$[Ag^+]$: _____

e. At this concentration of Ag^+, what is the potential of the silver electrode? What is the cell potential?

potential of silver electrode: _____

cell potential: _____

f. At the equivalence point of the I^- titration, when $[Ag^+] = [I^-]$, what is the $[Ag^+]$?

$[Ag^+]$: _____

g. At this concentration of Ag^+, what is the potential of the silver electrode? What is the cell potential?

potential of silver electrode: _____

cell potential: _____

h. When the AgCl begins to precipitate, what is the potential of the silver electrode? What is the cell potential?

potential of silver electrode: _____

cell potential: _____

i. When the $[Cl^-]$ drops to 1.2×10^{-3} M, what is the $[Ag^+]$?

$[Ag^+]$: _____

j. At this concentration of Ag^+, what is the potential of the silver electrode? What is the cell potential?

potential of silver electrode: _____

cell potential: _____

k. At the equivalence point of the Cl^- when $[Ag^+] = [Cl^-]$, what is the $[Ag^+]$?

$[Ag^+]$: _____

l. At this concentration of Ag^+, what is the potential of the silver electrode? What is the cell potential?

potential of silver electrode: _____

cell potential: _____