Quantification Halides and the Estimation of the Solubility Products of AgI and AgCl by Potentiometry

Background

The technique of Potentiometry measures the potential of an indicator electrode that is coupled with a suitable reference electrode. In this technique no current flows between the electrodes.

$$E_{cell} = E_{ind} - E_{ref}\,; \quad E_{ind} = E_{cell} - E_{ref}$$

The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component in the analyte solution. The potential difference that develops in the *electrochemical cell* is the result of the *free energy change* that would occur if the chemical phenomena were to proceed until the *equilibrium condition* has been satisfied.

$$\Delta G = -nFE_{cell}$$

Nernst Equation relates electrode potential to the activities of the species involved in a given electrode. The objective of the experiment is to quantify of each halide salt in a solid mixture of KI and KCl. In this experiment the mixture of halides can be titrated with $AgNO_3$ solution. The activity of Ag+ would vary during the titration in the reaction mixture and activity of Ag^+ is monitored as the titration proceeds using a $Ag|Ag^+(aq)$ electrode as the indicator (test) electrode.

$$E_{ind} = E_{Ag^+|Ag} = E^0_{Ag^+|Ag} - 2.303\frac{RT}{F}\log\frac{1}{a_{Ag^+}}$$

The trends in the variation of the E_{ind} and E_{cell} during the titration are the same;

$$E_{cell} = \left[E^0_{Ag^+|Ag} - 2.303\frac{RT}{F}\log\frac{1}{a_{Ag^+}}\right] - E_{ref} = (E^0_{Ag^+|Ag} - E_{ref}) - 2.303\frac{RT}{F}\log\frac{1}{a_{Ag^+}}$$

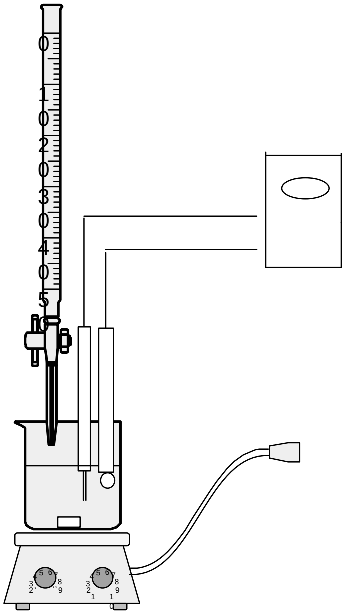
$$E_{cell} = k - 0.0591\log\frac{1}{a_{Ag^+}} \qquad \text{where } k = (E^0_{Ag^+|Ag} - E_{ref})$$

In the plot of E_{cell} vs. V_{Ag+}, which constitute a sigmoid, the values of V_{Ag+} at the steepest variation points of the plot would be the equivalence points. Plot of the second derivative of E_{cell} vs. V_{Ag+} would yield the two equivalent points.

Focusing on the reaction system before each equivalence point, the necessary theoretical background and expressions for an alternate means (Gran Plot) to determine the equivalence points and the K_{sp}'s is given in the appendix.

Apparatus:	Reference electrode, Ag electrode, beaker 150 mL, magnetic stirrer, pipette 25ml, burette 50ml, pH meter, connecting cables.
Chemicals:	0.4M bisulfate buffer (pH=2). $AgNO_3$(s).

Apparatus Setup:



Procedure:

1. Weigh accurately ~0.5g of the solid halide mixture and transfer carefully into a 100-mL volumetric flask quantitatively. Dissolve the solid in ~20 mL of water and dilute to the mark and homogenize the ‘unknown’ solution by mixing well.

2. Dry $AgNO_3$ at 105˚ C for 1 h and cool in a dessicator for 30 min with minimal exposure to light. Some discoloration is normal (and tolerable in this experiment) but should be minimized. Accurately weigh ~1.2 g and dissolve it in a 100-mL volumetric flask.

3. Set up the apparatus into carryout a potentiometric titration. The silver electrode is simply a 1-3-cm length of silver wire soldered to copper wire housed in a glass tube sealed with epoxy at the lower end with the silver wire protruding from the epoxy. The silver electrode is connected to the nominal pH sensing electrode of a pH meter. The reference electrode for this titration is a double junction Ag|AgCl(s)|KCl(sat)| electrode connected to the reference socket of the pH-meter. The silver electrode and the reference electrode are set inside the 150-mL beaker. The stir bar should not hit either electrode.

4. Pipette 25.00 mL of unknown into the beaker, add 3 mL of bisulfate buffer and initiate stirring. In all potentiometry experiments keep the stirring rate constant. Add ~1

mL of titrant to the beaker. Turn the pH meter to the mill volt scale and record the volume of dispensed titrant and corresponding cell voltage.

5. Proceed to titrate the halide mixture solution with ~1-mL aliquots until 50 mL of titrant have been added or until you can see two clear potentiometric end points. You need to allow ~10 s of “equilibration time” for each point. Record the volume and voltage at each point. Make a graph of E_{cell} (mV) versus V_{Ag+} (mL) as the experiment proceeds, to find the approximate positions (±1 mL) of the two end points.

6. Turn the pH meter to standby, remove the beaker, rinse the electrodes well with water, and blot them dry with a tissue. (Silver halide adhering to the glass electrode can be removed by soaking in concentrated sodium thiosulfate solution. This thorough cleaning is not necessary between Steps 6 and 7 in this experiment.) Clean the beaker and set up the titration apparatus again. The beaker need not be dry.

7. Now perform an accurate titration, using 1-drop aliquots near the end points (and 1-mL aliquots elsewhere).

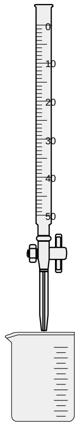
8. Prepare a graph of E_{cell} mV versus V_{Ag+} mL and locate the equivalence points via the second derivative plot. The Cl^- end point is the inflection point at the second break of the sigmoid. Compare the equivalence points extracted from the second derivative plot to those from the Gran plots (step 9).

9. Generate Gran plots for this experiment and determine the equivalence points and the solubility products. Calculate mole fraction of KI and KCl in your solid unknown.

G. Lisensky and K. Reynolds, J. Chem. Ed. 1991, 68, 334
R. Ramette, Chemical Equilibrium (Reading, MA: Addison-Wesley, 1981), p. 649.

Appendix:

A double 'sigmoid' would be the result of the plot of E_{cell} vs. V_{Ag} in this experiment. However the first fall in the plot is not satisfactory to determine the first equivalence point V_{e1} because AgCl(s) starts precipitating before the first nominal equivalence point is reached, pertaining to the completion of AgI(s) precipitation. Thus a Gran plot would be more suitable to determine the first equivalence point and for the second end equivalence point V_{e2} as well.



For the first reaction, at the equivalence point V_{e1}: $V_{e1}C_{Ag} = V_X C_I$

Before the first equivalence point: $[I] = \dfrac{V_X C_I - V_{Ag}C_{Ag}}{V_X + V_{Ag}}$

$$[I] = \frac{V_X C_I - V_{Ag}C_{Ag}}{V_X + V_{Ag}} = \frac{V_{e1}C_{Ag} - V_{Ag}C_{Ag}}{V_X + V_{Ag}}$$

Rearranging yields;

$$[I]\left(V_X + V_{Ag}\right) = V_{e1}C_{Ag} - V_{Ag}C_{Ag}$$

Substituting for [I] using the K_{sp} value;

$$\frac{K_{spAgI}}{[Ag]}\left(V_X + V_{Ag}\right) = V_{e1}C_{Ag} - V_{Ag}C_{Ag} \qquad (1)$$

Also; $E_{cell} = k - 0.0591\log\dfrac{1}{a_{Ag^+}}$ where k = $(E^0_{Ag^+|Ag} - E_{ref})$ and assume $a_{Ag^+} = [Ag]$

and $0.0591\log\dfrac{1}{[Ag]} = k - E_{cell} \quad \Rightarrow \quad \dfrac{1}{[Ag]} = 10^{\frac{k - E_{cell}}{0.0591}}$

Which used in the Eq. (1), $K_{spAgI}10^{\frac{k - E_{cell}}{0.0591}}\left(V_X + V_{Ag}\right) = V_{e1}C_{Ag} - V_{Ag}C_{Ag}$

$$10^{\frac{k - E_{cell}}{0.0591}}\left(V_X + V_{Ag}\right) = \frac{V_{e1}C_{Ag}}{K_{spAgI}} - \frac{C_{Ag}}{K_{spAgI}}V_{Ag}$$

Plot of $10^{\frac{k - E_{cell}}{0.0591}}\left(V_X + V_{Ag}\right)$ vs. V_{Ag} generates a straight line from which;

$V_{e1} = -\dfrac{\text{intercept}}{\text{slope}}$ and $K_{spAgI} = -\dfrac{C_{Ag}}{\text{slope}}$

For the second reaction, at the equivalence point, V_{e2}: $(V_{e2} - V_{e1})C_{Ag} = V_X C_{Cl}$

Before the first equivalence point: $[Cl] = \dfrac{V_X C_{Cl} - (V_{Ag} - V_{e1})C_{Ag}}{V_X + V_{Ag}}$

$$[Cl] = \frac{(V_{e2} - V_{e1})C_{Ag} - (V_{Ag} - V_{e1})C_{Ag}}{V_X + V_{Ag}} = \frac{V_{e2}C_{Ag} - V_{Ag}C_{Ag}}{V_X + V_{Ag}}$$

Rearranging yields;

$$[Cl]\left(V_X + V_{Ag}\right) = V_{e2}C_{Ag} - V_{Ag}C_{Ag}$$

Substituting for [Cl] using the K_{sp} value;

$$\frac{K_{spAgCl}}{[Ag]}\left(V_X + V_{Ag}\right) = V_{e2}C_{Ag} - V_{Ag}C_{Ag}$$

and $$\frac{1}{[Ag]} = 10^{\frac{k - E_{cell}}{0.0591}}$$

$$K_{spAgCl}10^{\frac{k - E_{cell}}{0.0591}}\left(V_X + V_{Ag}\right) = V_{e2}C_{Ag} - V_{Ag}C_{Ag}$$

$$10^{\frac{k - E_{cell}}{0.0591}}\left(V_X + V_{Ag}\right) = \frac{V_{e2}C_{Ag}}{K_{spAgCl}} - \frac{C_{Ag}}{K_{spAgCl}}V_{Ag}$$

Plot of $10^{\frac{k - E_{cell}}{0.0591}}\left(V_X + V_{Ag}\right)$ vs. V_{Ag} generates a straight from which;

$$V_{e2} = -\frac{\text{intercept}}{\text{slope}} \quad \text{and} \quad K_{spAgCl} = -\frac{C_{Ag}}{\text{slope}}$$

The Gran plot is made in the vicinity of the equivalence point, where an assumption can be that the activity coefficient remains practically constant.