Determining a Solubility Product Constant

Introduction

The solubility product constant, K_{sp}, is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound. Calcium iodate is slightly soluble in distilled water at room temperature

$$\text{Ca(IO}_3\text{)}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{IO}_3^-(aq)$$

The solubility product expression is

$$K_{sp} = [\text{Ca}^{2+}][\text{IO}_3^-]^2$$

If an analytical technique is used to determine the concentration of either the Ca^{2+} or IO_3^- ions in a saturated solution, the solubility product constant of Ca(IO_3)_2 can be calculated.

In this experiment the concentration of IO_3^- ions will be determined through titration with a standardized solution of thiosulfate ion (S_2O_3^{2-}) in the presence of iodide ion (I^-), using starch as an indicator near the end of the titration. Iodate ion reacts with iodide ions to give I_3^- (triiodide ion) as the sole product containing iodine:

$$\text{IO}_3^-(aq) + 8\text{I}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{I}_3^-(aq) + 3\text{H}_2\text{O}(l) \quad (1)$$

Triiodide reacts with S_2O_3^{2-} ions during the titration, according to

$$\text{I}_3^-(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightarrow 3\text{I}^-(aq) + \text{S}_4\text{O}_6^{2-}(aq) \quad (2)$$

Combining the two reactions gives the titration reaction of

$$\text{IO}_3^-(aq) + 6\text{S}_2\text{O}_3^{2-}(aq) + 6\text{H}^+(aq) \rightarrow \text{I}^-(aq) + 3\text{S}_4\text{O}_6^{2-}(aq) + 3\text{H}_2\text{O}(l) \quad (3)$$

Triiodide ion is a red-brown color and I^- is colorless, so no indicator is needed for most of the titration. Starch solution is added near the end of the titration (when most of the I_3^- ion has been consumed) because it reacts with I_3^- to give a more visible dark blue color. As I_3^- is consumed in the titration, the color will fade as the titration progresses. If the starch is added too early, the I_3^-/starch compound precipitates out of solution and is slow to react. First you will standardize the S_2O_3^{2-} solution, using a known volume of an IO_3^- solution whose molarity is known accurately. You will then use this S_2O_3^{2-} solution to analyze the saturated Ca(IO_3)_2 solution you will make.

I. Preparation of Saturated Ca(IO_3)_2 Solution.

1. Using the markings on a 100-mL beaker, prepare Ca(IO_3)_2 by adding 50 mL of 0.2 M KIO_3 to 20 mL of 1 M Ca(NO_3)_2.
2. Stir vigorously with a stirring rod. A white precipitate of Ca(IO₃)₂ should form. Let the mixture settle for a few minutes.

3. Use gravity filtration to collect the precipitate after decanting off most of the solution.

4. Wash the precipitate with 3 small (~5 mL) portions of distilled water.

5. Place all of the wet precipitate in a 250-mL beaker and add 100.0 mL of distilled water.

6. Stir thoroughly with a stirring rod and let the mixture stand for at least 30 minutes, leaving the stirring rod in the beaker. You are attempting to make a saturated solution of Ca(IO₃)₂. Go on to Part II.

II. Standardization of S₂O₃²⁻ Solution (approximately 0.04 M)

1. Rinse and fill a buret with the Na₂S₂O₃ solution. Remove air bubbles from the tip and record the initial volume to 0.01 mL accuracy. Be ready to titrate at step 3.

2. Pipet 10.00 mL of standardized KIO₃ (approximately 0.01 M (record the concentration to 4 significant figures)) into a clean 250-mL Erlenmeyer flask and add 20.0 mL of distilled water (graduated cylinder).

3. Measure about 0.2 g of solid KI (excess) in a small beaker (top loading balance) and dissolve in the solution above. Add 20 drops of 2 M HCl to the flask and swirl to obtain a homogeneous red-brown solution. Begin titrating immediately (I₂ is volatile).

4. Titrate until the solution becomes pale yellow. You do not need to record the volume used up to this color. You are still looking for the final colorless endpoint. Add 3–4 drops of 2% starch solution. Continue titrating until the blue solution just turns colorless (will not take much more titrant). Record the final volume of Na₂S₂O₃ solution to 0.01 mL accuracy.

5. Titrate two more samples of KIO₃. Calculate the molarity of the S₂O₃²⁻ from each of the titrations and obtain the mean molarity. A class average will be calculated. You are now ready to analyze the Ca(IO₃)₂ solution you made at the start of the experiment.

III. Determination of [IO₃⁻] and [Ca²⁺] in Saturated Ca(IO₃)₂ Solution.

Do not add water during filtration or sampling or the molarity of IO₃⁻ ions will change.

1. Gravity filter the solution from part I into a clean, dry 125-mL Erlenmeyer flask. Do not wash the precipitate on the filter paper.

2. Rinse a 10-mL pipet with a small amount of the filtrate.

3. Pipet 10.00 mL of the filtrate into a clean 250-mL Erlenmeyer flask. Add 20.0 mL of distilled water to the flask.
4. Measure about 0.2 g of solid KI in a small beaker and dissolve in the solution from step 3 above. Add 20 drops of 2 M HCl to the flask and swirl to obtain a homogeneous red-brown solution. Begin titrating immediately.

5. Titrate with standardized S\textsubscript{2}O\textsubscript{3}\textsuperscript{2–} until the solution becomes light orange to yellow. Add 3–4 drops of 2% starch solution. Continue titrating until the blue solution just turns colorless. Record the final volume of S\textsubscript{2}O\textsubscript{3}\textsuperscript{2–} solution to 0.01 mL accuracy.

6. Titrate two more 10.00 mL samples.

**Question**

1. Calculate the volume of 0.04000 M S\textsubscript{2}O\textsubscript{3}\textsuperscript{2–} solution that would be needed to titrate 10.00 mL of 0.01000 M IO\textsubscript{3}–, according to equation 3.

**Data Treatment and Discussion**

Determine the molarity of the S\textsubscript{2}O\textsubscript{3}\textsuperscript{2–} and give the average of your three trials. Indicate the class average molarity that you will use to determine the K\textsubscript{sp} of Ca(IO\textsubscript{3})\textsubscript{2}.

From the titrations in part III, determine of the molarity of IO\textsubscript{3}– in your saturated Ca(IO\textsubscript{3})\textsubscript{2} solution, and the average of the three trials. The molarity of the Ca\textsuperscript{2+} ion is based on the stoichiometry of the K\textsubscript{sp} reaction and the average concentration of IO\textsubscript{3}–.

Calculate the solubility product constant, K\textsubscript{sp}, of Ca(IO\textsubscript{3})\textsubscript{2}. Compare your value with a published value (give the reference). Suggest a reason for any error.

**Conclusion**

Give the K\textsubscript{sp} expression and value for Ca(IO\textsubscript{3})\textsubscript{2}.