Determining a Solubility Product Constant

Introduction

In general, the solubility product constant, \( K_{sp} \), is the equilibrium constant for the solubility equilibrium of a slightly soluble (or nearly insoluble) ionic compound. It equals the product of the equilibrium concentrations of the ions in the compound, each concentration raised to a power equal to the number of such ions in the formula of the compound. Lead(II) iodide is an example of a slightly soluble salt. The equilibrium in water is

\[
PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2 I^-(aq)
\]

The expression for the solubility product constant is

\[
K_{sp} = [Pb^{2+}][I^-]^2
\]

The equilibrium between solid \( \text{Ca(IO}_3\text{)}_2 \) and its ions in a saturated solution is

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

If some analytical technique is used to determine the concentration of either the Ca\(^{2+}\) or IO\(_3^-\) ions in the saturated solution, the solubility of \( \text{Ca(IO}_3\text{)}_2 \) will be known and the solubility product constant can be calculated.

In this experiment the concentration of IO\(_3^-\) ions is determined through titration with a standardized solution of thiosulfate ion (S\(_2\)O\(_3\)\(^{2-}\)) in the presence of iodide ion (I\(^-\)), using starch as an indicator near the end of the titration. Iodate ion reacts with the iodide ions to give I\(_3^-\) (triiodide ion) as the sole product containing iodine:

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

The triiodide reacts with S\(_2\)O\(_3\)\(^{2-}\) ions during the titration, according to

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

S\(_4\)O\(_6\)\(^{2-}\) is tetrathionate ion. Combining the two reactions gives a titration reaction of

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

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) in this titration because it reacts with I\(_3^-\) reversibly to form 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\(_2\)O\(_3\)\(^{2-}\) 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(IO$_3$)$_2$ 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(IO$_3$)$_2$. Go on to Part II.

II. Standardization of $S_2O_3^{2−}$ Solution (approximately 0.04 M)

1. Rinse and fill a buret with the Na$_2$S$_2$O$_3$ 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 KIO$_3$ (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 (I$_2$ 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 Na$_2$S$_2$O$_3$ solution to 0.01 mL accuracy.

5. Titrate two more samples of KIO$_3$. Calculate the molarity of the $S_2O_3^{2−}$ from each of the titrations and obtain the mean molarity. A class average will be calculated. You are now ready to analyze the Ca(IO$_3$)$_2$ 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 S₂O₃²⁻ 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 S₂O₃²⁻ solution to 0.01 mL accuracy.

6. Titrate two more 10.00 mL samples.

Question

1. Calculate the volume of 0.04000 M S₂O₃²⁻ solution that would be needed to titrate 10.00 mL of 0.01000 M IO₃⁻, according to equation 3.

Data Treatment and Discussion

Include the following. Be sure to include sample calculations.

1. Calculate the molarity of the S₂O₃²⁻ and give the average of your three trials.

2. Calculate of the molarity of IO₃⁻, and the average, in the saturated Ca(IO₃)₂ solution.

3. Calculate the molarity of the Ca²⁺ ion in the saturated Ca(IO₃)₂ solution (based on the stoichiometry of the Ksp reaction).

4. Calculate the solubility product constant, Ksp, of Ca(IO₃)₂. Compare your value with a published value (give the reference). Suggest a reason for any error.

Conclusion

Give the Ksp expression and value for Ca(IO₃)₂.