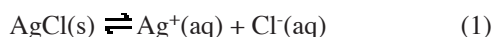

Solubility Constant

INTRODUCTION

For slightly soluble ionic compounds, equilibrium exists between a solid substance and its dissolved ions. For example, in a saturated solution of AgCl, about 0.002 grams of the substance dissolves in a liter of water. The equilibrium can be shown in the equation:

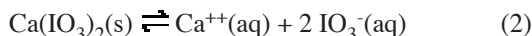


The equilibrium condition for this saturated solution is called the solubility constant, K_{sp} , and has the form:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

The solid AgCl is not used in the expression. If either the concentration of the Ag^+ or the Cl^- is increased by the addition of another ionic compound into the solution, the value of the K_{sp} remains the same, but the solubility of the AgCl decreases. This would take place, for example, if the AgCl were to be dissolved in a solution of NaCl or AgNO_3 . When an ionic substance is dissolved in a solution that already contains one of the ions, the *common ion effect* causes the solubility of the substance to decrease. Le Châtelier's principle helps to explain the effect of a common ion on solubility. In equation (1) above, if the concentration of either the Ag^+ or Cl^- increases, the reaction moves to the left.

In today's experiment, you will calculate the solubility of the ionic compound, calcium iodate, $\text{Ca}(\text{IO}_3)_2$. The solution equilibrium for the substance is:



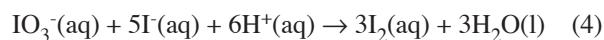
The equilibrium constant expression is:

$$K_{sp} = [\text{Ca}^{++}][\text{IO}_3^-]^2 \quad (3)$$

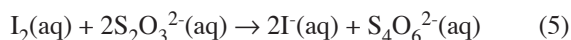
Two solutions of calcium iodate will be used. One is in pure deionized water. The other is in a water solution containing 0.0100M KIO_3 . You will measure the concentration of the iodate ion in each solution. In the first case, the solution in pure water, the solubility of the calcium iodate will be 1/2 the concentration of the iodate ion. In the other case, finding the solubility of the calcium iodate is a bit more involved. After finding the total concentration of the iodate ions in the solution of the calcium iodate in the water containing 0.0100M KIO_3 , 0.0100 will be subtracted, and 1/2 of the remaining iodate ion concentration will give the solubility of the calcium iodate. You will be asked to explain the reasoning behind this paragraph in the questions following the experiment.

DETERMINING THE SOLUBILITY

The solubility of $\text{Ca}(\text{IO}_3)_2$ will be determined using an indirect redox titration. The IO_3^- ion is an oxidizing agent. It reacts with iodide ions, I^- , to produce iodine molecules, I_2 . The iodine produced is then titrated with a standardized sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3$. This is an *iodometric titration*, a versatile method for experimentally measuring the amount of an oxidizing agent in a substance or solution. Iodine in water, particularly when there are I^- ions present, gives a deep reddish brown to a pale yellow color to the solution, depending on its concentration. If a starch solution is added to the iodine solution when the concentration of iodine is low, and the solution appears yellow, the iodine and the starch form an intensely blue colored complex. The disappearance of the blue color as sodium thiosulfate is added gives the endpoint in the titration. The reactions that take place are:



and then



In reaction (4), the I^- is provided by adding solid KI in excess, and the H^+ is provided by adding HCl solution. In reaction (4), the I_2 produced comes from the IO_3^- present. I^- alone will not produce I_2 , except by the slow oxidation caused by the oxygen in the air. There are 3 moles of I_2 produced for every 1 mole of IO_3^- present. In reaction (5), 2 moles of $\text{S}_2\text{O}_3^{2-}$ are required for every mole of I_2 present. The net result is that for every 6 moles of $\text{S}_2\text{O}_3^{2-}$ used in the titration, there must have been 1 mole of IO_3^- originally present. The sodium thiosulfate solutions have been standardized. You will use the molarity of the thiosulfate solution to calculate the molarity of the iodate in the calcium iodate solutions. In each titration, you will add 10.0 ml of the calcium iodate solution to a flask using a pipet. The sodium thiosulfate solution will be added from a buret, and the volume added will be carefully observed. The following relationship will be used to calculate the concentration of the IO_3^- ion from the data:

$$M_{\text{IO}_3^-} = \frac{\text{ml}_{\text{S}_2\text{O}_3^{2-}} \cdot M_{\text{S}_2\text{O}_3^{2-}}}{10.0 \text{ ml}_{\text{IO}_3^-}} \cdot \frac{1 \text{ IO}_3^-}{6 \text{ S}_2\text{O}_3^{2-}} \quad (6)$$

The number of ml of the $\text{S}_2\text{O}_3^{2-}$ and the M of the $\text{S}_2\text{O}_3^{2-}$ are the experimentally found values. The other numbers result from the conditions for this titration.

The two *important* measurements in the titration are the volume of the solution containing the IO_3^- ion and the volume of the solution containing the $\text{S}_2\text{O}_3^{2-}$ ion. The measurement of the mass of KI and the volume of the HCl, the two *developing reagents*, does not require great accuracy. You will use a pipet and a buret for the important volume measurements, and a graduated cylinder and one significant digit weighing accuracy for the developing reagent measurements.

EXPERIMENT

Supplies

- 1 stir bar
- 1 magnetic stirrer (and white paper if top is not white)
- 1 buret and buret stand
- 1 pipetting aide
- 2-10 ml volumetric pipet

From your drawer

- 1-250 ml flask
- 1-10 ml graduated cylinder
- 1 transfer pipet
- appropriately sized beakers to obtain reagents

From the reagent bottles

- 150 ml $\text{Na}_2\text{S}_2\text{O}_3$ solution (record the molarity)
- 30 ml of $\text{Ca}(\text{IO}_3)_2$ in water (record the temperature)
- 30 ml of $\text{Ca}(\text{IO}_3)_2$ in 0.0100 KIO₃ solution
- 45 ml 1M HCl
- 6 ml of 0.5% starch solution

Neatly arrange your work space. Beakers should be clearly marked for contents. Use the volume marks on the beakers to measure the volumes indicated above. Do not waste reagents by taking more than the amounts listed. Rinse the buret with five ml portions of sodium thiosulfate solution as instructed in the buret and pipet discussion on pages 103 and 104. You will do two titrations in each part of the experiment. Read and record the beginning and final volumes on the buret to the nearest 0.1 ml. After you finish with the first titration in a section, and you have used less than half of the solution in the buret, you do not have to refill the buret before beginning the second titration. In this case, the final volume reading of the first titration will be the initial volume reading of the second titration. Use one pipet in Part 1, the other pipet in Part 2. Rinse each pipet with the appropriate $\text{Ca}(\text{IO}_3)_2$ solution before filling. In Part 1, the solution is in pure water. In Part 2, the solution is in 0.0100M KIO₃.

General instructions for each sample titrated: For each titration, the developing reagents are used as follows: Rinse the 250 ml flask with deionized water and drain for a few seconds. Wipe the *outside* of the flask dry. Add 50 ml of deionized water. Use the volume mark on the flask to estimate this volume. Weigh out 0.5 g of solid KI. If you are using the electronic balances, do not waste time and effort by trying to get 0.500 g. Use a piece of weighing paper that has been folded to give it a crease which will help you

pour the solid into the flask. Make sure you tare out the weight of the paper. If you spill KI, sweep it away from the balance onto a piece of paper and put it into the “Dirty KI” container. Add the KI to the flask, put the stir bar in and place the flask on the magnetic stirrer. Adjust the speed so that there is good stirring but no splashing. Swirl the contents of the flask until the KI has completely dissolved. Measure 10 ml of the HCl in a graduated cylinder. Do not add it yet. The 10 ml volume can be roughly measured, within half a ml or so. Use the pipetting aide to pull up 10.0 ml of the calcium iodate solution into the pipet, add it to the flask, and then add the HCl. Position the buret and begin to add the sodium thiosulfate solution. Undue delay after preparing the solution and doing the titration can lead to errors caused by air oxidation of the I^- . Add thiosulfate solution until the color of the liquid in the flask has lost its red tint and appears yellow. Now use the mark on a transfer pipet to measure and add 1 ml of the starch solution to the flask. The solution will turn blue. Continue to add thiosulfate from the buret until one drop causes the solution to turn from blue to colorless. Take care that you do not overshoot the endpoint. After each titration, empty the contents of the flask into the sink. Rinse the flask with 2 small portions of deionized water. Allow excess water to drain. Do not allow the stir bar to fall into the sink.

Part 1: $\text{Ca}(\text{IO}_3)_2$ in Pure Water

Prepare the pipet and buret as instructed. Do two titrations. If the buret readings do not agree to within 0.3 ml, do a third titration. You will need to obtain 10 ml more of the $\text{Ca}(\text{IO}_3)_2$ in pure water solution if you have to do a third titration.

Part 2: $\text{Ca}(\text{IO}_3)_2$ in 0.0100 M KIO₃

Prepare the pipet and buret as instructed. Do two titrations. If the buret readings do not agree to within 0.3 ml, do a third titration. You will need to obtain 10 ml more of the $\text{Ca}(\text{IO}_3)_2$ in 0.0100 M KIO₃ if you have to do a third titration.

After the experiment: Pour excess solutions into the sink. Rinse the buret and pipet with deionized water. Fill the buret with deionized water, place the dust cap on top, set it as low as possible in the buret stand, and replace the stand with the buret on the shelf. Return stir motors to the shelf.

Calculations: For each titration, calculate the $[\text{IO}_3^-]$ using equation (6) on page 1. The “M of the IO_3^- ” and “ $[\text{IO}_3^-]$ ” both indicate the same value. In Part 1, the $[\text{Ca}^{2+}]$ will be 1/2 the $[\text{IO}_3^-]$ (see equation 2 on page 1). In Part 2, you must first subtract 0.0100 from the $[\text{IO}_3^-]$, and then the $[\text{Ca}^{2+}]$ will equal 1/2 of this value. The solubility of the calcium iodate and the concentration of the calcium ion are the same value. Calculate the K_{sp} 's for the calcium iodate from the two parts. Even though the solubility varies, the K_{sp} should stay constant.

Data Table

Concentration of Na ₂ S ₂ O ₃ solution _____M		Temperature of Saturation of Ca(IO ₃) ₂ Solutions _____°C		
Part 1	Ca(IO₃)₂ in Pure Water	Trial 1	Trial 2	<i>Trial 3</i>
	Initial buret reading (to the nearest 0.1 ml)	ml	ml	<i>ml</i>
	Final buret reading (to the nearest 0.1 ml)	ml	ml	<i>ml</i>
	Volume of Na ₂ S ₂ O ₃ used	ml	ml	<i>ml</i>
Part 2	Ca(IO₃)₂ in 0.0100M KIO₃			
	Initial buret reading (to the nearest 0.1 ml)	ml	ml	<i>ml</i>
	Final buret reading (to the nearest 0.1 ml)	ml	ml	<i>ml</i>
	Volume of Na ₂ S ₂ O ₃ used	ml	ml	<i>ml</i>

Calculations

Part 1	Ca(IO₃)₂ in Pure Water	Trial 1	Trial 2	<i>Trial 3</i>
	Molarity of the IO ₃ ⁻ (from equation 6)	M	M	<i>M</i>
	Average Molarity of the IO ₃ ⁻	M		
	Molarity of the Ca ²⁺ (1/2 the above value)	M		
	Value of K _{sp} for Ca(IO ₃) ₂ (equation (3) on page 1)	M ³		
Part 2	Ca(IO₃)₂ in 0.0100M KIO₃	Trial 1	Trial 2	<i>Trial 3</i>
	Molarity of the IO ₃ ⁻ (from equation 6)	M	M	<i>M</i>
	Average Molarity of the IO ₃ ⁻	M		
	Molarity of the Ca ²⁺ (1/2 the (above value - 0.0100))	M		
	Value of K _{sp} for Ca(IO ₃) ₂ (equation (3) on page 1)	M ³		

Compare [Ca²⁺] from Parts 1 and 2 (note: this is the solubility). Is Le Châtelier's law followed? Explain

Are the K_{sp}'s from Parts 1 and 2 consistent?

QUESTIONS

1. Explain the reasoning behind the statements about the relationship between the iodate concentration and the solubility in the last paragraph on the left side of page 1.
2. The last sentence on page 2 says that even though the solubilities of calcium iodate change in pure water and in 0.0100M potassium iodate, the K_{sp} values will stay the same. Explain why this is so. Use the Mass Action setup for the K_{sp} in the explanation.

3. The solution used in Part one was prepared at a temperature listed on the bottle. Here is a formula that will allow you to calculate what your value for the solubility (the $[Ca^{++}]$ from Part 1) would be at 25°C:

$$s_{25} = s_t \left[\frac{2 - 0.045(t - 25)}{2 + 0.045(t - 25)} \right]$$

s_t refers to the solubility, which is the $[Ca^{++}]$ from Part 1, at the temperature listed on the bottle. The t 's refer to this temperature as well. Watch your algebra, and calculate the solubility from your data converted to 25°C. To check your calculations, if the temperature listed on the bottle is below 25°C, then the value for the solubility should increase with the calculation.

4. The solubility of calcium iodate at 25°C is listed as 0.00798 moles per liter. Use the value calculated in question 3 to find the percent difference between your value for the solubility corrected to 25°C and this value: