

Experiment # 10 ARE INSOLUBLE SALTS REALLY INSOLUBLE?

Objectives: First, calculate the value of the solubility product constant (K_{sp}) of an insoluble salt, calcium iodate. Second, determine the effect of a common ion on the solubility of the insoluble salt.

Introduction

The precipitation and dissolving of ionic solids are phenomena that are occurring constantly in the world around us. For example, limestone which is principally calcium carbonate is slowly dissolved in rain and ground water and is re-precipitated as the water evaporates. This process leads to erosion of rock as well as to formation of spectacular structures in caves and to silt in lakes and rivers. Tooth enamel is slightly soluble in the acidic environment produced by the bacteria that live in our mouths leading to tooth decay. Both of these processes involve the slow dissolution of “insoluble” salts.

Many ionic compounds are soluble in water at room temperature. However, there are many compounds that are only slightly soluble. Most general chemistry textbooks give a list of rules that a chemist can use to predict the solubility of the most common ionic compounds. According to these rules, many ionic salts are classified as insoluble or slightly soluble. Solubility rules predict that insoluble salts will precipitate out of solutions as a result of double displacement reactions. If we state that a compound is insoluble it suggests that no ions representing the solid will be present in the solution after the salt has precipitated. How is it possible then, to form more solid in a saturated solution of a salt by adding a solution of one of the ions present in that salt? Think back to the Equilibrium lab in which you precipitated sodium chloride from a saturated aqueous solution by adding hydrochloric acid. How were the sodium ions for this reaction produced? Small amounts of so called insoluble ionic compounds dissolve to form very low concentrations of the corresponding cations and anions. As it turns out, “insoluble” is a relative term that depends on multiple factors. Even the most insoluble compounds are soluble to some extent depending on the equilibrium between the dissolved ions and the solid. If the system is disturbed, for example by increasing the concentration of one of the ions, the equilibrium will shift to form more precipitate until new equilibrium conditions are reached.

The equilibrium concentrations of the dissolved ions in an aqueous solution can be determined from the equilibrium constant, K_{sp} . K_{sp} is also called the solubility product constant (or often just the solubility product). The K_{sp} for dissolution of any ionic compound depends only on the temperature. The solubility product equals the product of the molar concentrations of the ions involved in the equilibrium, each raised to the power of their coefficient in the balanced chemical equation. For example, for the hypothetical reaction:

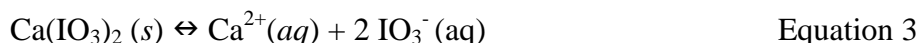


The solubility product constant, K_{sp} is:

$$K_{sp} = [M^{+2}][A^-]^2 \quad \text{Equation 2}$$

Remember that the amount of solid does not affect the solubility. That is, the activity of a solid equals one so there is no need to include the solid MA_2 in the denominator of the equilibrium constant expression.

Let's take a look at a sparingly soluble salt, calcium iodate, $Ca(IO_3)_2$. When the salt is placed in water and stirred, a saturated solution is formed and the following equilibrium is established:



The equilibrium equation for this system may be written as:

$$K_{sp} = [Ca^{2+}][IO_3^-]^2 \quad \text{Equation 4}$$

What is the practical meaning of K_{sp} ? What implications would the K_{sp} value have in developing a precipitation method for the assessment of low concentrations of heavy metal ions (such as silver) in the analysis of water samples? Would you be able to use just any concentration of the anion to precipitate the salt? Or is there a certain minimal concentration of the anion required to detect a given concentration of the metal cation? Is there a detection limit (the lowest concentration of metal ion that produces a precipitate)?

The value of K_{sp} for an insoluble salt is determined experimentally using an appropriate analytical method to measure the concentration of one or both ions in a saturated solution of that salt. It is often easier to determine the concentration of one of the ions, and then use the stoichiometry to find the concentration of the other ion. For example, the dissociation reaction for calcium iodate (Equation 3) indicates that in a saturated solution of $Ca(IO_3)_2$:

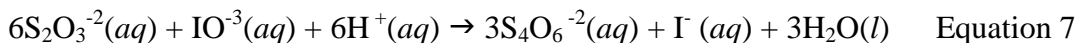
$$[Ca^{2+}] = 0.5[IO_3^-] \text{ or } [IO_3^-] = 2[Ca^{2+}] \quad \text{Equation 5}$$

Thus, if you determine the concentration of iodate in the solution it is then easy to calculate the calcium ion concentration and then K_{sp} . By substituting equation 5 into equation 4, K_{sp} for $Ca(IO_3)_2$ can be expressed in terms of iodate alone:

$$K_{sp} = 0.5[IO_3^-][IO_3^-]^2 = 0.5[IO_3^-]^3 \quad \text{Equation 6}$$

About this experiment

The concentration of iodate ions is determined by redox titration. The titrant is a standard solution of sodium thiosulfate ($Na_2S_2O_3$). However, you are not titrating the iodate ions directly. First, you must add potassium iodide and sulfuric acid to your sample of saturated calcium iodate solution producing aqueous brown molecular iodine, $I_2(aq)$. Next, the amount of iodine formed in the first step is determined by titration with sodium thiosulfate in the presence of a starch indicator. The overall net ionic equation for this multi-step process is described by the following equation:



The cations (Na^+ , Ca^{2+} , K^+) are in the solution, of course, but are spectator ions.

Based on the molar ratio of thiosulfate ions to iodate ions in Equation 7 and the volume and molarity of the thiosulfate used for the titration one can easily calculate the concentration of iodate ions. Finally, once the iodate ion concentration is known, the calculation of K_{sp} can be performed.

PROCEDURE

1. a. Place a small amount (no need to weigh) of calcium iodate in a 50 ml beaker containing about 10 ml of distilled water. Swirl gently, you should have a visible amount of undissolved $\text{Ca}(\text{IO}_3)_2$ in the beaker. Label the beaker W.

b. Place another small portion of the salt in a second 50 ml beaker (labeled Ca) containing 10 ml of Ca^{+2} solution (calcium nitrate or chloride will be provided). Let both beakers (W and Ca) stand at room temperature for about 15 minutes, swirling once in a while (3 to 4 times during 15 minute period).

2. Prepare two clean, dry funnels and place a fluted filter paper in each (see the instructions at the end of this document or go to <http://www.chem.ubc.ca/courseware/235/danalabsess/flutedfilterpaper.html>). Filter solutions W and Ca into two separate dry test tubes (labeled W and Ca, respectively).

3. Wash a burette (if necessary) then rinse it with a small amount (about 5 ml) of sodium thiosulfate solution. Fill it to the 0.0 ml mark with $\text{Na}_2\text{S}_2\text{O}_3$. Make sure that there are no air bubbles in the tip, and that your burette is not leaking.

Record the exact concentration of sodium thiosulfate (displayed on the label).

4. Using a volumetric pipette, transfer *exactly* 1.0 ml of solution W into a 125 ml Erlenmeyer flask and add 10-15 ml of distilled water. Add 1.0 ml of KI solution followed by 5-6 drops of dilute sulfuric acid. Swirl the flask to mix it then titrate the contents of the flask with sodium thiosulfate until the solution turns pale yellow. Do not over titrate. Add 3-4 drops of starch and finish the titration of the resulting dark navy blue solution (very carefully, using the “drop and swirl” procedure) until the solution is colorless. If there are some dark particles in the colorless solution at the end of titration, continue the titration until they are gone. Record the initial and final volumes in the burette.

5. Repeat step 4 two more time using 2.0 mL of solution W each time.

6. Repeat step 4 using 2.0 mL of solution Ca. Do it once only.

CLEANUP

Clean the burettes as in previous titration experiments. Never take the burette off the stand while performing the rinse with tap water.

Calculations

Calculate:

1. the molar concentration of iodate ion, $[\text{IO}_3^-]$, for each titration of the filtrate W,

then calculate the average $[\text{IO}_3^-]$.

2. the K_{sp} based on the average $[\text{IO}_3^-]$. Remember that $K_{sp} = 0.5[\text{IO}_3^-]^3$

3. $[\text{IO}_3^-]$ in filtrate Ca based on the titration with $\text{S}_2\text{O}_3^{2-}$.

4. the solubilities of calcium iodate for filtrates W and Ca, in mol/L as well as in mg/mL.

Report

SHOW ALL CALCULATIONS. Organize and label all calculations.

In the discussion, state the final results and include an evaluation of the common ion effect on the solubility of the salt (compare appropriate results). Evaluate possible experimental error sources. Re-check and correct all calculations as needed.

Chemistry 1225, experiment 10 Prelab

Name _____

A saturated aqueous solution of a slightly soluble salt, barium iodate $[\text{Ba}(\text{IO}_3)_2]$, was prepared and titrated with sodium thiosulfate (according to the same procedure used in your experiment). Based on the data tabulated below, calculate the indicated quantities in questions 1-5.

Volume of saturated barium iodate solution (filtered solution), mL	Initial (before titration) volume of thiosulfate in the burette, mL	Final (after titration) volume of thiosulfate in the burette, mL	Molarity of titrant (thiosulfate solution), mol/L
1.0	0.0	6.5	0.01
2.0	6.8	20.1	
3.0	20.3	46.8	

Organize your calculations using the steps below, but first determine and write the proper chemical equation.

1. Calculate the number of moles of thiosulfate used in each titration: $n \text{S}_2\text{O}_3^{2-} =$

2. Calculate the number of moles of iodate titrated: $n \text{IO}_3^- =$

3. Calculate the molar concentration of iodate ions: $[\text{IO}_3^-]$

4. Calculate the average molar concentration of iodate ions: $\text{Avg} [\text{IO}_3^-] =$

5. Calculate K_{sp} for the dissolution of $\text{Ba}(\text{IO}_3)_2$: $K_{\text{sp}} =$

1. Will any changes be observed in a saturated solution of BaSO_4 if some barium chloride solution is added? Write a balanced equation to support your answer. Explain.

2. The measured volume of saturated $\text{Ca}(\text{IO}_3)_2$ solution (filtrate W) was believed to be 1.0 ml and this volume was used in calculations, but due to improper use of a pipette, the actual volume delivered and used for titration was lower. Will the calculated solubility product constant of $\text{Ca}(\text{IO}_3)_2$ increase, decrease or remain unchanged. Justify your answer.

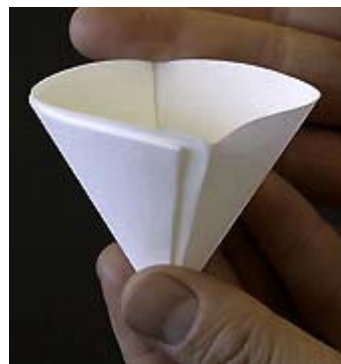
3. Why does the saturated solution of calcium iodate have to be filtered before titration?
Hint: think about the equilibrium....

4. A water sample collected from a household faucet in Park City was known to contain Ag^+ . Sodium iodide solution was used to detect Ag^+ in this water sample. The K_{sp} for silver iodide (AgI) is 1.5×10^{-16} . If the $[\text{I}^-]$ concentration has to reach 0.067 M in this water sample before a precipitate can be detected, what is the detection limit for the silver ion in mol/L as well as in ppm?



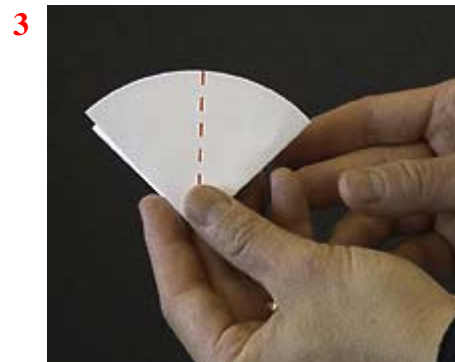
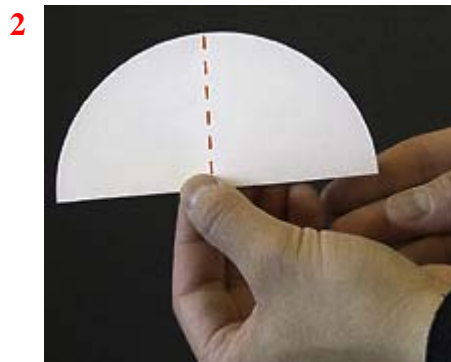
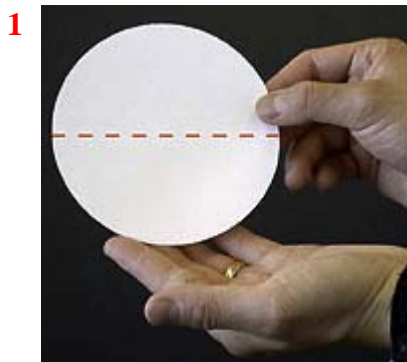
“Fluted “ filter paper (LEFT) is used when you wish to separate a liquid and a solid, keeping the liquid and discarding the solid. This arrangement of folds in the filter paper will allow the liquid to pass through it very quickly and give you a lot of surface area on which to collect the solid “impurity”.

If you wished to keep the solid sample and discard the liquid, you would make a simple cone of the filter paper (RIGHT). This would make it much easier to remove the solid from the filter paper than if it was on a fluted filter paper.

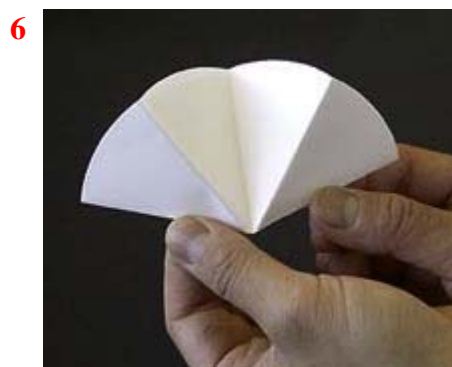
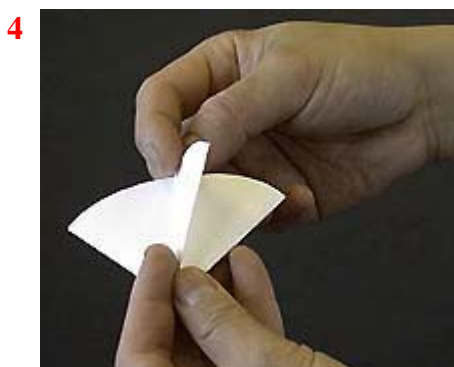


To “flute” filter paper, you do the following:

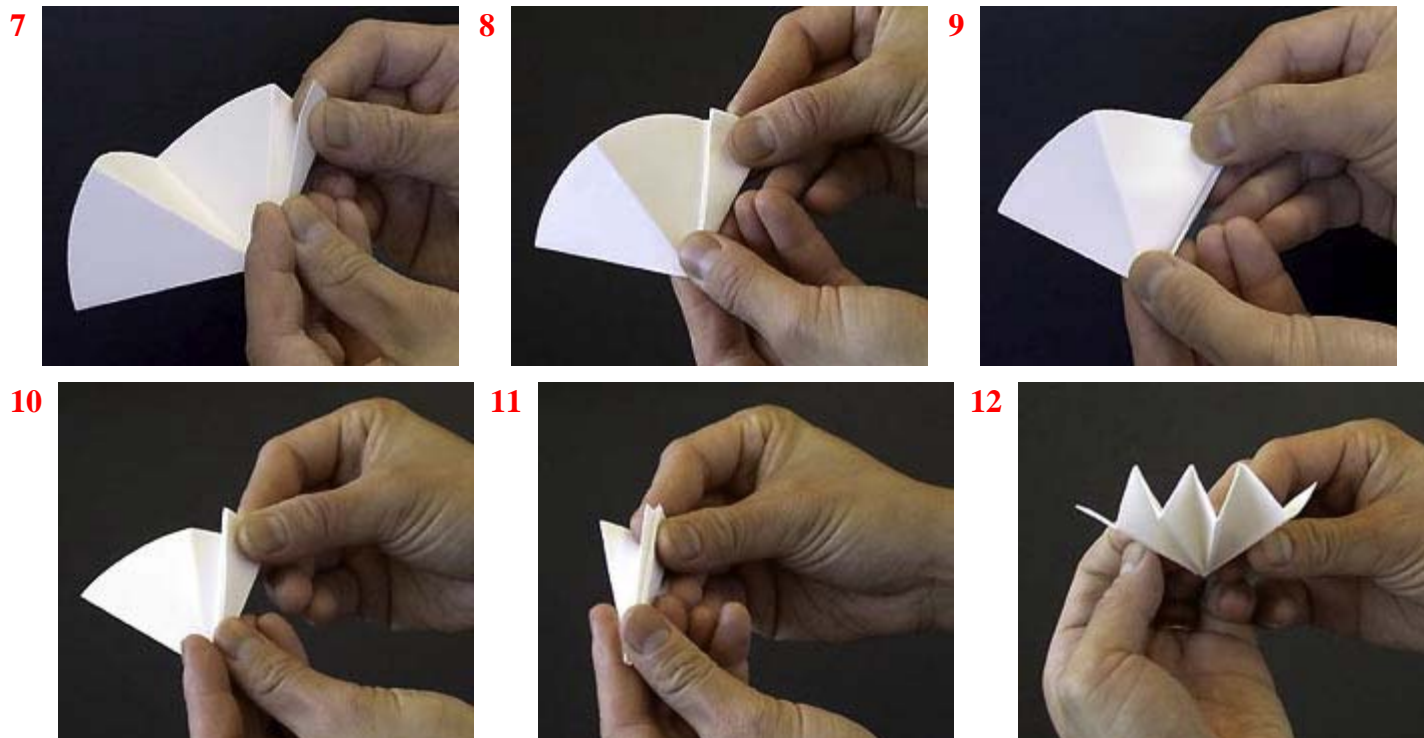
Fold the large circle of filter paper in half (2), then in quarters (3) being careful not to press the creases too hard as this tends to weaken the paper and cause possible tears later on.



Take the straight edge on one side and fold back to the centre fold (4). Do the same on the other side (5). You should now have a “fan” with alternating folds. Open the “fan” up with the centre fold going away from you (6).



Starting at one side, fold the straight edge up towards the first fold (7). Fold back along the preformed fold and then fold again towards the centre fold (8). Reverse the direction of the centre fold (9). Continue folding back and forth until you get another smaller-sized fan. (10, 11, 12)



Open the “fan” and look for the two areas called the “boxes”, where there are two folds going in the same direction instead of alternating (13). Pinch the paper (14) to make another fold between the two folds in each box (15). Then invert the filter paper before you place it in the glass funnel. [NOTE: inverting the filter paper will insure that any grease or dirt transferred from your fingers will be on the “inside” of the filter paper rather than the “outside”, when it is being used. Whatever is collected on the inside of the filter paper is something that will be disposed of.]



Copied from: <http://www.chem.ubc.ca/courseware/235/danalabsess/flutedfilterpaper.html>