

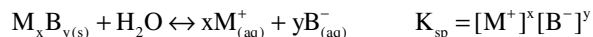
EXPERIMENT 7

Precipitation and Complex Formation

Introduction

Precipitation is the formation of a solid in a solution as the result of either a chemical reaction, or supersaturating a solution with a salt resulting in solid material collecting on the bottom of a beaker. The solid formed is called the **precipitate**. Precipitation is an indication that the solution has been *supersaturated* by a compound and no more material can be supported by the solution. In most situations, the solid "falls" out of the solute phase, and sinks to the bottom of the solution. However, if the precipitate is less dense than the aqueous solution, it may float on top of the solution or be suspended within the solution. In this latter case, the heterogeneous mixture is called a **suspension** and can be identified by the fact that the solution will not be clear, but rather cloudy.

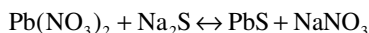
The chemical reaction describing this precipitation is that of the solid salt breaking into its ions in an aqueous solution. The equilibrium constant associated with this reaction is called the K_{sp} , or solubility product constant. By convention, the K_{sp} is always written as the solid breaking apart into ions, so that the numerator in the K_{sp} expression contains the ion concentrations, raised to the coefficients given in the chemical reaction (x and y below). There is no denominator. In equilibrium constant expressions, solids and pure liquids are not used, so their values are taken to be 1. Since the reactants consist of a solid salt and pure water, the K_{sp} is based solely on the concentrations of the anion and cation in the solution, not on the initial amount of material added to water.



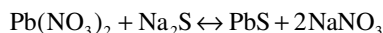
Determining the K_{sp} as a Result of a Chemical Reaction

When precipitation is the result of a chemical reaction rather than simply dissolving a salt, the situation becomes more complicated. First, you need to determine what is reacting and what the new products would be. If you are mixing two aqueous solutions of chemicals, you need to determine if one or more of the products will not dissolve, resulting in a precipitate. This is done by performing the following steps.

First, find the new products by swapping the cations of each reactant as shown in the example below.



Next balance the equation

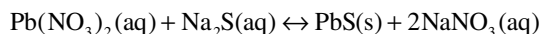


Finally, use the solubility rules listed below to determine if one or more of the products is insoluble.

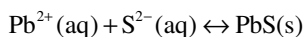
Always soluble	Ammonium (NH_4^+) Hydrogen ion (H^+) Alkali Metal (group 1A) Nitrate (NO_3^-) Perchlorate (ClO_4^-) Acetate ($C_2H_3O_2^-$)	Always soluble Always soluble Always soluble Always soluble Always soluble Always soluble
Sometimes soluble	Halide (Cl^- , Br^- , I^- & F^-) Sulfate (SO_4^{2-})	Soluble except: Pb^{2+} , Hg_2^{2+} , Hg^{2+} , Ag^+ , Cu^+ Soluble except: Pb^{2+} , Hg_2^{2+} , Ba^{2+} , Ca^{2+} , Sr^{2+}
Sparingly Soluble (Insoluble)	Sulfide (S^{2-}) Hydroxide (OH^-) Oxide (O^{2-}) Carbonate (CO_3^{2-}) Phosphate (PO_4^{3-})	Only if cation is soluble Only if cation is soluble Only if cation is soluble Only if cation is soluble Only if cation is soluble

According to this table, sulfides, salts containing the anion, S^{2-} , are insoluble unless combined with a group 1 cation, ammonium ion or hydrogen ion. Since the product, lead sulfide, PbS , does not contain any of these cations, it will precipitate out of the solution. Conversely, the salt $NaNO_3$ will be soluble for two reasons: First, it has a group 1 cation, Na^+ , that would indicate immediately that it is soluble, and second, it contains nitrate ion, NO_3^- , which is also very soluble. Therefore, solid $NaNO_3$ will not form a precipitate, but rather will remain in its ionic form in the solution. The chemical

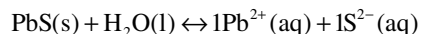
equation can be adjusted to show these changes by adding in the subscripts, (s) for a solid and (aq) for an aqueous solution.



Since the Na^+ and NO_3^- ions do not interact in the solution, they are considered spectator ions and will not play any part in the equilibrium reaction. As a result, they can be removed from the chemical equation so that only the reacting ions will be included when the K_{sp} is written.



Once you have determined the chemical equation for the formation of a solid precipitate, you can reverse the reaction to write the K_{sp} according to the convention of the salt dissolving. This relationship can then be used to determine the concentrations of lead and sulfide ion necessary to precipitate PbS. Tables of K_{sp} values can be found in the appendix of your text book.

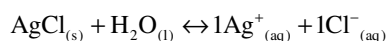


$$K_{\text{sp}} = [\text{Pb}]^1[\text{S}]^1$$

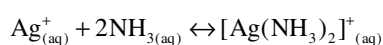
Complex Formation

Complexes are soluble compounds that form in aqueous solutions that can often increase the solubility of an insoluble salt. They are formed from a cation that surrounds itself with either negatively charged anions, or molecules, such as water or ammonia that have one or more pairs of electrons that become attracted to the positively charged cation. These anions or molecules are referred to as ligands when forming a complex with the metal cation. Commonly used ligands are water and ammonia molecules and anions such as hydroxide, chloride, thiosulfate and cyanide.

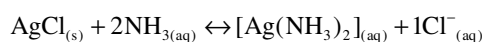
In terms of solubility the formation of a complex lowers the concentration of the cation in the solution, and if a precipitate containing that cation is present, will begin to dissolve the precipitate by pulling the cation out of the solid salt and forcing the anion into the solution. The chemical equations and equilibrium constants are given below for the example of solid silver chloride, AgCl, dissolving first in water and then in an ammonia solution. Note that first the solid dissolves, so only the K_{sp} is involved. The second equation would be for an already soluble silver ion put into an ammonia solution, the anion is not involved. The final equation involves actually dissolving some of the precipitate due to using up the silver ion that is produced due to the equilibrium of the silver chloride in water (first equation). As a result, the equilibrium constant, K_{c} , associated with the solid silver chloride dissolving is a between the equilibrium of the silver chloride dissolving and then the equilibrium that results when the silver ion reacts with the ammonia to remove it from solution. Note that in the final K_{c} equation, no silver ion is associated with the equilibrium. In this case, all of the silver ion dissociated from the salt is used up by the ammonia, leaving only the chloride ion free in solution.



$$K_{\text{sp}} = [\text{Ag}]^1[\text{Cl}]^1$$



$$K_{\text{f}} = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}]^1[\text{NH}_3]^2}$$

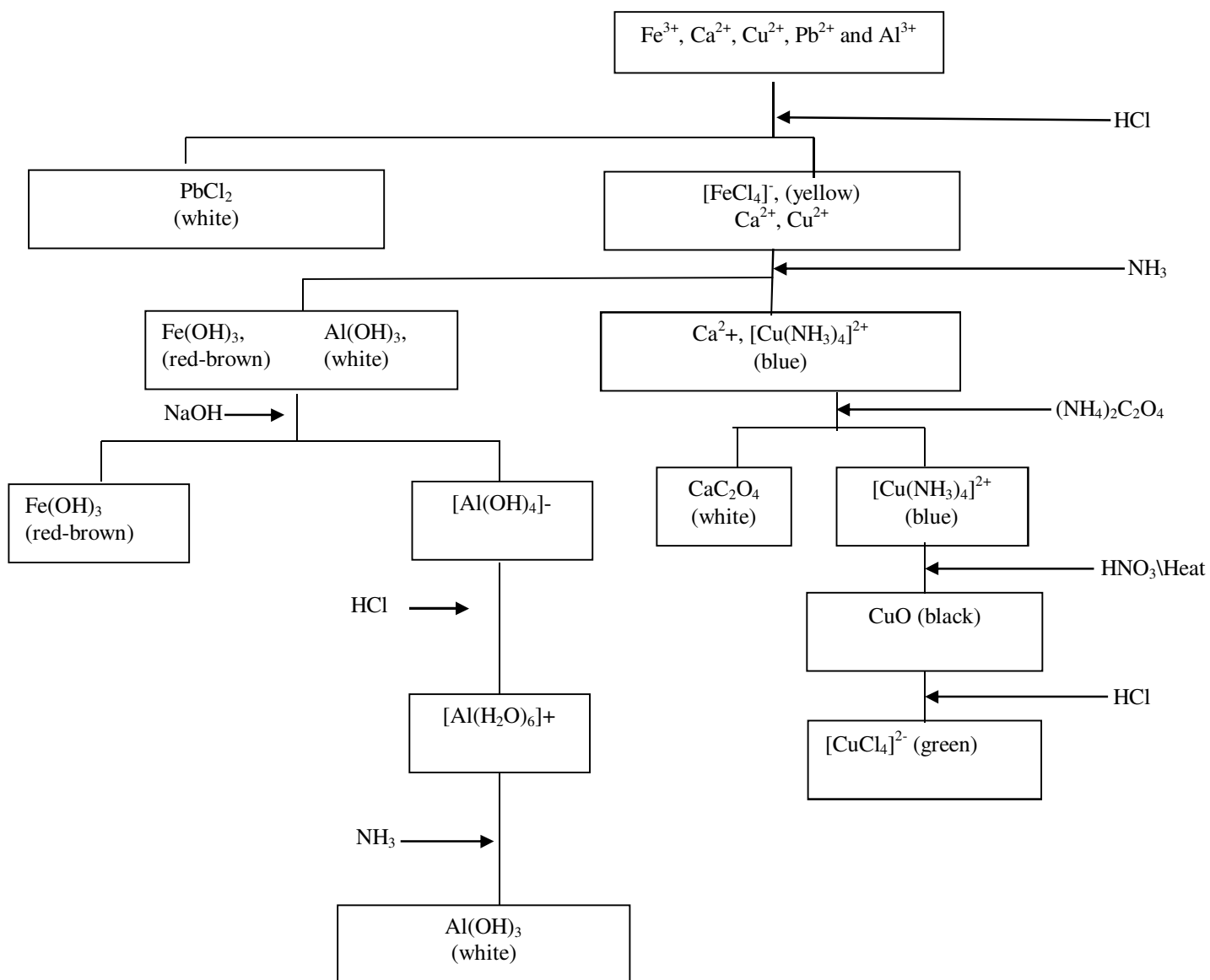


$$K_{\text{c}} = K_{\text{sp}} \times K_{\text{f}} = \frac{[\text{Ag}(\text{NH}_3)_2]^+[\text{Cl}^-]}{[\text{NH}_3]^2}$$

In Your Lab...

In this experiment, you will start with an standard aqueous solution of 5 different cations all with nitrate as an anion, thus all the cations are soluble. The solution is acidified with nitric acid to keep the ions from precipitating. You will also have a test solution containing between 2 and 5 of the same cations that are in the standard solution. You will then add different reagents that will cause precipitation or complexation of other ions that will allow you to separate the 5 ions in the solution. Your results will be based on your observations during these separations. The color of the precipitate or solution, as well as the type of precipitate, solid, fluffy, etc. can be used to identify each of the ions in the original solutions. Be sure to list all observations in your laboratory notebook and use the flow chart on the following page to follow what is happening to each cation at each stage during the experiment.

Flow Chart of Cation Separation



Experimental Procedure

Your TA must sign your data before leaving lab or you will not receive credit for attending the lab. One person will do the test sample and the other the standard sample. Do these tests simultaneously to observe the results.

Part 1: Sample Preparation

1. In a small test tube, obtain 10 drops of a solution that is 0.1M in each of the standard cation mixture.
2. In a second test tube, obtain 10 drops of one of the test sample solutions. The test sample contains between 2 and 5 of these cations.
3. Apply the following instructions to both test tubes and then determine which cations are present in your test sample based on the precipitation and complexation results.

Part 2: Separation of Pb^{2+}

**Goals: Formation of Soluble Chloride Complex, $[\text{FeCl}_4]^-$,
Precipitation of Insoluble Chloride, PbCl_2**

1. Add 10 drops of 6M HCl. Stir thoroughly with a spatula. Solution should turn yellow due to the formation of $[\text{FeCl}_4]^-$ with a white precipitate.
2. Centrifuge for 2 minutes to separate the precipitate from the liquid. The white precipitate is PbCl_2 and is considered a positive test for Pb^{2+} .
3. Record all observations on data sheet.
4. Decant the solution containing the Fe^{3+} , Ca^{2+} , Cu^{2+} and Al^{3+} ions into a clean test tube.
5. Label test tube containing liquid " Fe^{3+} , Ca^{2+} , Cu^{2+} and Al^{3+} " and set aside.
6. Discard solid PbCl_2 into waste container and rinse out the test tube with distilled water.

Part 3: Separation of Fe^{3+}

**Goals: Formation of Soluble Ammonia Complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}$
Precipitation of Insoluble Hydroxides, $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$
Formation of Soluble Hydroxide Complex, $[\text{Al}(\text{OH})_4]^-$**

1. Add 6M NH_3 dropwise to the test tube containing " Fe^{3+} , Ca^{2+} , Cu^{2+} and Al^{3+} " until the solution is no longer acidic. Test with blue litmus paper after each drop is added. Count the drops as you add them.
2. Add the same number of drops of 6M NH_3 again to make a basic buffered solution.
3. Mix solution well.
4. Centrifuge the test tube and contents for 2 minutes. You should have a clear blue liquid, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and Ca^{2+} , and a brown precipitate containing $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$.
5. Record all observations on data sheet.
6. Decant supernatant liquid containing Ca^{2+} , Cu^{2+} into a clean test tube. Label test tube containing liquid " Ca^{2+} , Cu^{2+} " and set aside.
7. Rinse the precipitate with 10 drops of distilled water.
8. Centrifuge 2 minutes and decant the rinse liquid into the waste container.
9. Add 6 drops of 6M NaOH to the precipitate.
10. Stir thoroughly and centrifuge 2 minutes.

- Decant the supernatant liquid into a test tube and label $[\text{Al}(\text{OH})_4]^-$ and set aside.
- Add 3 drops of 6M HCl to the remaining brown precipitate. Precipitate should dissolve, leaving a yellow solution of $[\text{FeCl}_4]^-$. If the brown precipitate does not dissolve add a few more drops of 6M HCl until it does.
- Both the brown precipitate and the yellow solution are positive tests for Fe^{3+} .
- Discard $[\text{FeCl}_4]^-$ in the waste container.

Part 4: Separation of Al^{3+}

Goal: Precipitation of Insoluble Hydroxide, $\text{Al}(\text{OH})_3$

- Add 6M HCl dropwise to the supernatant liquid containing $[\text{Al}(\text{OH})_4]^-$ until it tests acidic to pH paper.
- Add 6M NH_3 solutions dropwise until basic to pH paper.
- Centrifuge for 2 minutes.
- A white precipitate is a positive test for the Al^{3+} ion.
- Record all observations on data sheet.
- Discard solution and precipitate in waste container.

Part 5: Separation of Ca^{2+}

Goal: Precipitation of Insoluble Oxalate, CaC_2O_4

- Add 3 drops of 0.5M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution to the test tube labeled " Ca^{2+} , Cu^{2+} " and stir thoroughly.
- Centrifuge test tube for 2 minutes. You should have a blue liquid ($\text{Cu}(\text{NH}_3)_4^{2+}$) and a white solid (CaC_2O_4). The white solid is a positive identification for Ca^{2+} .
- Record all observations on data sheet.
- Decant supernatant liquid containing $\text{Cu}(\text{NH}_3)_4^{2+}$ into a clean test tube. Label test tube containing liquid " Cu^{2+} " and set aside.
- Discard solid CaC_2O_4 into waste container.

Part 6: Positive identification of Cu^{2+} :

**Goal: Formation of Soluble Chloride Complex, $[\text{CuCl}_4]^{2-}$
Precipitation of Insoluble Oxide, CuO**

- Transfer solution in the test tube labeled " Cu^{2+} " to a 50 mL beaker
- In the fume hood, heat contents to dryness on a hot plate.
- Cool beaker and contents for 5 minutes.
- Add 6 drops of concentrated HNO_3 and heat in the fume hood until the precipitate begins to blacken. This black precipitate is CuO and is a positive test for Cu^{2+} .
- Cool beaker and contents for 5 minutes.
- Add 6 drops of 6M HCl to dissolve CuO residue
- Transfer green solution (CuCl_4^{2-}) to clean test tube. The green solution is a positive test for Cu^{2+} .
- Record all observations.
- Discard solution into waste container.

Laboratory Data

Create a table for observations for each part of the experiment. Record the following observations during lab in pen. You need to record observations for both the test solution and the standard.

Color of any precipitate or solution, cloudiness of solution, type of precipitate, granular, fluffy, etc.

Phase, solid, liquid or gas produced

Tentative formula and name of ions or precipitates formed during a particular step of the reaction.

You may need more than a 1 line description for a multi-step separation

Include the **signed** copy of this data when you turn in your lab report.

Laboratory Results

Create a table with the following data that conclusively identifies the presence or absence of each cation in your test solution. If the cation is not present, list no change under the observation.

Example:

<u>Cation:</u>	<u>Procedure</u>	<u>Observation</u>	<u>Compound produced</u>
Pb ²⁺	Addition of HCl	White solid	PbCl ₂ (s)

Calculations

There are no calculations necessary for this lab report.

Consolidate your observations into a table for each section with a short comparative description between the cation standard solution and your test solution.

Include for each part whether the cation associated with that section of the experiment is present or absent based on your observations. If the test is inconclusive, (does not show positive in the standard solution), state that your results for that cation are inconclusive.

Discussion Questions

You must use your data to answer these questions. If the answer you give does not reflect YOUR data and results, you will receive no credit for the question.

1. What cations were present in your test solution? Describe the observations you used to determine the presence or absence of each of the 5 possible cations.
2. Write the chemical equations describing the equilibrium in water of $\text{Fe}(\text{OH})_3$ and $[\text{FeCl}_4]^-$. These will be 2 different chemical equations.
3. The concentration of aluminum ion in the test solution was 0.10M. Using the K_{sp} given in your textbook for aluminum (III) hydroxide, calculate the concentration of hydroxide needed to precipitate aluminum hydroxide. From the concentration of the hydroxide, calculate the pH of the solution needed to cause precipitation of aluminum hydroxide.
4. If excess hydroxide is added to the solution in question 3, a complex will form that will dissolve the solid aluminum hydroxide, $\text{Al}(\text{OH})_3$. Write the chemical equation that would be associated with the complex that will form from adding additional sodium hydroxide solution to solid $\text{Al}(\text{OH})_3$.
5. PbCl_2 is approximately 3 times more soluble in hot water than in cold water. What observation could be seen after the addition of the HCl solution and the PbCl_2 precipitate if the solution was heated to boiling?