EXPERIMENT 4

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.

Sometimes adding a second chemical to a solution can cause the precipitate to dissolve. **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.

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

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.

$$M_xB_y\text{ (s)} + \text{H2O(l)} \leftrightarrows x\text{M+(aq)} + y\text{B}^-\text{(aq)}$$

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.

$$\text{Pb(NO}_3\text{)}_2\text{(aq)} + \text{Na}_2\text{S (aq)} \leftrightarrows \text{PbS (s)} + \text{NaNO}_3\text{ (aq)}$$

Next balance the equation:

$$\text{Pb(NO}_3\text{)}_2\text{(aq)} + \text{Na}_2\text{S (aq)} \leftrightarrows \text{PbS (s)} + 2\ \text{NaNO}_3\text{ (aq)}$$

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

Always soluble	Ammonium (NH_4^+)	Always soluble
	Hydrogen ion (H^+)	Always soluble
	Alkali Metal (group 1A)	Always soluble
	Nitrate (NO_3^-)	Always soluble
	Perchlorate (ClO_4^-)	Always soluble
	Acetate ($C_2H_3O_2^-$)	Always soluble

Sometimes soluble	Halide (Cl^-, Br^-, I^- & F^-)	Soluble except: Pb^{2+}, Hg_2^{2+}, Hg^{2+}, Ag^+, Cu^+
	Sulfate (SO_4^{2-})	Soluble except: : Pb^{2+}, Hg_2^{2+},Ba^{2+}, Ca^{2+},Sr^{2+}

Sparingly	Sulfide (S^{2-})	Soluble if cation is soluble
Soluble	Hydroxide (OH^-)	Soluble if cation is soluble
(Insoluble)	Oxide (O^{2-})	Soluble if cation is soluble
	Carbonate (CO_3^{2-})	Soluble if cation is soluble
	Phosphate (PO_4^{3-})	Soluble 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.

$$Pb(NO_3)_2(aq) + Na_2S\ (aq) \leftrightarrows \mathbf{PbS\ (s)} + 2\ NaNO_3\ (aq)$$

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.

$$PbS\ (s) \leftrightarrows Pb^{2+}(aq) + S^{2-}\ (aq)$$

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. These Ksp values and expressions can be used to solve for the concentrations of ions in a saturated solution.

$$PbS\ (s) \leftrightarrows Pb^{2+}(aq) + S^{2-}\ (aq) \qquad K_{sp} = [Pb^{2+}][S^{2-}]$$

Complex Formation and K_f

The equilibrium constant associated with a complex is called a **formation constant** and uses the symbol, **K_f.** The format for writing a chemical equation for K_f is defined by the complex that is formed. The reactants will always be a single metal cation + however many ligands are needed to make the complex. The product is always 1 mole of the complex. An example is given below for $[Ag(NH_3)_2]^+$.

$$Ag^+_{(aq)} + 2NH_{3(aq)} \leftrightarrow [Ag(NH_3)_2]^+{}_{(aq)} \qquad K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+]^1[NH_3]^2}$$

In terms of solubility the formation of a complex lowers the concentration of the free cation in the solution. 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. As with all equilibrium reactions, it you add chemical equations together to get a final equation, you need to multiply the equilibrium constants. 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.

$$AgCl_{(s)} + H_2O_{(l)} \leftrightarrow 1Ag^+{}_{(aq)} + 1Cl^-{}_{(aq)} \qquad K_{sp} = [Ag^+]^1[Cl^-]^1$$

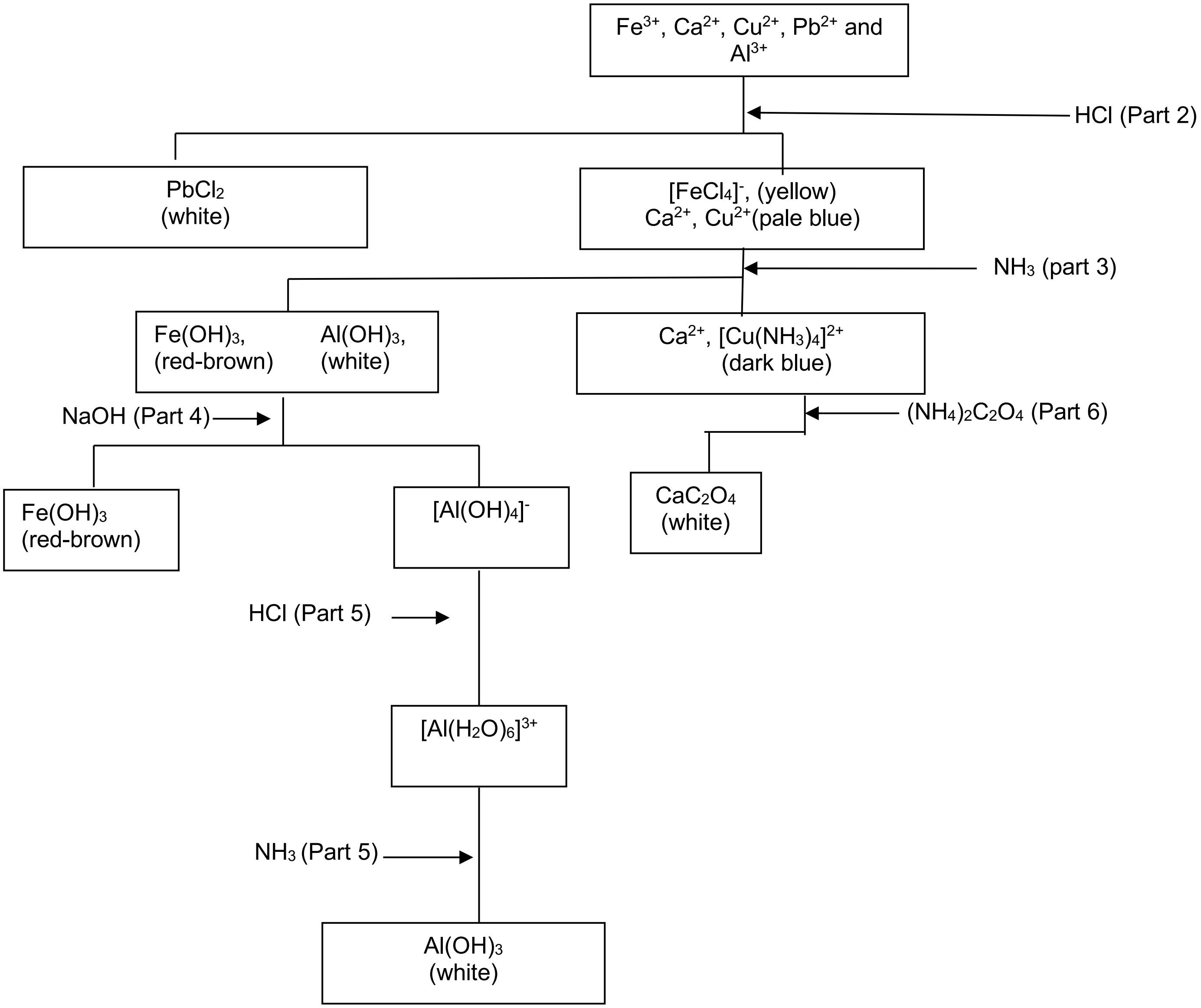
$$Ag^+_{(aq)} + 2NH_{3(aq)} \leftrightarrow [Ag(NH_3)_2]^+{}_{(aq)} \qquad K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+]^1[NH_3]^2}$$

$$AgCl_{(s)} + 2NH_{3(aq)} \leftrightarrow [Ag(NH_3)_2]_{(aq)} + 1Cl^-{}_{(aq)} \qquad K_c = K_{sp} x\ K_f = \frac{[Ag(NH_3)_2]^+[Cl^-]}{[NH_3]^2}$$

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 data and use the flow chart on the following page to follow what is happening to each cation at each stage during the experiment. You will not be given this flow chart on your concept review but will be expected to generate it based on the procedures and your data.

Flow Chart of Cation Separation



Experiment 4: Prelab Worksheet
Submit via Brightspace before coming to lab

Name: ______________________________ Date: ________ Section: ________ Grade: ________

Record all values with the correct number of significant figures and units.
Place all answers on the line next to the question.
Show calculations for any numerical answers.
See any 114 TA via webex before your prelab is due if you have any questions.

1. What is the pH of a 3.0M solution of HCl?

2. Write the K_{sp} expression for aluminum hydroxide

3. Calculate the concentration of aluminum in a saturated solution of aluminum hydroxide. The K_{sp} of aluminum hydroxide is $1x10^{-33}$.

4. Write the K_f expression for the aluminum tetrahydroxide ion.

5. Calculate K_c for the aluminum tetrahydroxide ion created from a saturated solution of aluminum hydroxide and 1.0M sodium hydroxide. The K_f for aluminum tetrahydroxide is $3x10^{33}$ and the K_{sp} for aluminum hydroxide is $1.9x\ 10^{-33}$. Show the chemical equation associated with this reaction.

6. Write the chemical reactions associated with adding NH_3 to a solution containing iron. This will be a 2-step process that results in a red-brown precipitate of $Fe(OH)_3$. The first step involves the base dissociating in water (chemical equation for K_b) and the second is the hydroxide reacting with the iron ion.

7. What color is the solution if you add HCl to a solution containing iron?

8. Give the chemical formula for each of the complexes formed in this experiment

9. Give the chemical formula for each of the precipitates formed in this experiment.

10. If you have a green test solution, what cations could you guess are probably present?

Experiment 4: Experimental Procedures and Data Sheet
Submit via Brightspace as part of Informal Report

Name: ______________________________ Date: ________ Section: ________

TA Signature: __________________________

All data must be written in pen at the time it is collected. **Pencil is not allowed!!**
Record all measurements with the correct number of significant figures and units.
TA signature and TA initials on any changes made to the data must be present or your data is invalid

Part 1: Sample Preparation

1. In a small test tube, 1 lab partner obtains 10 drops of a solution of the standard cation mixture.

2. In a second test tube, the other lab partner obtains 10 drops of one of the test sample solutions. The test sample contains between 2 and 5 of these cations. Record the code of the test sample on the data sheets of both partners.

Test Sample Code: __________________

3. Each lab partner should 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. Do each step together and compare the test tubes at each step to be sure you are doing the experiment correctly.

Part 2: Separation of Pb^{2+}

Goals: Formation of Soluble Chloride Complex, $[FeCl_4]^-$,
Precipitation of Insoluble Chloride, $PbCl_2$

1. Add 10 drops of 6M HCl. Stir thoroughly with a spatula. The standard solution should turn yellow due to the formation of $[FeCl_4]^-$ 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+}.The K_{sp} for $PbCl_2$ is very dependent on temperature, so if no precipitate is seen at room temperature, cool the test tubes in a cold water bath to confirm no lead is present in the test solution. The K_{sp} for lead chloride is significantly lower at cooler temperatures.

3. Decant the solution containing the Fe^{3+}, Ca^{2+}, Cu^{2+} and Al^{3+} ions into a clean test tube.

4. Label test tube containing liquid "Fe^{3+}, Ca^{2+}, Cu^{2+} and Al^{3+}" and set aside.

5. Discard solid $PbCl_2$ into waste container and rinse out the test tube with distilled water.

	Standard cation mixture	Test sample
Color of liquid:	__________________	________________
Color of precipitate:	__________________	________________

Part 3: Precipitation of Fe^{3+} and Al^{3+} from complex formation of Cu^{2+}

Goals: Formation of Soluble Ammonia Complex, $[Cu(NH_3)_4]^{2+}$
Precipitation of Insoluble Hydroxides, $Fe(OH)_3$ and $Al(OH)_3$

1. Add 6MNH_3 dropwise (it usually takes approximately 10-20 drops) 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, $[Cu(NH_3)_4]^{2+}$ and Ca^{2+}, and a brown precipitate containing $Fe(OH)_3$ and $Al(OH)_3$. Record observations below.

	Standard cation mixture	Test sample
Color of liquid:	___________________	_________________
Color of precipitate:	___________________	_________________

Part 4: Identification of Fe^{3+}

Goals: Precipitation of Insoluble Hydroxides, $Fe(OH)_3$
Formation of Soluble Hydroxide Complex, $[Al(OH)_4]^-$

1. Decant the blue supernatant liquid containing Ca^{2+}, Cu^{2+} into a clean test tube. Label test tube containing liquid “Ca^{2+}, Cu^{2+} and set aside.

2. Rinse the precipitate with 10 drops of distilled water.

3. Centrifuge 2 minutes and decant the rinse liquid into the waste container.

4. Add 6 drops of 6M NaOH to the precipitate.

5. Stir thoroughly and centrifuge 2 minutes.

6. Decant the supernatant liquid into a test tube and label $[Al(OH)_4]^-$ and set aside.

5. Add 3 drops of 6M HCl to the remaining brown precipitate. The precipitate should dissolve, leaving a yellow solution of $[FeCl_4]^-$. If the brown precipitate does not dissolve add a few more drops of 6M HCl until it does. Discard $[FeCl_4]^-$ in the waste container after recording observations.

7. Both the brown precipitate and the yellow solution are positive tests for Fe^{3+}. Record observations.

	Standard cation mixture	Test sample
Color of liquid:	___________________	_________________
Color of precipitate:	___________________	_________________

Part 5: Identification of Al^{3+}

Goal: Precipitation of Insoluble Hydroxide, $Al(OH)_3$

1. Add 6M HCl dropwise to the supernatant liquid containing $[Al(OH)_4]^-$ until it tests acidic to pH paper.
2. Add 6M NH_3 solutions dropwise until basic to pH paper.
3. Centrifuge for 2 minutes.
4. A white precipitate is a positive test for the Al^{3+} ion. Record observations.

	Standard cation mixture	Test sample
Color of liquid:	____________________	__________________
Color of precipitate:	____________________	__________________

5. Discard solution and precipitate in waste container.

Part 6: Identification of Ca^{2+}

Goal: Precipitation of Insoluble Oxalate, CaC_2O_4

1. Add 3 drops of 0.5M $(NH_4)_2C_2O_4$ solution to the test tube labeled “Ca^{2+}, Cu^{2+}” and stir thoroughly.
2. Centrifuge test tube for 2 minutes. You should have a blue liquid ($Cu(NH_3)_4{}^{2+}$) and a white solid (CaC_2O_4). The white solid is a positive identification for Ca^{2+}. Record observations.

	Standard cation mixture	Test sample
Color of liquid:	____________________	__________________
Color of precipitate:	____________________	__________________

3. Decant supernatant liquid containing $Cu(NH_3)_4{}^{2+}$ into a clean test tube. Label test tube containing liquid “Cu^{2+}” and set aside.
4. Discard solid CaC_2O_4 into waste container.

Grading

Points

Neatness and Clarity of Data	5pts	___________pts
Significant figures and units	5pts	___________pts
All data is present	10pts	___________pts

Deductions (sliding based on TA discretion)

Lab area left unclean	20pts	___________pts
Improper waste disposal	20pts	___________pts
Disruptive behavior	20pts	___________pts
Other: ____		___________pts

Grade for Experimental Procedures and Data ________pts

Experiment 4: Results Table
Submit via Brightspace as part of Informal Report

Name: ____ Date: ________ Section: ________

Record all results with the correct number of significant figures and units

Part 2 **Addition of HCl**

Results	Standard sample (Liquid)	Standard sample (Precipitate)	Test sample (Liquid)	Test sample (Precipitate)
Presence and color of solid (write "none" if no solid)				
Color of liquid				
Possible product(s)				
Cation(s) present				

Part 3 **Addition of NH_3**

Results	Standard sample (Liquid)	Standard sample (Precipitate)	Test sample (Liquid)	Test sample (Precipitate)
Presence and color of solid (write "none" if no solid)				
Color of liquid				
Possible product(s)				
Cation(s) present				

Part 4 **Addition of NaOH**

Results	Standard sample (Liquid)	Standard sample (Precipitate)	Test sample (Liquid)	Test sample (Precipitate)
Presence and color of solid (write "none" if no solid)				
Color of liquid				
Possible product(s)				
Cation(s) present				

Part 5 **Addition of HCl**

Results	Standard sample (Liquid)	Standard sample (Precipitate)	Test sample (Liquid)	Test sample (Precipitate)
Presence and color of solid (write "none" if no solid)				
Color of liquid				
Possible product(s)				
Cation(s) present				

Part 6 **Addition of $(NH_4)_2C_2O_4$**

Results	Standard sample (Liquid)	Standard sample (Precipitate)	Test sample (Liquid)	Test sample (Precipitate)
Presence and color of solid (write "none" if no solid)				
Color of liquid				
Possible product(s)				
Cation(s) present				

Final Results **Test Sample Code:**

Cation	Present	Present	Absent	Absent
Lead				
Iron				
Aluminum				
Copper				
Calcium				

Calculations

There are no calculations necessary for this lab report but you should be able to use K_{sp} and K_f values to solve equilibrium problems similar to those in the prelab.

Grading

Points

Significant figures and units	5pts	__________pts
Table is neat and legible	5pts	__________pts
All results are present	10pts	__________pts

Deductions (sliding based on TA discretion)

Results do not make sense	20pts	__________pts
Results do not match data	20pts	__________pts
Other: ______________________________________		__________pts

Plagiarism!!! Results are identical to another student 100pts __________pts

Grade for Results Table ________pts

Experiment 4 Questions:
Submit as part of your Informal Report

1. The K_{sp} of aluminum hydroxide is $1.8\text{x}10^{-5}$.
   a.) If you have a saturated solution of $Al(OH)_3$ with an equilibrium concentration of Al^{3+} equal to 0.0045M, what is the concentration of OH^- ions? Show all work for your calculation.

   Answer: ________________

   b.) Write the balanced chemical equation describing the equilibrium that results when $Al(OH)_3$ is added to water. Include the phases of all chemicals in the equation.

   c.) Write the K_{sp} expression associated with $Al(OH)_3$.

2. Identify which cations were present in your solution and which were not present in your solution. For each cation, briefly explain how you knew that it was/was not present. Include the code for your test sample in your answer.

3. a.) Write the chemical equation for the process of dissolving solid $CuCO_3$ ($K_{sp} = 1.4x10^{-10}$) in a 1.5M solution of ammonia to form the $Cu(NH3)_4^{2+}$ complex ($K_f = 1.1x10^{13}$). Include all of the phases in your equation.

b.) Write the equilibrium expression for this process.

d.) Calculate the equilibrium constant for the overall reaction.

Answer: ________________

4. a.) What is the molar solubility of $PbCl_2$ ($K_{sp} = 1.6x10^{-5}$)?

Answer: ________________

b.) What is the molar solubility of $PbCl_2$ ($K_{sp} = 1.6x10^{-5}$) in a 0.250M solution of NaCl?

Answer: ________________

c.) What is the solubility of $PbCl_2$ ($K_{sp} = 1.6x10^{-5}$) in a 0.250M solution of $Pb(NO_3)_2$?

Answer: ________________