6 Qualitative Analysis I: Cations I

Version: February 22, 2005

- **Apply acid-base, solubility, and complex ion equilibrium principles to the identification of cations in solution.**
- **Learn some of the descriptive chemistry of some common cations.**

DISCUSSION

In Experiment 5, you learned how to separate mixtures of ions in solution, and you saw how reagents can be used to produce colored solutions or precipitates when certain ions are present. Using such techniques to determine what components are present in a sample is called qualitative analysis. This experiment and four of the five remaining experiments are devoted to qualitative analysis.

Historically, most qualitative analysis was done at a lab bench, with beakers, test tubes, centrifuges, etc. In recent years, however, sophisticated instruments have been developed which are more sensitive, more accurate, and more efficient than most of the old "wet chemistry" techniques. Many of you will become familiar with these instrumental techniques as you continue your education. There is still much value in doing the outdated "wet chemistry," however, because as you do these experiments you will see many examples of acid-base, solubility, oxidation-reduction, and complex ion equilibria, and you will learn some descriptive chemistry of the elements as you determine the composition of solutions given to you for analysis.

This experiment and Experiment 7 focus on the analysis of some common cations. Experiments 9 and 10 will teach you how to detect the presence of several common anions in solution. Then, in Experiment 11, you will be given an ionic solid and will be asked to determine the cations and anions present in the solid. As you do these experiments, look for examples of the equilibrium principles you are studying in the lecture portion of the course.

The cations to be studied include some common alkali metals (Na^+ and K^+) and some alkaline earth metals (Mg^{2+}, Ca^{2+}, and Ba^{2+}), along with Zn^{2+}, Al^{3+}, and NH_4^+. These ions are not colored in solution, and most of their compounds are white. It is impossible therefore to use colors of solutions or precipitates (as you did in the last experiment) to indicate which of these cations is present in solution. Instead, in this experiment, you will use differences in solubilities to separate the cations from each other. Na^+, K^+, and NH_4^+ ions form very few insoluble compounds. Experiment 7 will illustrate other techniques for identifying these cations.

If you will take a moment to review the solubility rules you have learned, you will realize that the sulfates of the cations listed above are all soluble, with the exception of barium sulfate. Calcium sulfate is slightly soluble and will not precipitate under the conditions of this experiment. Thus adding sulfate to a mixture of these cations will allow you to detect barium and remove it from solution.

Four of the other cations form insoluble hydroxides. (Calcium hydroxide is slightly soluble, but will precipitate in a strongly basic solution.) Two of these, however, are amphoteric and will dissolve in a strongly basic solution to form complex ions (see Experiment 5). By making the solution strongly basic, then, two of the remaining cations will precipitate, while two more will be converted to complex ions. The two which precipitate can be separated due to differences in the solubilities of their oxalates. One of them will precipitate when ammonium oxalate is added. The other will then be precipitated by adding NaH_2PO_4*(aq)*.

The solution containing the complex ions will then be acidified, then neutralized with NH_3*(aq)*. In this weakly basic solution one of the amphoteric hydroxides will precipitate, while the other forms a complex ion with NH_3*(aq)*. Finally, this last cation is precipitated with sulfide ion.

PROCEDURE

1. Preliminary Observations

Into five small test tubes, place 2 mL samples of 0.1 *M* aqueous solutions of salts of Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+} and Al^{3+}. Use nitrates or chlorides. Test each solution to see if it is acidic, basic, or neutral by transferring a drop to some red and blue litmus paper with a stirring rod. Red litmus turns blue in basic solution (above about pH 8), blue litmus turns red in acidic solution (below about pH 5), and neither will change color if the solution is close to neutral (between about pH 5 and 8). Record your observations on the report. Although some of the solutions will be acidic due to hydrolysis of the cations, not all of them will be acidic enough to change the color of litmus paper.

a. Add to each test tube 1 drop of 1 *M* Na_2SO_4*(aq)*. Write the formula for the precipitate on the report.

b. To each of the four remaining test tubes, add 1 mL of 6 *M* NaOH*(aq)* and stir well. Refer to Experiment 5, if necessary, and write the formulas of the products on the report (two precipitates and two complex ions). Save the two test tubes containing complex ions for part ***e***.

c. Centrifuge the two test tubes containing precipitates, and discard the solution in each of these tubes. Notice the appearance of the two precipitates. Dissolve each with ½ mL of 6 *M* HCl*(aq)*. If the precipitate doesn't dissolve completely, add more HCl, a drop at a time with stirring, until it does. Then add 6 *M* NH_3*(aq)* a drop at a time until the solution is slightly basic. If a precipitate forms, add 1 *M* HCl*(aq)* dropwise until it just dissolves. (You will need to prepare your own 1 *M* HCl*(aq)* by dilution of 6 *M* HCl*(aq)* in your 10 mL graduated cylinder. Mix well before using.) Add 1 drop of 0.25 *M* $(NH_4)_2C_2O_4$*(aq)* to each test tube. Write the formula of the precipitate on the report.

d. To the test tube from Part ***c*** where no precipitate formed with ammonium oxalate, add 2 drops of 6 *M* NH_3*(aq)* and a few drops of 0.1 *M* NaH_2PO_4*(aq)*. The precipitate, which may form slowly, has the formula $\mathbf{M}NH_4PO_4$, where **M** is the metal ion. Write the formula of the precipitate on the report.

e. To the two test tubes from Part **b** containing complex ions, add 1.5 mL of 6 *M* HCl*(aq)*. Test with litmus paper. If any precipitate remains, or if the solutions are not distinctly acidic, add more HCl until any precipitate present is dissolved and the solutions are acidic. Then add 6 *M* NH_3*(aq)* (at least 1 mL) until the solutions are distinctly basic and have a strong odor of ammonia. Stir well. Write the formula of the precipitate on the report. In the other test tube a new complex ion has been formed. Write its formula on the report. (Refer to Experiment 5 if necessary.)

f. Finally, add several drops of 0.1 *M* Na_2S*(aq)* to the last test tube. Write the formula of the precipitate on the report. Discard the contents of this test tube in the small sink under the hood. In contact with acid in the drains, H_2S*(g)* (rotten egg gas) is formed, which is not only unpleasant but poisonous.

- **CAUTION: Barium compounds are very toxic. Avoid skin contact with all chemicals in the lab, but be especially careful to avoid contact with solutions containing barium compounds.**
- **CAUTION: Remember to wear safety glasses at all times in the lab. You will be working with 6 *M* NaOH *(aq)* and 6 *M* HCl*(aq)*, both of which are corrosive and can damage eyes quickly.**

2. Preparation of the Flowchart

On the second page of the lab report is a flowchart which summarizes the procedures to be followed in analyzing an unknown solution containing any of the cations studied above. Before starting the analysis of the unknown solutions, fill out the flowchart by referring to your preliminary observations and by studying the procedure below. When the flowchart is filled out, have it initialed by the lab instructor before proceeding.

3. Analysis of the Unknowns

Obtain two test tubes at the stockroom window containing unknown solutions. (Leave two of your clean test tubes in their place). These solutions contain one or more of the cations studied in the preliminary observations. Immediately record the unknown numbers on the report. Proceed as outlined below, referring to the flowchart and recording your observations and conclusions on the report. Doing both unknowns at the same time will save time, providing you label your test tubes.

Mix each unknown thoroughly before beginning the analysis. It may have been prepared by combining solutions of the different cations, so you need to make sure it is a uniform mixture. Check the unknowns with litmus paper before beginning the analysis. Draw any conclusions you can about the presence or absence of certain ions.

a. To a 2 mL sample of your unknown in a small test tube, add 1 drop of 1*M* Na_2SO_4*(aq)*. If no precipitate forms, continue with part *b*. If a precipitate forms, add an additional ½ mL Na_2SO_4*(aq)*. Centrifuge the solution. Test for completeness of precipitation by adding another drop of sodium sulfate. If necessary, continue to add the reagent until no more precipitate forms, then centrifuge again. Discard the precipitate and proceed to Part ***b*** with the solution. (Unless otherwise directed, always make sure precipitation reactions are complete before centrifuging and separating the precipitate from the solution.)

b. To the solution from Part ***a*** add ½ mL 6 *M* NaOH*(aq)* and stir well. If there is no precipitate, proceed to part *e*. If there is a precipitate, add another 1 mL NaOH*(aq)* and stir. If the precipitate redissolves, proceed to Part ***e***. If it doesn't redissolve, centrifuge, decant, and save the solution for Part ***e***. Proceed to part ***c*** with the precipitate.

c. Add ½ mL 6 *M* HCl*(aq)*, or more as needed, to dissolve the precipitate. Then add 1 mL of water, then 6 *M* NH_3*(aq)*, dropwise, until the solution is just basic. (If a precipitate forms at this point, the solution is too basic. Add 1 *M* HCl*(aq)* dropwise with stirring until the precipitate just dissolves.) Then add 3 drops of 0.25 *M* $(NH_4)_2C_2O_4$*(aq)*. If a precipitate forms, add 1 mL or more as needed to complete the precipitation. Centrifuge and discard the precipitate.

d. To the solution add 2 drops of 6 *M* NH_3*(aq)* and ½ mL of 0.1 *M* NaH_2PO_4*(aq)*. If no precipitate forms immediately, warm the test tube in hot water for a few minutes.

e. To the solution from Part ***b***, add 6 *M* HCl*(aq)* until it is distinctly acidic and any precipitate formed has redissolved. Then add 6 *M* NH_3*(aq)* (at least 1 mL) until the solution is distinctly basic and has a strong odor of ammonia. Centrifuge and discard any precipitate.

f. To the solution from Part ***e***, add several drops of 0.1 *M* Na_2S*(aq)*. Dispose of the contents of this test tube in the sink under the hood.

4. Confirming the Analysis

Now that you have some results for your unknowns, it is wise to doublecheck them. Prepare solutions that match the suspected composition of your unknowns by mixing equal volumes of the reagents you used in Part 1. Then repeat Part 3 with the knowns, comparing the results with your recorded observations and conclusions for your unknowns. If there are discrepancies, repeat the analysis with your unknowns.

6 Qual Analysis I: Cations I

Name ______________________________
Section __________________Locker ____
Instructor ___________________________

Preliminary Observations

Which solutions are acidic to litmus?	
Which solutions are basic to litmus?	

Explain why some salt solutions are not neutral.

Write the formulas of the products in the spaces provided.

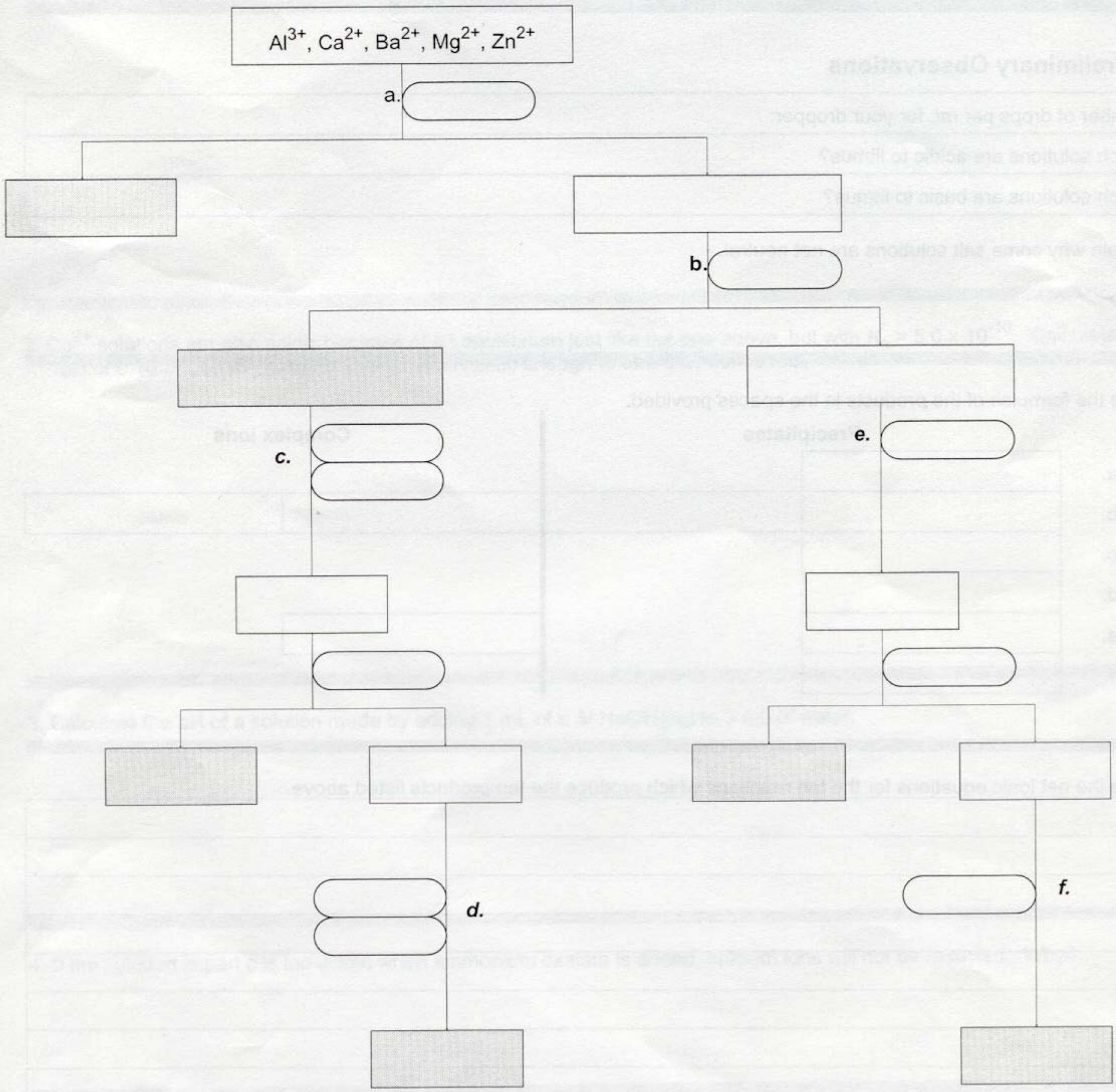
	Precipitates		Complex ions	
a.				
b.				
c.				
d.				
e.				
f.				

Write the net ionic equations for the ten reactions which produce the ten products listed above.

1.
2.
3.
4.
5.
6.
7.
8.
9
10.

Preparation of Flowchart

Each branch indicates the separation of precipitate (shaded box) from the solution (open box) by centrifuging. Place formulas of products with the rectangular boxes, and put the formulas of the added reagents within the rounded boxes. Letters in bold face refer to steps in the procedure.


Al^{3+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Zn^{2+}
a.
b.
c.
d.
e.
f.

Analysis of the Unknowns

Complete the following table for your unknowns:

Unknown	**Step**	**Observations**	**Conclusions**

Summarize your analysis in the following table:

Unknown Number	**Ions Found**

Confirming the Analysis

Describe below what you did to confirm that your analysis is correct.

APPLICATION OF PRINCIPLES

1. Solutions of Cu^{2+} turn blue litmus red because of the equilibrium

$$Cu(H_2O)_6^{2+} + H_2O(l) = Cu(H_2O)_5(OH)^{+} + H_3O^{+}$$

for which $K_a = 1.0 \times 10^{-8}$. Calculate the pH of 0.10 *M* $Cu(NO_3)_2$*(aq)*.

2. Co^{2+} solutions are also acidic because of an equilibrium just like the one above, but with $K_a = 5.0 \times 10^{-10}$. Calculate the pH of 0.10 *M* $Co(NO_3)_2$*(aq)*. Is this solution acidic enough to turn blue litmus red?

3. Calculate the pH of a solution made by adding 1 mL of 6 *M* NaOH*(aq)* to 3 mL of water.

4. If the solution in part c is too acidic when ammonium oxalate is added, calcium ions will not be detected. Why?

5. Barium ions are toxic, yet when the stomach or intestines are X-rayed, they are first filled with a suspension of $BaSO_4$. Why doesn't this poison the patient?