1. *Qualitative Analysis of Mg^{2+}, Ca^{2+}, Ba^{2+}, and Al^{3+} Ions*

Introduction

Some of the similarities and differences in the chemical behaviors of the first three main-group families (Ebbing/Gammon, Chapter 22) can become very clear during qualitative analysis by chemical methods.

Purpose

You will learn to separate and identify each cation in a mixture of Mg^{2+}, Ca^{2+}, Ba^{2+}, and Al^{3+} ions. Your studies will allow you to determine which of these ions are present in an unknown mixture. This mixture may contain any or all of these cations.

Concept of the experiment

The characteristic chemical behaviors of Mg^{2+}, Ca^{2+}, Ba^{2+}, and Al^{3+} ions will become clearer to you as you learn to separate and identify each cation. You will discover different chemical behaviors within a family by comparing the behavior of Mg^{2+}, Ca^{2+}, and Ba^{2+} ions. You will discover differences between cations in different families but in the same period from the behaviors of Mg^{2+} and Al^{3+} ions.

There are four principal tasks in this experiment:

1. The separation of the cation from Group III (Al^{3+}) from the cations belonging to Group II (Mg^{2+}, Ca^{2+}, and Ba^{2+})
2. The identification of Al^{3+} by characteristic chemical reactions
3. The separation of the cations in Analytical Group II
4. The identification of these cations by characteristic chemical reactions

Each of these tasks will be discussed in turn.

The separation of Groups II and III

This separation will be brought about by the precipitation of $Al(OH)_3$. The precipitation must be selective, because $Mg(OH)_2$ is also essentially insoluble and $Ca(OH)_2$ is only slightly soluble. The solubility product constants for these substances are given in Table 1.1.

Table 1.1 Solubility Product Constants

Compound Formula	Compound Name	K_{sp}
$Al(OH)_3$	Aluminum hydroxide	4.6×10^{-23}
$Mg(OH)_2$	Magnesium hydroxide	1.8×10^{-11}
$Ca(OH)_2$	Calcium hydroxide	5.5×10^{-6}
$Ba(OH)_2$	Barium hydroxide	Soluble
$MgCrO_4$	Magnesium chromate	Soluble
$CaCrO_4$	Calcium chromate	7.1×10^{-4}
$BaCrO_4$	Barium chromate	1.2×10^{-10}
MgC_2O_4	Magnesium oxalate	8.5×10^{-5}
CaC_2O_4	Calcium oxalate	2.3×10^{-9}
BaC_2O_4	Barium oxalate	1.6×10^{-7}

You will achieve selective precipitation by using a buffered solution of NH_3, a weak base, rather than a solution of a strong base, such as NaOH. The buffer (Ebbing/Gammon, Section 17.6) will fix the hydroxide ion concentration so that only $Al(OH)_3$, the most insoluble hydroxide in Table 1.1, will precipitate.

To prepare the buffer, a *limited* amount of HCl is added to an *excess* quantity of NH_3. Because the reaction of these substances yields NH_4Cl, a buffer containing NH_3 and NH_4^+ will result. The hydroxide ion concentration is fixed at a desired value by the relative molar quantities of the base and its conjugate acid.

The amphoteric nature of $Al(OH)_3$ (Ebbing/Gammon, Section 22.4) provides another reason for using the buffer solution. If a strong base were used, $Al(OH)_3$ would precipitate, as you would expect. However, this precipitate would dissolve in the presence of any excess hydroxide ions because of the reaction

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$$

The identification of Al^{3+}

The characteristic reactions that are used to provide positive identification of Al^{3+} are based on the amphoteric nature of $Al(OH)_3$ and on the insolubility of this substance in a solution of the weak base NH_3.

The separation of the cations in Group II

The chromates and oxalates of Mg^{2+}, Ca^{2+}, and Ba^{2+} play important roles in the separation of these cations. The solubility product constants for these compounds are given in Table 1.1.

You will notice that the solubilities of the chromates decrease from Mg^{2+} through Ba^{2+}. The solubilities of these compounds are influenced by the acidity because of the equilibrium between yellow CrO_4^{2-} (chromate ion) and orange $Cr_2O_7^{2-}$ (dichromate ion):

$$2CrO_4^{2-}(aq) + 2H_3O^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + 3H_2O(l)$$

Nevertheless, K_{sp} for $BaCrO_4$ is sufficiently small that this substance precipitates even from a weakly acidic solution. Precipitation of $MgCrO_4$ and $CaCrO_4$ does not occur under this condition.

There is no regular trend in the solubilities of the oxalates, but CaC_2O_4 is the most insoluble of these substances. Oxalic acid is a weak diprotic acid, so an equilibrium between $C_2O_4^{2-}$ and $HC_2O_4^-$ exists in a weakly acidic solution:

$$C_2O_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HC_2O_4^-(aq) + H_2O(l)$$

Consequently, the acidity of the solution again affects the solubilities. Unlike MgC_2O_4 and BaC_2O_4, CaC_2O_4 precipitates from a weakly acidic solution because K_{sp} for this compound is very small.

Now consider a weakly acidic solution of Mg^{2+}, Ca^{2+}, and Ba^{2+}. The addition of K_2CrO_4 will cause $BaCrO_4$ to precipitate and allow the separation of Ba^{2+} from Mg^{2+} and Ca^{2+}. Subsequently, the addition of $K_2C_2O_4$ will result in the precipitation of CaC_2O_4 and allow the separation of Ca^{2+} from Mg^{2+}.

The identification of Mg^{2+}, Ca^{2+}, and Ba^{2+}

After $BaCrO_4$ is dissolved in a solution containing a strong acid, Ba^{2+} will be precipitated once again as white $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$) by the addition of Na_2SO_4. This reaction will confirm the presence of Ba^{2+}.

A strong acid will be used to dissolve CaC_2O_4. This substance will be precipitated again by making the solution basic. This reaction will confirm the presence of Ca^{2+}.

Finally, Mg^{2+} will be precipitated as $Mg(OH)_2$. Although this compound is usually colorless when it is freshly precipitated, it will be stained yellow in this experiment because of the presence of yellow CrO_4^{2-}. This precipitate will be dissolved in an acidic solution. White $MgNH_4PO_4$ ($K_{sp} = 2.5 \times 10^{-12}$) will then be precipitated. Both of these will be used to confirm the presence of Mg^{2+}.

Procedure

Getting started

1. Obtain 6 small test tubes.
2. Obtain your unknown mixture and record its identification number.
3. Obtain 1 mL of the known mixture. This solution contains $Mg(NO_3)_2$ (0.2 *M*), $Ca(NO_3)_2$ (0.2 *M*), $Ba(NO_3)_2$ (0.2 *M*), and $Al(NO_3)_3$ (0.2 *M*).

CAUTION: Wash your hands thoroughly after using the solution containing barium because it is poisonous.

4. Conduct the analysis of the known and unknown solutions simultaneously so that you can compare the results.
5. Use labeled test tubes throughout the experiment so that you do not confuse the known and unknown solutions and precipitates at any time.

6. If necessary, obtain instructions for using the centrifuges in your laboratory.

CAUTION: When you use a centrifuge, do not attempt to stop the centrifuge rotor with your finger or anything else.

7. Obtain directions for discarding the solutions that you will use in this experiment.
8. Take care in handling the solutions used in this experiment.

CAUTION: The 6 *M* solutions of ammonia, hydrochloric acid, and sodium hydroxide can cause chemical burns in addition to ruining your clothes. If you spill any of these on you, wash the contaminated area thoroughly with water and report the incident to your instructor. You may require further treatment.

Doing the analysis

1. Take 1 mL of the known mixture and 1 mL of the unknown mixture in separate small test tubes.
2. Each of the subsequent additions and operations should be conducted on both the known and the unknown mixtures unless the instructions indicate otherwise.
3. Add 6 drops of 6 *M* NH_3 and 4 drops of 6 *M* HCl to each test tube to make buffer solutions. Look carefully for a precipitate because sometimes it is difficult to see.
4. If no precipitate forms, proceed with Step 8. If a precipitate forms, stir the mixture with a clean stirring rod. Centrifuge the mixture for about 1 min.
5. Decant (pour off) the solution into a clean test tube. Save this solution for Step 8. Use the precipitate in the following step.
6. Wash the precipitate by adding 1 mL of distilled water, 6 drops of 6 *M* NH_3, and 4 drops of 6 *M* HCl and stirring vigorously. Centrifuge the mixture, save the precipitate, and discard the solution.
7. Dissolve the precipitate by gently shaking it with 4 drops of 6 *M* NaOH. Add drops of 6 *M* HCl until a drop of the solution on a clean stirring rod will turn blue litmus paper pink. A white precipitate may appear briefly during this operation. Add drops of 6 *M* NH_3 until a white precipitate appears. These reactions confirm the presence of Al^{3+}.
8. Add 1 *M* acetic acid by drops to the solution from either Step 4 or Step 5 until a drop of the solution on a clean stirring rod turns blue litmus paper pink. Avoid using excess acetic acid.
9. Add 8 drops of 1 *M* K_2CrO_4 to the solution and stir the mixture thoroughly with a clean stirring rod.
10. If no precipitate has formed, proceed with Step 13. If a yellow precipitate has formed, centrifuge the mixture, save the solution for Step 13, and use the precipitate in the next step.
11. Dissolve the precipitate in 3 drops of 6 *M* HCl and 3 drops of distilled water.

12. Add 20 drops of 0.1 *M* Na_2SO_4. A white precipitate in a yellow solution will result. To show that the precipitate is white, centrifuge the mixture and discard the solution. You may wash the precipitate with distilled water if desired. The formation of this precipitate confirms the presence of Ba^{2+}.
13. Add 10 drops of 1 *M* $K_2C_2O_4$ to the solution from Step 10.
14. If a white precipitate does not appear within 10 min, proceed with Step 17. If a precipitate does appear, go on to the next step.
15. Stir the mixture with a clean stirring rod. Centrifuge the mixture and decant the solution. Save the solution for Step 17 and use the precipitate in the following step.
16. Dissolve the precipitate in 4 drops of 6 *M* HCl and add 20 drops of distilled water. Add another drop of 1 *M* $K_2C_2O_4$, and make the solution basic to litmus paper with 6 *M* NaOH. A white precipitate confirms the presence of Ca^{2+}.
17. Add 6 drops of 6 *M* NaOH to the solution from either Step 14 or Step 15. Stir and then centrifuge the mixture. Examine the mixture carefully. If no precipitate has formed, you have completed the analysis. If a translucent, pale yellow precipitate has formed, decant and discard the solution, and use the precipitate in the next step.
18. Dissolve the precipitate by adding 3 drops of 6 *M* HCl.
19. Add drops of 6 *M* NH_3 until the solution is basic to litmus.
20. Add 10 drops of 1 *M* Na_2HPO_4. A white precipitate, which may form slowly, confirms the presence of Mg^{2+}.
21. Record the cations that are present in the unknown mixture.

CAUTION: Wash your hands thoroughly. Oxalate solutions are poisonous.

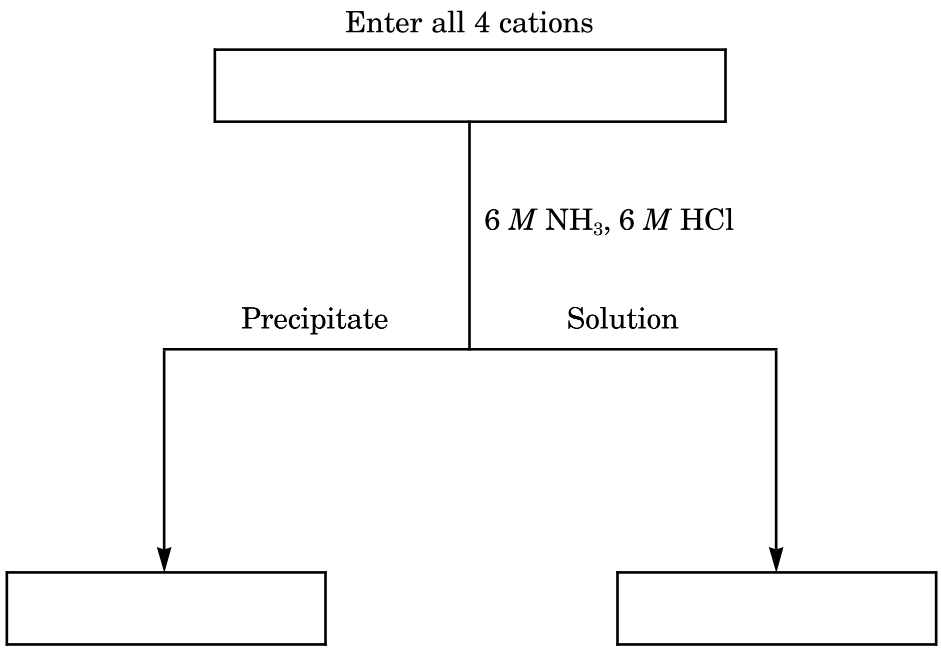
Qualitative Analysis of Mg^{2+}, Ca^{2+}, Ba^{2+}, and Al^{3+} Ions

Date:	....	Student name:	....
Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

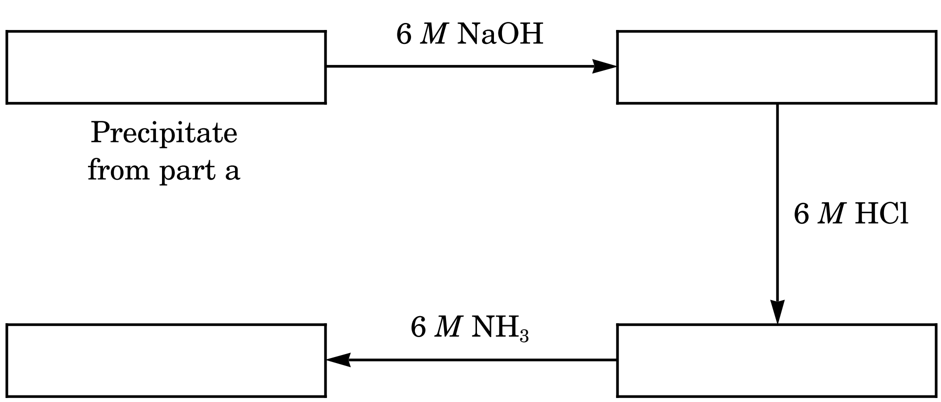
Prelaboratory assignment

1. Complete the following flow diagrams by filling in the boxes with the correct cations or precipitates.

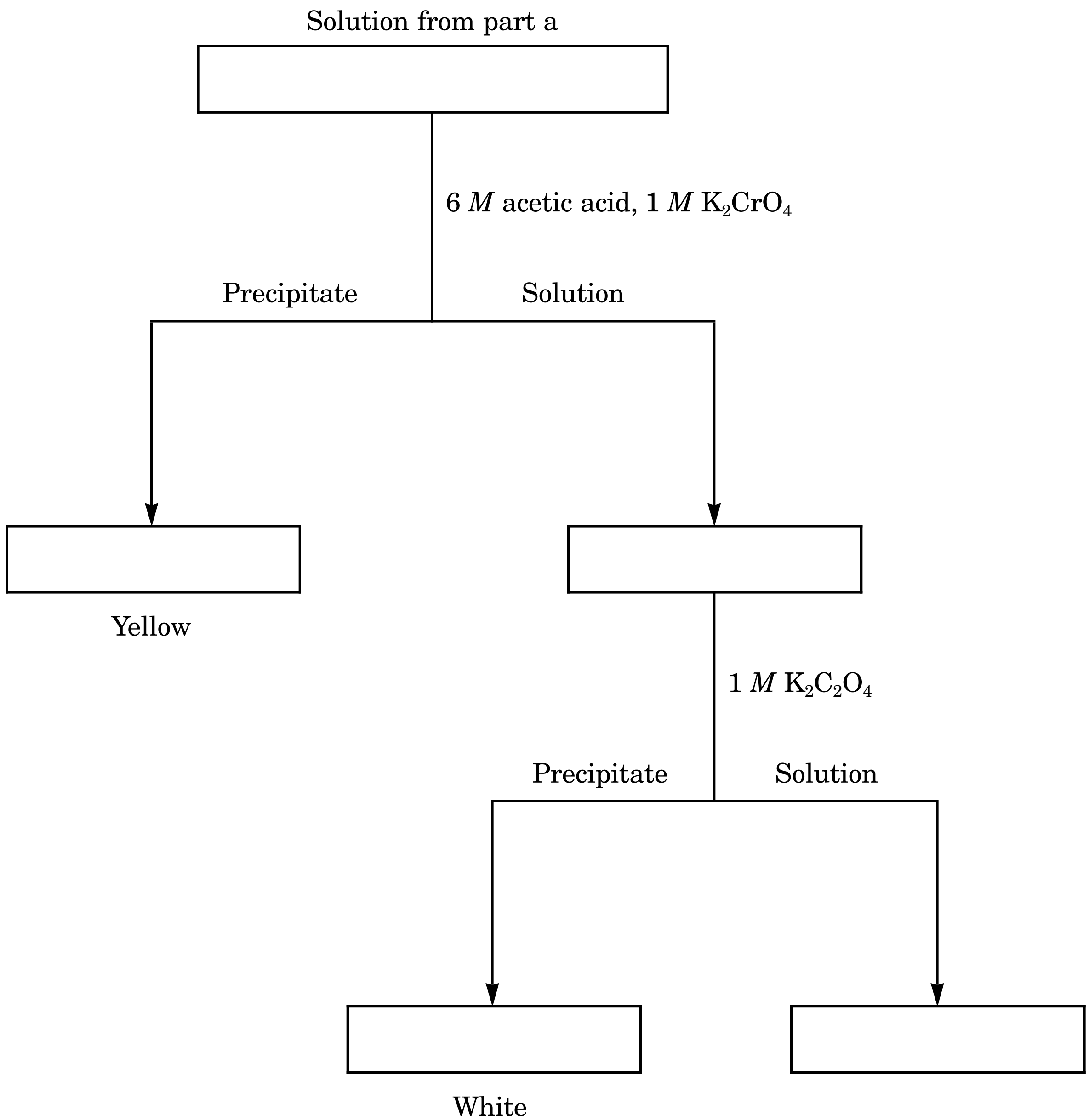
   a.



   b. Identification of cation from Group III:



c. Separation of cations from Group II:



d. Devise a flowchart that shows the identification of the cation in the yellow precipitate from part c. Give the colors of any precipitates.

e. Devise a flowchart that shows the identification of the cation in the white precipitate from part c. Give the colors of any precipitates.

f. Devise a flowchart that shows the identification of the remaining cation from part c. Give the colors of any precipitates.

2. Describe the purpose of the buffer solution used in this experiment.

3. a. What is an amphoteric substance?

b. What is the only substance in this experiment that is amphoteric?

4. What special safety precautions are cited in this experiment?

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Instructor:	....		....

Results

Unknown no.: ....

Ions present: ....

Questions

1. a. Write a balanced equation for each precipitation reaction that was used to separate the four cations.

   b. Write a balanced equation for each reaction that was used to confirm the identity of each cation.

2. a. Suppose a mixture contained only Al^{3+} and Mg^{2+}. How would you *separate* these cations?

b. Suppose a mixture contained only Al^{3+} and Ba^{2+}. An unbuffered solution of NH_3 will allow these cations to be separated. Why?

c. Suppose a mixture contained only Mg^{2+} and Ba^{2+}. What would happen upon the addition of 1 *M* NaOH? 1 *M* K_2CrO_4? 1 *M* $K_2C_2O_4$? Use Table 1.1.