EXPERIMENT 10

Analysis of a Cation Mixture

Objective

This experiment illustrates the procedures used in developing a scheme for separating and identifying a selected group of cations.

Introduction

A chemist uses inorganic qualitative analysis to detect the various elements that are present in a sample of material. For ionic substances this is usually done by putting the substance in aqueous solution and testing for various cations and anions.

In this experiment, you will look at part of the chemistry of six cations: Ag^+, Ni^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, and Cr^{3+}. You will initially compare the reactions of each of these with various reagents to see which form precipitates, which are amphoteric, and which form ammonia complex ions. You will use these results to develop a scheme for separating these cations when they are present in a mixture. You will also look at some specific reactions for each of these cations that allow you to identify each cation when you know that other cations are absent.

Predicting reaction products:

You are asked to complete and balance the equations for each of the reactions occurring. The reactants are given in each case.

With the exception of one reaction which is oxidation-reduction, all the reactions in this experiment are of three types:

1. formation of an insoluble salt (precipitation reaction)
2. formation of ammine complex ions
3. formation of hydroxide complex ions (amphoteric cations).

To predict the formula of an insoluble precipitate, use the cation under study and the anion from the reagent added. For example, if you mix Pb^{2+} solution with 3 *M* HCl, you observe a white precipitate. The net-ionic equation is

$$Pb^{2+} + 2Cl^{-} \rightarrow PbCl_2(s) \qquad \textbf{(EQ 10.1)}$$

When adding either NaOH or NH_3 solution and a precipitate forms, it is the metal hydroxide as both these solutions are bases.

Hydroxides such as $Zn(OH)_2$ and $Al(OH)_3$, which dissolve in either strong base or strong acid, are referred to as being **amphoteric**. You will test for amphoteric behavior of a cation by first adding just enough NaOH to make a solution basic (in which case most metal hydroxides precipitate) and then adding excess NaOH to see if the metal hydroxide dissolves. For example, if you add 1 drop NaOH to Pb^{2+} solution, you see a white precipitate which dissolves when an excess of 8 - 10 drops of NaOH is added.

The net-ionic equations are:

$$Pb^{2+} + 2OH^{-} \rightarrow Pb(OH)_2(s) \qquad \textbf{(EQ 10.2)}$$

$$Pb(OH)_2(s) + 2OH^{-} \rightarrow Pb(OH)_4^{2-} \qquad \textbf{(EQ 10.3)}$$

The ion $Pb(OH)_4^{2-}$ is called a complex ion. Of the ions you are studying in this experiment, *those that are amphoteric complex with four* OH^- *in each case*.

You will test for the formation of ammine complex ions by first adding just enough NH_3 solution to make the cation solution basic (in which case most metal hydroxides precipitate), then by adding excess NH_3 to see if the metal hydroxide dissolves. For example, if you added 1 drop of NH_3 solution to a Cd^{2+} solution, you would see a white precipitate which dissolves on adding 8 - 10 drops excess NH_3. The net-ionic equations are:

$$Cd^{2+} + 2NH_3 + 2H_2O \rightarrow Cd(OH)_2(s) + 2NH_4^{+} \qquad \textbf{(EQ 10.4)}$$

$$Cd(OH)_2 + 4NH_3 \rightarrow Cd(NH_3)_4^{2+} + 2OH^{-} \qquad \textbf{(EQ 10.5)}$$

The ion $Cd(NH_3)_4^{2+}$ is an ammine complex. Many of the transition metal cations form ammine complexes as well as complex ions with other groups besides NH_3 or OH^- (called ligands). The number of ligands attached to a metal is called the **coordination number**. The cations in this study have the following coordination numbers when they form complex ions. **Ag^+(2), Ni^{2+}(6), Fe^{3+}(6), Cr^{3+}(4), Zn^{2+}(4)**. Use these coordination numbers to determine the number of NH_3 groups bonded to the metal for any of the cations you observe forming ammine complexes.

Frequently, in qualitative analysis, we need to bring a precipitate back into solution. There are many different ways to dissolve a precipitate. Most of these involve chemical recations which compete with precipitate formation. Common methods involve forming a complex ion with the cation (as in the above examples) or adding H^+ if the insoluble salt contains the anion of a weak acid. An example of this is

$$NiS(s) + 2H^{+} \rightarrow Ni^{2+} + H_2S \qquad \textbf{(EQ 10.6)}$$

The only oxidation-reduction reaction you will observe is that of $Cr(OH)_4^-$ with H_2O_2 in basic solution. The products are CrO_4^{2-} from the $Cr(OH)_4^-$ and OH^- from the H_2O_2. Using this information, you can balance the redox equation.

General Techniques

Centrifuge. A centrifuge is an instrument used to rapidly separate a solid from a liquid. A mixture of solid and liquid in a test tube is placed in a slot in the centrifuge and spun at high speed. This concentrates the solid in the bottom of the test tube in 30 - 50‘ seconds of spinning. After centrifuging, one can easily pour off the clear supernatant above the solid.

> **Caution:** A centrifuge must be balanced to spin properly. To balance a centrifuge, use a second test tube filled with water to the same depth as your sample tube. These two test tubes should be placed on opposite sides of the centrifuge. Most centrifuges have sufficient slots to allow 2 or 3 samples to be spun simultaneously.

Mixing of reagents. A dropper should be used to add small quantities of one reagent to another. For qualitative analysis, the general rule of thumb is that 1 mL = 20 drops, using a standard size dropper (**not a Pasteur Pipet**). On mixing 2 or more reagents, always stir the mixture before drawing any conclusions about the reaction.

Precipitation. To detect the formation of a precipitate, it is essential that the reagents being mixed together are clear. A clear solution is transparent but may be colored. Several of the cation solutions you will study are colored.

Heating of solutions in test tubes. The safest, simplest way to heat a small amount of solution in a small test tube is in a boiling water bath. For the 4" test tubes, use a 250 mL beaker with 1½ inches boiling water. Put the test tube in the boiling water for about 5 minutes, stir a couple of times during the 5 minutes.

Testing acidity. To test a solution for acidity, stir it with a stirring rod and touch the wet rod to a piece of litmus paper. Litmus is red in acid and blue in base. Never immerse the litmus paper in the solution in the test tube.

Experimental Procedure

Part I. You will study the reactions of the six cations Ag^+, Fe^{3+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, and Ba^{2+} with various reagents. Record all observations such as initial colors, precipitate formations, color changes, etc. Table 10.2 on page 66 of the write-up is for a summary of all reactions observed. It will be used to develop a scheme for separating these cations, using the reagents studied. Copy this table into your lab notebook.

1. Reaction with dilute HCl. To 10 drops of each cation solution, add 1 mL (20 drops) of 3 *M* HCl. Any precipitates formed are metal chlorides.
2. Reaction with $NH_3 + H_2O$.
    a. To 10 drops of each cation solution, add 1 drop of 1 *M* NH_3 solution and mix. Test each solution for acidity. To any mixture which is not basic, add additional 1 *M* NH_3 dropwise until just basic. Any precipitates formed are metal hydroxides.
    b. To the above basic mixtures, add 10 drops of 15 *M* NH_3. Note any color changes or precipitates that dissolve to detect the formation of ammine complex ions.
3. Reaction with NaOH and Oxidation with H_2O_2.

- **a.** To 10 drops of each cation solution, add 1 drop of 6 M NaOH and mix. Test each solution for acidity. To any mixture which is not basic, add additional 6 M NaOH dropwise until just basic. Any precipitates formed are metal hydroxides.
- **b.** To the above mixtures, add 20 drops of 6 *M* NaOH and mix. Note any color changes and any precipitates that dissolve to detect the formation of any hydroxide complex ions.
- **c.** To the above test tubes, add 10 drops of 3% H_2O_2 and heat for 5 minutes in a boiling water bath. Stir a couple of times while heating. Note any changes which occur. Immediately test for Cr^{3+}as in "7" below.

4. Reaction with H_2SO_4.

- **a.** To 10 drops of each cation solution, add 5 drops of 3 *M* H_2SO_4 and mix. Any precipitates that form are metal sulfates.

The following are tests which can be used to confirm the presence of each of these cations when you have only one cation present. Note all color changes and precipitates.

5. Ag^+ test. The formation of white AgCl on addition of HCl as in (1) above is sufficient to confirm Ag^+.

6. Fe^{3+} test. To an Fe^{3+} solution (10 drops), add 5 drops of 0.2 *M* KSCN. This will form the complex ion $Fe(SCN)^{2+}$, a deep red complex ion.

7. Cr^{3+} test. To a CrO_4^{2-} solution (10 drops), add 6 *M* $HC_2H_3O_2$ until acidic; then add 2 - 3 drops 0.1 *M* $Pb(C_2H_3O_2)_2$ solution. A yellow ppt of $PbCrO_4$ forms.

8. Ni^{2+} test. Take 10 drops of Ni^{2+} solution; make it just basic with 6 *M* NH_3. To this mixture, add 10 drops of dimethylglyoxime. The formation of red precipitate confirms Ni^{2+}.

9. Zn^{2+} test. To 10 drops of Zn^{2+} solution, add 6 *M* HNO_3 until just acidic; then add 10 drops of $K_4Fe(CN)_6$. Formation of a pale yellow precipitate of $K_2ZnFe(CN)_6$ confirms Zn^{2+}.

10. Ba^{2+} test. The formation of white $BaSO_4$ precipitate, noted in part (4) above on addition of 3 *M* H_2SO_4, is sufficient to confirm Ba^{2+}.

Part II. Before your lab meets next session you must develop a scheme in flow chart form for separating and identifying these six cations in a mixture. **You must get your flow chart approved by your instructor before lab starts**. You will not be issued an unknown until your flow chart is approved. You will use it to analyze your unknown.

To develop your scheme for separating the ions, use the reagents and results from parts (1) - (4) above. Ideally, you would add a reagent that will precipitate out only one cation which can then be separated by centrifugation. That isn't entirely possible with these reagents. You will at some point have to separate the group of ions into two smaller groups with some cations in the precipitate you form and others left in solution. These mixtures can then be further treated to completely separate the cations. It is helpful to run the known mixture of cations at the same time that you are analyzing your unknown solution, so that you can compare results.

You can add 6 *M* HNO_3 dropwise to neutralize excess base. To dissolve metal hydroxide precipitates, add 10 drops of water, then 6 *M* HNO_3 with stirring until dissolved. Once you have separated one cation from the others, you need to run a confirmatory test to prove its presence, use the tests in parts (5) - (10) above.

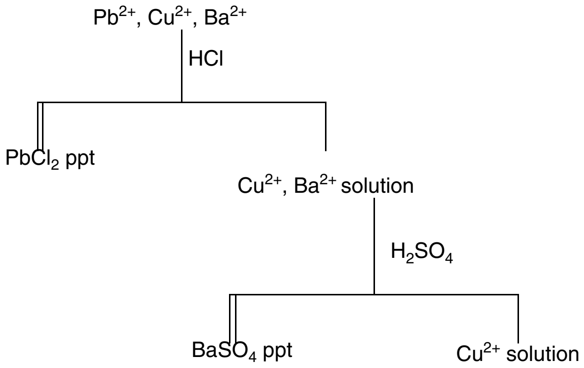
Flow charts

The simplest method of showing a separation scheme is in flow chart form. Table 10.1 gives you an example of three cations with various reagents and a flow chart (see Figure 10.1) developed from the table for separating these three ions from each other.

TABLE 10.1

Reagent	Pb^{2+}	Cu^{2+}	Ba^{2+}
HC1	white ppt	no reaction	no reaction
Na_2CO_3	white ppt	pale blue ppt	white ppt
H_2SO_4	white ppt	no reaction	white ppt

FIGURE 10.1 **Sample Flow Chart**


Pb^{2+}, Cu^{2+}, Ba^{2+}
HCl
$PbCl_2$ ppt
Cu^{2+}, Ba^{2+} solution
H_2SO_4
$BaSO_4$ ppt
Cu^{2+} solution

You will be issued an unknown solution containing one or more of these six cations. You will analyze the unknown, using your approved flow chart.

Observations and Data

1. Record your observations on all reactions in your notebook using Table 10.2 as an example.

TABLE 10.2 **Sample Matrix**

Reagents	A g$^+$	Fe^{3+}	Cr^{3+}	Ni^{2+}	Zn^{2+}	Ba^{2+}
3 *M* HCl						
1 *M* NH_3 until basic						
15 *M* NH_3 excess						
6 *M* NaOH until basic						
6 *M* NaOH excess						
6 *M* NaOH in excess, H_2O_2 and heat						
3 *M* H_2SO_4						

SAMPLE

2. Record the observed results for each of the individual cation tests in your notebook.
   - a. Ag$^+$ test:
   - b. Fe^{3+} test:
   - c. Cr^{3+} test:
   - d. Ni^{2+} test:
   - e. Zn^{2+} test:
   - f. Ba^{2+} test:
3. Construct a flow chart and get it approved by your instructor.

Reaction Equations

Complete and balance the following equations (reactants given) in net-ionic form. **Be sure to indicate the phase**.

1. $Ag^+ + Cl^- \rightarrow$
2. $Ag^+ + NH_3 + H_2O$ (until basic) $\rightarrow$
3. $Ag(OH)_{(s)} + NH_3$ (excess) $\rightarrow$
4. $Ag^+ + NH_3$ (excess) $\rightarrow$
5. $Ag^+ + OH^- \rightarrow$
6. $Fe^{3+} + NH_3 + H_2O \rightarrow$
7. $Fe^{3+} + OH^- \rightarrow$
8. $Fe(OH)_{3(s)} + H^+ \rightarrow$
9. $Fe^{3+} + SCN^- \rightarrow$
10. $Cr^{3+} + NH_3 + H_2O \rightarrow$
11. $Cr^{3+} + OH^-$ (until basic) $\rightarrow$
12. $Cr^{3+} + OH^-$(excess) $\rightarrow$
13. $Cr(OH)_{3(s)} + OH^- \rightarrow$

14. $Cr(OH)_{3(s)} + H^+ \rightarrow$

15. $Cr(OH)_4^- + H_2O_2 + OH^- \rightarrow$

16. $CrO_4^{2-} + Pb^{2+} \rightarrow$

17. $Zn^{2+} + NH_3 + H_2O$ (until basic) $\rightarrow$

18. $Zn(OH)_2(s) + NH_3$ (excess) $\rightarrow$

19. $Zn^{2+} + NH_3$ (excess) $\rightarrow$

20. $Zn^{2+} + OH^-$ (until basic) $\rightarrow$

21. $Zn(OH)_2(s) + OH^-$ (excess) $\rightarrow$

22. $Zn^{2+} + OH^-$ (excess) $\rightarrow$

23. $Zn(OH)_2 + H^+ \rightarrow$

24. $Zn^{2+} + K^+ + Fe(CN)_6^{4-} \rightarrow$

25. $Ni^{2+} + NH_3 + H_2O$ (until basic) $\rightarrow$

26. $Ni(OH)_2(s) + NH_3$ (excess) $\rightarrow$

27. $Ni^{2+} + NH_3$ (excess) $\rightarrow$

28. $Ni^{2+} + OH^- \rightarrow$

29. $Ni(OH)_{2(s)} + H^+ \rightarrow$

30. $Ba^{2+} + SO_4^{2-} \rightarrow$

Questions

1. What hydroxide concentration must be exceeded in order to precipitate the corresponding metal hydroxides of 0.050 *M* Ni^{2+} and 0.050 *M* Ba^{2+}?

$$K_{sp}\ Ni(OH)_2 = 1.6\times10^{-16} \text{ and } Ba(OH)_2 = 2.2\times10^{-2}$$

  a. You used 10 drops of 0.050 *M* N^{i2+} and 10 drops of 0.050 *M* Ba^{2+} and added 6 *M* NaOH until basic (assume it took 2 drops in each case to become basic). What was the concentration of each of these ions in the respective mixtures you observed?

  b. Are the results from parts1 and (a) above consistent with your observations? Be specific.

2. What concentration of NH_3 is needed to convert all the cation in 0.050 *M* $Ni(NO_3)_2$ into the ammonia complex, $Ni(NH_3)_6^{2+}$? (Assume the Ni^{2+} drops from 0.050 *M* to 1.0×10^{-6} *M*.)

$$K_d \text{ of } Ni(NH_3)_6^{2+} = 1.8\times10^{-9} \quad \text{or} \quad K_f = 5.6\times10^{8}$$