SEPARATION AND IDENTIFICATION OF METAL CATIONS

As you have seen in the laboratory this semester, if a metal ion is alone in solution, it can be identified by one or more simple tests. If you have a mixture of cations, however, it is usually necessary to separate them chemically before being able to identify the ions. There are several approaches to this problem, the main one being to precipitate a mixture of ions with some reagent and then to use another reagent to selectively redissolve some of the ions. By repeating this procedure several times, you may be able to separate a reasonably large group of cations so that each ion ends up in a separate test tube where it may then be identified.

SEPARATION SCHEMES

How do you go about designing a scheme for separating a mixture of ions? Obviously you need to know something about the combinations of reagents that lead to precipitates or the reagents that will redissolve those precipitates. In this experiment you will have only the following reagents available to bring about the ion separations:

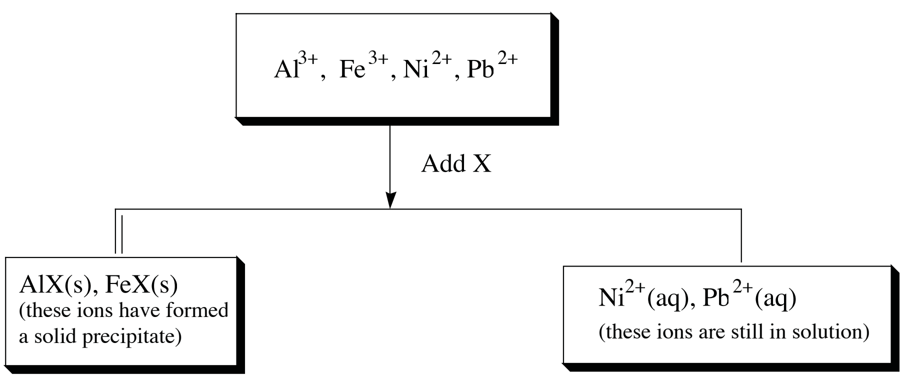
6 M HCl   6 M NH_3 6 M NaOH

These will be used to form precipitates, or to dissolve precipitates once they have been formed, in order to separate the following metal cations:

Al^{3+} Fe^{3+} Ni^{2+} Pb^{2+}

Available Reagents:
HCl, NH_3, and NaOH
Ions to be separated and identified:
Al^{3+}, Fe^{3+}, Ni^{2+}, and Pb^{2+}.

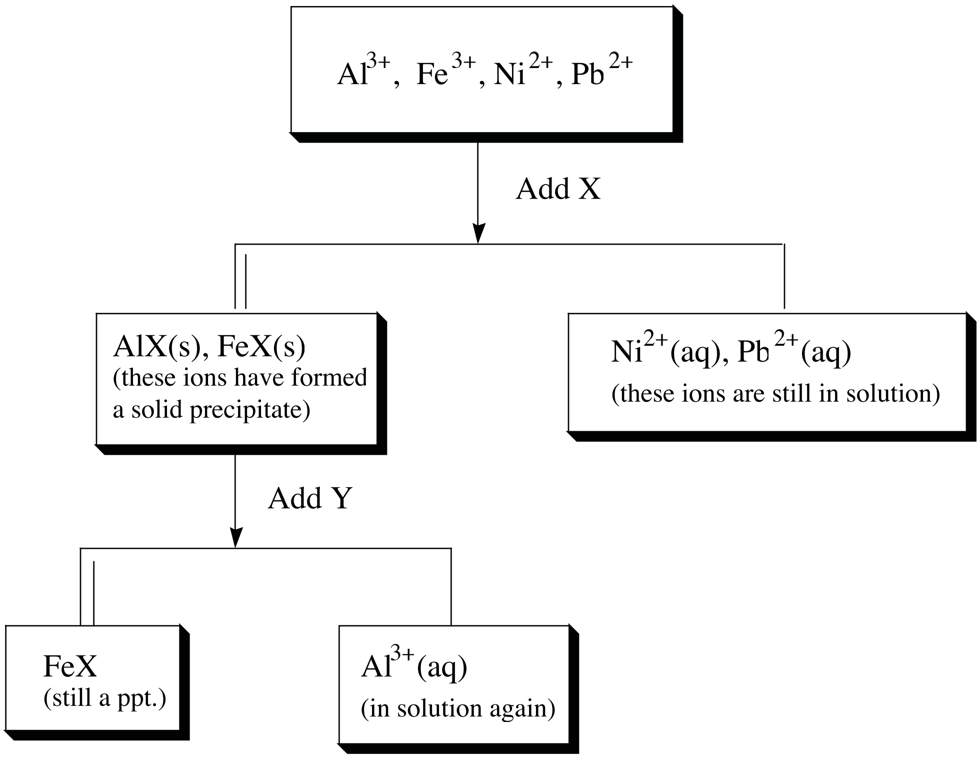
Now to work out a separation scheme for the ions above. Suppose you have a reagent X that you know will precipitate Al^{3+} and Fe^{3+} as insoluble salts but not Ni^{2+} or Pb^{2+}. You can show the results on a flow chart such as the one below.



See *Chemistry & Chemical Reactivity*, pages 890-892 for more on separation schemes.

In the laboratory you can then centrifuge the solid precipitate (containing AlX and FeX) so that it packs into the bottom of the test tube, and the liquid (now containing only the ions Ni^{2+} and Pb^{2+}) can be decanted into another test tube.

Suppose you now find another reagent Y that will dissolve AlX but not FeX. This will of course enable you to separate Al^{3+} from Fe^{3+}, and the flow chart would now look like



You have now reached the point where at least Fe^{3+} and Al^{3+} are in separate test tubes. The next step would be to test for the presence of Al^{3+} in the solution and to redissolve FeX so that you can test for Fe^{3+}.

The hypothetical scheme above has allowed you to separate Fe^{3+} and Al^{3+} from the other two ions and to find a way to test for the presence of the iron(III) and aluminum ions in your unknown. The next step would be to work out a method of separating Ni^{2+} and Pb^{2+} from one another and testing for their presence.

EXPERIMENTAL PROCEDURE

A. DEVELOPING A SEPARATION SCHEME

1. Using the three reagents: NaOH, NH_3, and HCl

Before you can develop a flow scheme for analyzing an unknown, you need to know how each of the four ions to be tested (Al^{3+}, Fe^{3+}, Ni^{2+}, and Pb^{2+}) will react with each of the three reagents to be used (6 M HCl, 6 M NH_3, and 6 M NaOH). You should proceed as outlined below. *Be sure to record your observations in your notebook in an organized manner so that you can draw useful conclusions later on.* (See the directions below for recording your observations.)

This is a two-week experiment. In the first week you will carry out the tests outlined here and develop a separation scheme. In the second week you will test your scheme and then use it to solve an unknown.

Step 1. Prepare a set of 4 test tubes, each test tube containing a few drops of one of the four ions to be tested.

In some cases, the first drop of reagent, say NaOH, will lead to a precipitate. Adding more reagent, however, will redissolve the precipitate. This is an important observation and can be used later in devising a separation scheme.

Step 2. Add one drop of one of the reagents, 6 M NaOH, for example, to each of the four test tubes. Observe the result. If no precipitate has formed, add 4-5 more drops of the reagent. This reagent (NaOH, HCl, or NH_3) will lead to precipitates, such as $Fe(OH)_3$, with some or all of the ions.

$$Fe^{3+}(aq) + 3\ OH^-(aq) \rightarrow Fe(OH)_3(s)$$

Step 3. If an ion has formed a precipitate with the reagent added in Step 2, you have to know what will dissolve this precipitate. Therefore, you should centrifuge to collect the precipitate, decant the supernatant liquid, and wash the precipitate with a few drops of distilled water. (***NOTE:*** If no precipitate has formed, you may proceed to another ion.)

When combining reagents, make sure you mix and stir thoroughly!

Step 4. Now you want to see what reagent will dissolve the precipitate formed in Step 2 (and washed in Step 3). Because there are three reagents that can possibly dissolve the precipitate, you will need 3 test tubes, each containing some of the precipitate. Therefore, if you have not already done so, prepare 3 batches of washed precipitate as described in Steps 2 and 3.

Step 5. To each of the three test tubes containing one of the precipitates from Steps 3 and 4, say $Fe(OH)_3(s)$, add a few drops of one of the three reagents. For example, to test tube 1 add 6 M HCl, to test tube 2 add 6 M NH_3, and to test tube 3 add 6 M NaOH. Some or all of the added reagents will dissolve the $Fe(OH)_3$. You should try as hard as possible to dissolve each precipitate. It may take excess reagent or heating. *Remember to stir thoroughly* in any event.

When adding HCl, recall that Pb^{2+} forms an insoluble chloride, $PbCl_2$. However, the solubility is affected by temperature. Therefore, when Pb^{2+} and Cl^- are reacted, put the test tube in an ice bath.

2. Keeping records

It is very important here to keep accurate records. You want to know what happens when combining each of four ions with each of three reagents (Step 2). This means there are ***12 possible precipitates*** that can form, and so you should have a table that has 12 boxes to record your initial observations.

Reagent	Al^{3+}	Fe^{3+}	Ni^{2+}	Pb^{2+}
NaOH				
NH_3				
HCl				

You will find that each of the three reagents may form precipitates with some or all of the ions. Each of these precipitates must then be tested with an excess of each of the three reagents (Steps 4 and 5). Therefore, for each precipitate that you observed above, you should have another table. For example, you will see that Al^{3+} reacts with aqueous ammonia, NH_3, to precipitate $Al(OH)_3$.

$$Al^{3+}(aq) + 3\ NH_3(aq) + 3\ H_2O(\ell) \rightarrow Al(OH)_3(s) + 3\ NH_4^+(aq)$$

Therefore, you will want to test this precipitate with an excess of each of the three reagents, recording your observations in a smaller table.

Reagent	Precipitate from Al^{3+} + NH_3
NaOH	
NH_3	
HCl	

Each of the precipitates you observed in your testing (Step 2) must be tested with each of the three reagents. Each set of tests should be outlined in a table such as that above.

3. The Separation Scheme

Based on a knowledge of how various precipitates can form, and what reagents can be used to dissolve them, you should be able to build a separation scheme of the type outlined in the introduction to this experiment. That is, you now know enough chemistry to be able to begin with a test tube containing all four ions in solution and separate those ions so that you end up with the four ions each in a separate test tube.

At least three or four different separation schemes are possible. Experience has shown, though, that the most successful schemes involve separating the Pb^{2+} ion from the mixture as early in the scheme as possible.

In designing a separation scheme you should generally try to separate the lead(II) ion from the others as soon as possible.

B. CONFIRMATORY TESTS

After you have carried out the separation of a mixture of ions in solution, you must be able to confirm the presence or absence of a single ion in a solution. To do this, you must carry out confirmatory tests on individual ions. As you carry out the tests outlined below, be sure to *record your observations* in your notebook.

Test for aluminum, Al^{3+}. Using a few drops of the solution containing Al^{3+}, make it distinctly acidic with 6 M HCl. Add 1 drop of aluminon dye, and then add 6 M NH_3 dropwise until the solution is basic to litmus paper. (Avoid adding an excess of NH_3.) If present, Al^{3+} will form a gelatinous precipitate of $Al(OH)_3$ that absorbs the red dye to give what is commonly called an "aluminum lake."

Note carefully: Aluminon dye can also dye the precipitates of $Ni(OH)_2$ and $Pb(OH)_2$ red. However, you can distinguish $Al(OH)_3$ from $Ni(OH)_2$ by adding excess NH_3. $Ni(OH)_2$ dissolves, while $Al(OH)_3$ does not. Finally, if the color of the solution or precipitate is purple, you do not have aluminum in the solution.

Test for iron(III), Fe^{3+}. Make the solution acidic with 6 M HCl. Add 1 drop of $K_4Fe(CN)_6$ solution. A blue precipitate of $Fe_4[Fe(CN)_6]$ (usually called "Prussian blue") confirms the presence of iron(III).

Test for lead, Pb^{2+}. Make the solution to be tested neutral. Then add 2 drops of 0.2 M K_2CrO_4. Mix and centrifuge. A yellow precipitate of $PbCrO_4$ indicates the presence of lead ion.

Test for nickel(II), Ni^{2+}. Make the solution basic with 6 M NH_3 (if it is not already basic). Add several drops of a solution of the ligand dimethylglyoxime (from a bottle probably labeled DMG) and mix well. (If no precipitate forms, try adding a few more drops of 6 M NH_3.) If Ni^{2+} is present, a strawberry-red precipitate will form.

C. THE UNKNOWN

This experiment is designed to last two laboratory periods. During the first week you will investigate the chemistry of the ions. On the basis of this chemistry you will work out a flow scheme, and then test the scheme in the second week. After testing it, you will be given ***an unknown consisting of at least two of the ions in one solution.*** You will use the scheme you have developed to separate and identify the ions in the unknown.

There are several important things to note:

1. Your instructor will not give you an unknown until he or she has checked your notebook and has verified that you have kept complete, accurate, and organized records.
2. Experience has shown that the best schemes for solving the unknown are those that use some method of removing any lead(II) ions from the solution as early in the scheme as possible. Lead removal should probably be the first or second step you carry out.
3. You will achieve the best results if you come to the second laboratory period prepared with more than one possible scheme. You should test your schemes as thoroughly as possible before you try the best one on an unknown.
4. When you have completed the unknown, save your test tubes containing the confirmatory tests you did. If you have made an error, your instructor can help you find the source of the error if he or she can see the results of these tests.

D. DEVELOPING AND USING A FLOW SCHEME FOR SEPARATING THE CATIONS

Write your flow scheme in your laboratory note book. Each substance must be represented by its correct formula, for example Al^{3+} or $Al(OH)_4^-$ for ions or $Al(OH)_3$ for a precipitate of aluminum hydroxide. *Show your flow scheme to your instructor before trying it on an unknown.*

More hints for developing a scheme:

(a) Three steps are needed to achieve a separation of the four cations from each other. Use one of the reagents (HCl, NH_3, or NaOH) in each step.

(b) It is best to separate Pb^{2+} ion from the others in the first step.

(c) When your scheme calls for NH_3 or NaOH, use an excess of the reagent.

(d) There are several ways to achieve separation and identification. No single scheme is better than others.

Using your flow scheme:

1. When precipitating $PbCl_2$ chill the test tube with ice to achieve complete precipitation. Test for completeness of precipitation. Do not use an excess of HCl (or the precipitate may redissolve) but do add enough HCl to ensure that the solution is acidic.
2. Wash all precipitates with water (using chilled water for $PbCl_2$).
3. If your scheme calls for dissolving $Ni(OH)_2$ with NH_3, first dissolve the precipitate with HCl, and then use enough NH_3 to make the solution basic.
4. Precipitates must be redissolved before confirmatory tests can be done. Use hot water to redissolve $PbCl_2$. Use HCl to redissolve $Fe(OH)_3$.
5. When doing a confirmatory test, always stir thoroughly. Centrifuge in order to get a good look at the precipitate.

After your instructor approves your flow scheme in your notebook, *test* the scheme on a *known* solution containing all four cations. Make this solution using equal parts of the four cation solutions. Use 5-6 drops of the known solution to begin testing. Record each step, including observations and conclusions, in your notebook. Do a confirmatory test for each cation to make sure they work properly when included in a flow scheme for all ions.

THE LABORATORY NOTEBOOK

More than any other, this experiment demands that you keep accurate records of your work. It is very helpful to make up tables in which you organize your information. In addition, you must answer the questions listed below:

1. Write net ionic equations for
   (a) the reaction of nickel(II) ion with 6 M NaOH to give $Ni(OH)_2$.
   (b) the reaction of iron(III) with 6 M NaOH to give iron(III) hydroxide.
   (c) the reaction of Ni^{2+} with aqueous ammonia to give $Ni(OH)_2$.

2. (a) Refer to your notes from the previous experiment ("Complex Ions and Amphoterism") and explain why you can dissolve $Ni(OH)_2$ in aqueous ammonia.
   (b) Explain how the reaction of $Ni(OH)_2$ with NH_3 would enable you to separate a mixture iron(III) and nickel(II) hydroxide.
   (c) Could you use excess NaOH to separate a mixture of the precipitates of $Fe(OH)_3$ and $Ni(OH)_2$? Explain briefly why or why not.

In each box below indicate what occurs on adding one drop and then on adding 5 drops of each reagent to each ion.

Ion	**HCl**	**NH_3**	**NaOH**
Al^{3+}			
Fe^{3+}			
Ni^{2+}			
Pb^{2+}			

Below list the precipitates you have observed and test each precipitate with each of the three reagents.
