ANALYSIS OF THE SILVER GROUP CATIONS

One problem often faced in qualitative analysis is to test for one ion in a mixture of many ions. To find a test for one ion that is not interfered with by another ion is nearly impossible. Therefore, if one has a mixture of a large number of ions, the usual approach is to use a chemical method to separate the mixture into subgroups that consist of just a few ions. Then it may be possible to test for one particular ion in the presence of just one or two others. Alternatively, each subgroup of just a few ions may be separated further so that each ion in the subgroup ends up in a different test tube where its presence can be confirmed by other chemical tests.

The chemical reactions encountered in qualitative analysis fall conveniently into four categories: (i) acid-base (proton transfer), (ii) precipitation, (iii) complex formation, and (iv) oxidation-reduction (electron transfer). Precipitation reactions are of particular importance in qualitative analysis (as you have already seen in the analysis of anions), and they are important in the silver group. In addition, acid-base, complexation, and even oxidation-reduction reactions are useful.

The silver group of ions — silver(I) (Ag⁺), lead(II) (Pb²⁺), and mercury(I) (Hg₂²⁺) — is a chemically related subgroup of ions. In this experiment we want to focus on this small group to show how to use the basic reaction types—especially precipitation, acid-base, and complex formation—to separate one ion from another and to confirm the presence of that ion.

CHEMISTRY OF THE SILVER GROUP CATIONS

Silver(I), lead(II), and mercury(I) are grouped together in qualitative analysis schemes because they are the only common metal cations that form insoluble precipitates with chloride ion. For example,

\[
\text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightarrow \text{AgCl(s)}
\]

This means that, in a mixture of metal cations, these three metal ions can be separated from all others by precipitating them as their insoluble chlorides, usually with 6 M HCl.

Once the precipitates of AgCl, PbCl₂, and Hg₂Cl₂ have been dissolved in water...

The structure of solid AgCl. Note that this model of the unit cell of AgCl has a net of 4 Ag⁺ ions and 4 Cl⁻ ions. As you will see in Chapter 13 of Chemistry & Chemical Reactivity, the structure can be thought of as a face centered cubic lattice of Cl⁻ ions with Ag⁺ ions in the octahedral holes (like NaCl). See the Models folder on the General Chemistry Interactive CD-ROM.
isolated from the solution containing the other metal cations, the three insoluble chlorides can be separated from one another by chemical means. To do this, we exploit differences in the chemistry of the three ions according to the separation scheme given on a separate sheet and in the table.

As you can see in the table of properties of the three silver group chlorides, PbCl2 is by far the most soluble of the three in water. Therefore, the first step in separating the three chlorides is to treat the solid mixture with hot water to selectively dissolve PbCl2 and to leave AgCl and Hg 2Cl2 as a solid mixture. Once Pb2+ is back in aqueous solution, the presence of this ion in this solution can be confirmed by the addition of potassium chromate, K2CrO4. The Pb2+ ion and the chromate ion, CrO 4^{2-}, combine to form the bright yellow, insoluble solid lead(II) chromate, PbCrO4. 

\[
Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(bright\ yellow\ solid)
\]

Silver(I) and mercury(I) chlorides are too insoluble in water to be redisolved in water, even when the water is boiled. Therefore, we turn to another useful trick for dissolving precipitates: we take advantage of the tendency of transition metal ions such as Ag+ to form water-soluble complex ions with ammonia, NH3. Here the ammonia uses the lone pair of electrons of the N atom to form a bond with the Ag+ ion.

\[
[H_3N :Ag^{+} \leftrightarrow NH_3],\ a\ water-soluble\ complex\ ion
\]

When a large enough concentration of NH3 is added to an insoluble precipitate of AgCl, the ammonia binds to the Ag+ ion and forms the complex ion. The net result is that the AgCl dissolves.

\[
AgCl(s) + 2 NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)
\]

In this way, the silver(I) ion is separated from the mercury(I) ion, as noted on the attached separation scheme.

When relatively concentrated ammonia is added to the mixture of solids AgCl and Hg2Cl2, the silver chloride precipitate is dissolved. However, Hg2Cl2 also reacts with NH3, but in a different manner. Mercury(I) chloride can undergo what is known as a disproportionation reaction. That is, the mercury(I) ion is both oxidized [to mercury(II), Hg^{2+}] and reduced (to metallic mercury).

\[
Hg_2Cl_2(s) \rightarrow Hg(liq) + Hg^{2+}(aq) + 2 Cl^-(aq)
\]

This reaction is induced by the presence of ammonia. In addition, when ammonia and Cl^- ion are present, the Hg^{2+} ion forms a rather strange compound, an amido salt HgClNH2. The latter is an insoluble white solid.

\[
Hg^{2+}(aq) + NH_3(aq) + Cl^-(aq) + H_2O(liq) \rightarrow HgClNH_2(s) + H_3O^+(aq)
\]
Therefore, when NH₃ is added to the AgCl/Hg₂Cl₂ mixture the AgCl dissolves, as described above, and the Hg₂Cl₂ turns into black or gray finely-divided mercury metal and the white insoluble solid HgClNH₂. The net reaction for Hg₂Cl₂ is

\[ \text{Hg}_2\text{Cl}_2 (s) + 2 \text{NH}_3(aq) \rightarrow \text{HgClNH}_2(s) + \text{Hg}(0)(s) + \text{NH}_4\text{Cl(aq)} \]

Notice that a second molecule of the base NH₃ is used to “collect” the H⁺, an acid, that is produced when Hg²⁺ reacts with NH₃; the product is of course the salt NH₄Cl. The importance of this reaction is that it provides confirmation of the presence of the mercury(I) ion, Hg₂⁺, in a solution of unknown composition.

If we had started with a mixture of AgCl, PbCl₂, and Hg₂Cl₂, we have now reached the point where the Pb²⁺ ion has been separated and identified, the Hg₂Cl₂ has been converted to Hg(0) and HgClNH₂, and the silver(I) ion is in solution in the form of the complex ion \([\text{Ag(NH}_3]_2^+\) (see the Separation Scheme attached to this experiment). To prove that silver is present, we make the solution containing the complex ion acidic with nitric acid. The acid (H⁺) reacts with the base (NH₃) to form the very stable ammonium ion. Thus, the NH₃ is no longer bound to Ag⁺. Because Cl⁻ is still present in solution, the Ag⁺ ion and the Cl⁻ can once again combine to form the insoluble precipitate AgCl.

\[ [\text{Ag(NH}_3]_2^+(aq) + 2 \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl(s) + 2 NH}_4^+(aq) + 2 \text{H}_2\text{O(liq)} \]

A white precipitate at this point confirms that Ag⁺ was in the original solution.

THE SILVER GROUP LABORATORY EXPERIMENT

To understand the chemistry of the silver group, you will first take a solution that contains all three of the ions, the known solution, and perform the separation given on the attached separation scheme. As indicated on the scheme, begin with about 1 mL of the solution; follow the directions given on the scheme and in the accompanying notes.

When you have completed separating and identifying the ions of the known solution, and recording your observations, you are ready for an unknown. Obtain the unknown from your instructor and determine the contents of the solution, again being certain to write down all of your observations. Summarize your results in your notebook as follows:

- Cations probably present _______________________
- Cations probably absent _______________________

Show your instructor your results before leaving the laboratory, and they will be checked for you.

WRITING UP THE NOTEBOOK

As you went through the experiment you described your observations and intermediate conclusions. There is a final portion to the experimental write-up that can be done outside of the laboratory. This consists of writing bal-
balanced equations for at least some of the reactions you observed and answering some other questions regarding the experiment. Your grade on the laboratory book depends on the overall quality of your write-up and on your answers to the final questions.

For this experiment, write answers to the following questions in your laboratory book.

1. Write the balanced, net ionic equation for the reaction occurring when
   (a) Cl⁻ is added to a solution containing Pb²⁺
   (b) Cl⁻ is added to a solution containing Hg₂²⁺

2. Write a balanced equation for the reaction that occurs on adding excess aqueous ammonia to AgCl.
Begin with about 1 mL of known or unknown solution. Add 3-5 drops of chilled 6 M HCl. Centrifuge and test for complete precipitation with another drop of 6 M HCl. Centrifuge and decant.

Ppt. is AgCl, PbCl₂, Hg₂Cl₂

Add 20 drops (about 1 mL) of hot water. Mix well. Heat in a boiling water bath, stirring vigorously to dissolve all the PbCl₂.

Centrifuge immediately (so the solution does not cool) and decant.

Precipitate is AgCl and Hg₂Cl₂

Wash twice with hot water to remove any remaining PbCl₂.

Add 10 drops of 6 M NH₃. Mix well. Centrifuge and decant.

Gray precipitate is HgNH₂Cl + Hg Indicates presence of Hg²⁺ ion in original solution. If a white ppt. is observed here it is probably Pb(OH)Cl from Pb²⁺ that was not removed completely.

Solution contains Pb²⁺

Test for Pb²⁺: Add 2 drops of 0.2 M K₂CrO₄. Mix and centrifuge. Yellow precipitate of PbCrO₄ confirms presence of Pb²⁺.

Solution contains [Ag(NH₃)₂]⁺

Add 6 M HNO₃ dropwise until solution is acidic. (Be sure to stir before testing.) A white ppt. is AgCl and indicates that Ag⁺ was present in the original solution.
NOTES OF SILVER GROUP ANALYSIS

1. Some observations that may be made early in the analysis often turn out to be useful later. For example, AgCl acquires a slight purplish tint on standing in light for a while. Also, the crystals of PbCl₂ look more like snow than the denser solid, AgCl.

2. In separating these ions from others, it is important to add enough HCl to get complete precipitation. Cold HCl is used because this gives a more complete precipitation of the more soluble salt PbCl₂. An excess of HCl must be avoided because soluble complex ions such as AgCl₂⁻ or PbCl₄²⁻ may be formed.

3. PbCl₂ may be slow to dissolve on heating. Stir well and make every effort to make sure it is completely dissolved. Then you should centrifuge and decant as quickly as possible, before the solution has a chance to cool and reprecipitate the PbCl₂.

4. If the Pb²⁺ ion is not completely separated from AgCl and Hg₂Cl₂, addition of NH₃ will produce an insoluble white basic salt, Pb(OH)Cl. This is soluble in HNO₃ so it should not interfere with the confirming test for silver, but it should not be confused with the white salt HgClNH₂ in the confirmation of Hg₂²⁺.

5. If the solution is quite basic from the addition of NH₃, a substantial amount of HNO₃ may be needed to precipitate AgCl. Stir the solution well before testing for acidity. Remember that blue litmus paper turns red in acid.

6. The yellow K₂CrO₄ solution should not be mistaken for the yellow PbCrO₄ precipitate. Centrifuge before concluding that Pb²⁺ is present or absent.