

ANALYSIS OF THE SILVER GROUP CATIONS

Ag⁺ Pb²⁺ Hg₂²⁺ Analysis of a Mixture of Cations

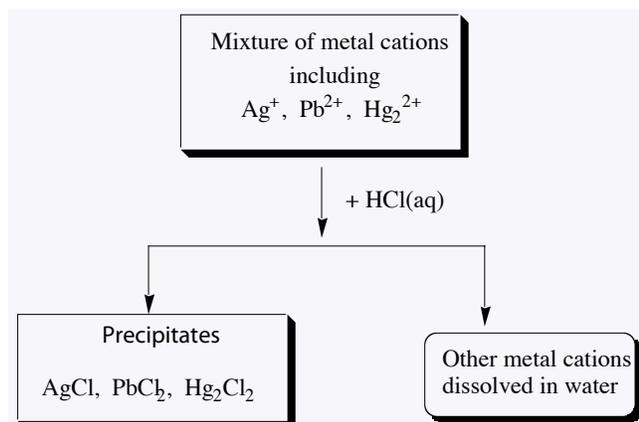
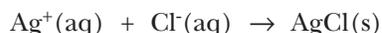
One problem often faced in **qualitative analysis** is to test for one ion in a mixture of many ions. To find a test for one ion that is not interfered with by another ion is nearly impossible. Therefore, if one has a mixture of a large number of ions, the usual approach is to use a chemical method to 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.

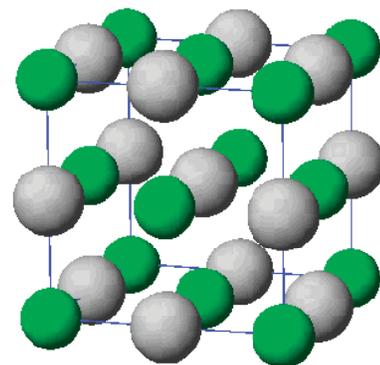
CHEMISTRY OF THE SILVER GROUP CATIONS

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,



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



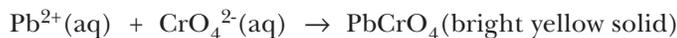
The structure of solid AgCl. Note that this model of the unit cell of AgCl has a net of 4 Ag⁺ ions and 4 Cl⁻ ions. As you will see in Chapter 13 of *Chemistry & Chemical Reactivity*, the structure can be thought of as a face centered cubic lattice of Cl⁻ ions with Ag⁺ ions in the octahedral holes (like NaCl). See the Models folder on the *General Chemistry Interactive CD-ROM*.

Properties of the Chlorides of Silver Group Cations

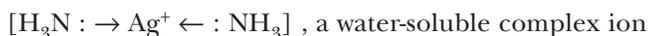
Compound	Color	Solubility (20 °C) per 100 g H ₂ O	Solubility (100 °C) per 100 g H ₂ O	Reaction with Ammonia
AgCl	white	0.00015 g	0.0021 g	forms colorless soluble complex
PbCl ₂	white	1.0 g	3.3 g	forms white ppt. Pb(OH)Cl
Hg ₂ Cl ₂	white	0.0002 g	0.001 g	redox reaction; see text

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.

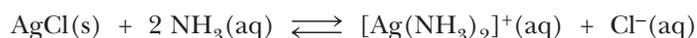
As you can see in the table of properties of the three silver group chlorides, PbCl₂ is by far the most soluble of the three in water. Therefore, the first step in separating the three chlorides is to treat the solid mixture with hot water to selectively dissolve PbCl₂ and to leave AgCl and Hg₂Cl₂ as 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, CrO₄²⁻, combine to form the bright yellow, insoluble solid lead(II) chromate, PbCrO₄.



Silver(I) and mercury(I) chlorides are too insoluble in water to be redissolved 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.



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.

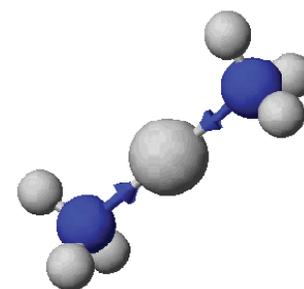
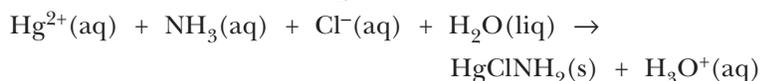


In this way, the silver(I) ion is separated from the mercury(I) ion, as noted on the attached separation scheme.

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), Hg²⁺] and reduced (to metallic mercury).



This reaction is induced by the presence of ammonia. In addition, when ammonia and Cl⁻ ion are present, the Hg²⁺ ion forms a rather strange compound, an amido salt HgClNH₂. The latter is an insoluble white solid.



The silver-ammonia complex ion, Ag(NH₃)₂⁺.

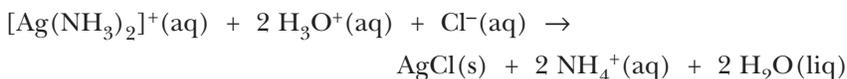
The reaction of aqueous ammonia with AgCl is illustrated and described on page 779 of Chemistry & Chemical Reactivity (6e).

Therefore, when NH_3 is added to the $\text{AgCl}/\text{Hg}_2\text{Cl}_2$ mixture the AgCl dissolves, as described above, and the Hg_2Cl_2 turns into black or gray finely-divided mercury metal and the white insoluble solid HgClNH_2 . The net reaction for Hg_2Cl_2 is



Notice that a second molecule of the base NH_3 is used to “collect” the H^+ , an acid, that is produced when Hg^{2+} reacts with NH_3 ; the product is of course the salt NH_4Cl . The importance of this reaction is that it provides confirmation of the presence of the mercury(I) ion, Hg_2^{2+} , in a solution of unknown composition.

If we had started with a mixture of AgCl , PbCl_2 , and Hg_2Cl_2 , we have now reached the point where the Pb^{2+} ion has been separated and identified, the Hg_2Cl_2 has been converted to $\text{Hg}(\text{l})$ and HgClNH_2 , and the silver(I) ion is in solution in the form of the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ (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 (NH_3) to form the very stable ammonium ion. Thus, the NH_3 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 .



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.

Be sure to record your observations at each stage in your notebook.

WRITING UP THE NOTEBOOK

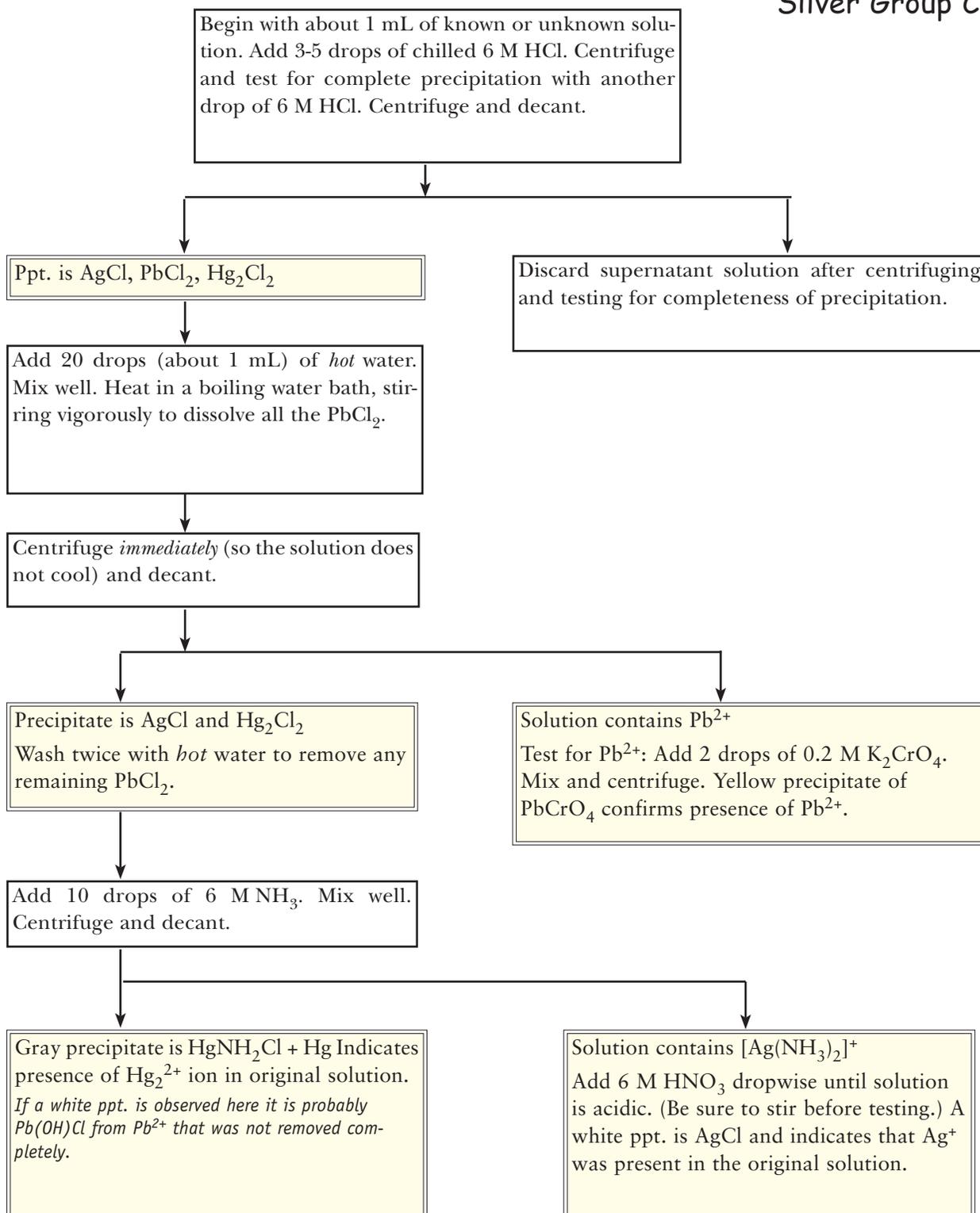
As you went through the experiment you described your observations and intermediate conclusions. There is a final portion to the experimental write-up that can be done outside of the laboratory. This consists of writing bal-

anced 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.

Scheme for Analysis of Silver Group Cations



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.