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Experiment #10 – Qualitative Analysis of Group I Cations

Qualitative analysis is a branch of analytical chemistry that identifies particular substances in a given sample of material. In the analysis of inorganic substances, this branch involves the analysis of both metallic constituents as cations and nonmetallic constituents as anions. Qualitative analysis has remained an important part of the laboratory experience in general chemistry for a number of years even though such analytical methods have been replaced by sophisticated instrumental methods for practical analysis.

In this experiment, you will analyze a known solution that contains all the Group I cations—silver, lead (II), and mercury(I)—and an unknown solution to determine which ions are present and which are absent.

The chlorides of Ag^{+}, Pb^{2+}, and Hg_2^{2+} are all insoluble in cold water. They can be removed as a group from solution by the addition of HCl. The reactions that occur are simple precipitations and can be represented by the equations:

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s) \qquad (1)$$

$$Pb^{2+}(aq) + 2\,Cl^{-}(aq) \rightarrow PbCl_2(s) \qquad (2)$$

$$Hg_2^{2+}(aq) + 2\,Cl^{-}(aq) \rightarrow Hg_2Cl_2(s) \qquad (3)$$

It is important to add enough HCl to ensure complete precipitation, but not too large an excess. In concentrated HCl solution, these chlorides tend to dissolve, producing chloro-complexes such as $AgCl_2^{-}$.

Lead (II) chloride is separated from the other two chlorides by heating with water. The K_{sp} for $PbCl_2$ greatly increases with temperature, favoring less solid and more ions, therefore the $PbCl_2$ dissolves in hot water:

$$PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2\,Cl^{-}(aq) \qquad (4)$$

Once Pb^{2+} has been put into solution, we can check for its presence by adding a solution of K_2CrO_4. The chromate ion, CrO_4^{2-}, gives a yellow precipitate with Pb^{2+}:

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow \underset{\text{yellow}}{PbCrO_4(s)} \qquad (5)$$

The other two insoluble chlorides, AgCl and Hg_2Cl_2, can be separated by adding aqueous ammonia. Silver chloride dissolves, forming the complex ion $Ag(NH_3)_2^+$:

$$AgCl(s) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad (6)$$

Ammonia also reacts with Hg_2Cl_2 via a rather unusual oxidation-reduction reaction. The products include finely divided metallic mercury, which is black, and a compound of formula $HgNH_2Cl$, which is white:

$$\underset{\text{white}}{Hg_2Cl_2(s)} + 2\ NH_3(aq) \rightarrow \underset{\text{black}}{Hg(l)} + \underset{\text{white}}{HgNH_2Cl(s)} + NH_4^+(aq) + Cl^-(aq) \qquad (7)$$

As this reaction occurs, the solid appears to change color, from white to black or grey.

The solution containing $Ag(NH_3)_2^+$ needs to be further tested to establish the presence of silver. The addition of a strong acid (HNO_3) to the solution destroys the complex ion and reprecipitates silver chloride. We may consider that this reaction occurs in two steps:

$$Ag(NH_3)_2^+(aq) + 2\ H^+(aq) \rightarrow Ag^+(aq) + 2\ NH_4^+(aq)$$

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

+

$$Ag(NH_3)_2^+(aq) + 2\ H^+(aq) + Cl^-(aq) \rightarrow \underset{\text{White}}{AgCl(s)} + 2\ NH_4^+(aq) \qquad (8)$$

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Procedure

Wear your safety glasses while performing this experiment. Lead and mercury salts are toxic, and chromates are known to be carcinogenic. Silver ion is corrosive and leaves a black stain on the skin. Make certain to wash your hands thoroughly when you leave the laboratory. Work with two separate solutions in test tubes, (1) a known solution that contains all three ions and (2) a separate test solution with unknown ions. Label your solutions and your stirring rods well with different colored tape to avoid cross contamination between your known and unknown samples.

1. Precipitation of Group I Ions. Add 2 drops of 6 M HCl to 1 mL of each test solution in separate small test tubes. Centrifuge the solution, being careful to balance the centrifuge by placing test tubes containing equal volumes on opposite sides of the centrifuge. Add one more drop of the 6 M HCl to each solution to test for completeness of precipitations. Centrifuge again if necessary, and decant the supernatant solution from the chloride precipitate. The solution should be saved for further study if ions from other groups may be present and need testing. (For this experiment we are done with the solution and it is now waste.)

2. Separation of Pb^{2+}. Add 1 mL of distilled water to the precipitate in the test tube and place in a 100 mL beaker that is half full of boiling water*. Allow the tube to remain in the boiling water bath for a few minutes and stir occasionally with a glass rod. The higher temperature should start dissolving the $PbCl_2$ solid

   Centrifuge the hot solution and pour it into another test tube and **save the solution for step 3**. **Save the remaining precipitate for testing in step 4**.

   *Note: Watch the level of water in the beaker. Add water when it is low. Never add water to a dry hot beaker as the glass is likely to break.

3. Identification of Pb^{2+}. To the **solution from step 2**, add one drop of 6 M acetic acid and a few drops of 1 M K_2CrO_4. If Pb^{2+} is present in the solution, a yellow precipitate of $PbCrO_4$ will form.

4. Separation and Identification of Hg_2^{2+}. To the **precipitate from step 2**, add 15 to 20 drops of 6 M NH_3 and stir thoroughly. Centrifuge the solution and decant. (**Save the decanted solution for step 5!)** A gray or black precipitate, produced by reaction of Hg_2Cl_2 with ammonia to produce metallic mercury, will establish the presence of Hg_2^{2+}.

5. Identification of Ag^+. To the **solution from step 4**, add 6 M HNO_3 until it is acidic toward litmus paper. (*Remember you previously added 15-20 drops of base).* Test for acidity by dipping the end of your stirring rod in the solution and then touching it to a piece of blue litmus paper (red in acid solution). If Ag^+ is present in the acidified solution, a white precipitate of AgCl will form.

6. If you analyzed ONLY the known solution, then obtain an unknown and analyze it for the possible presence of Ag^+, Pb^{2+}, and Hg_2^{2+}.

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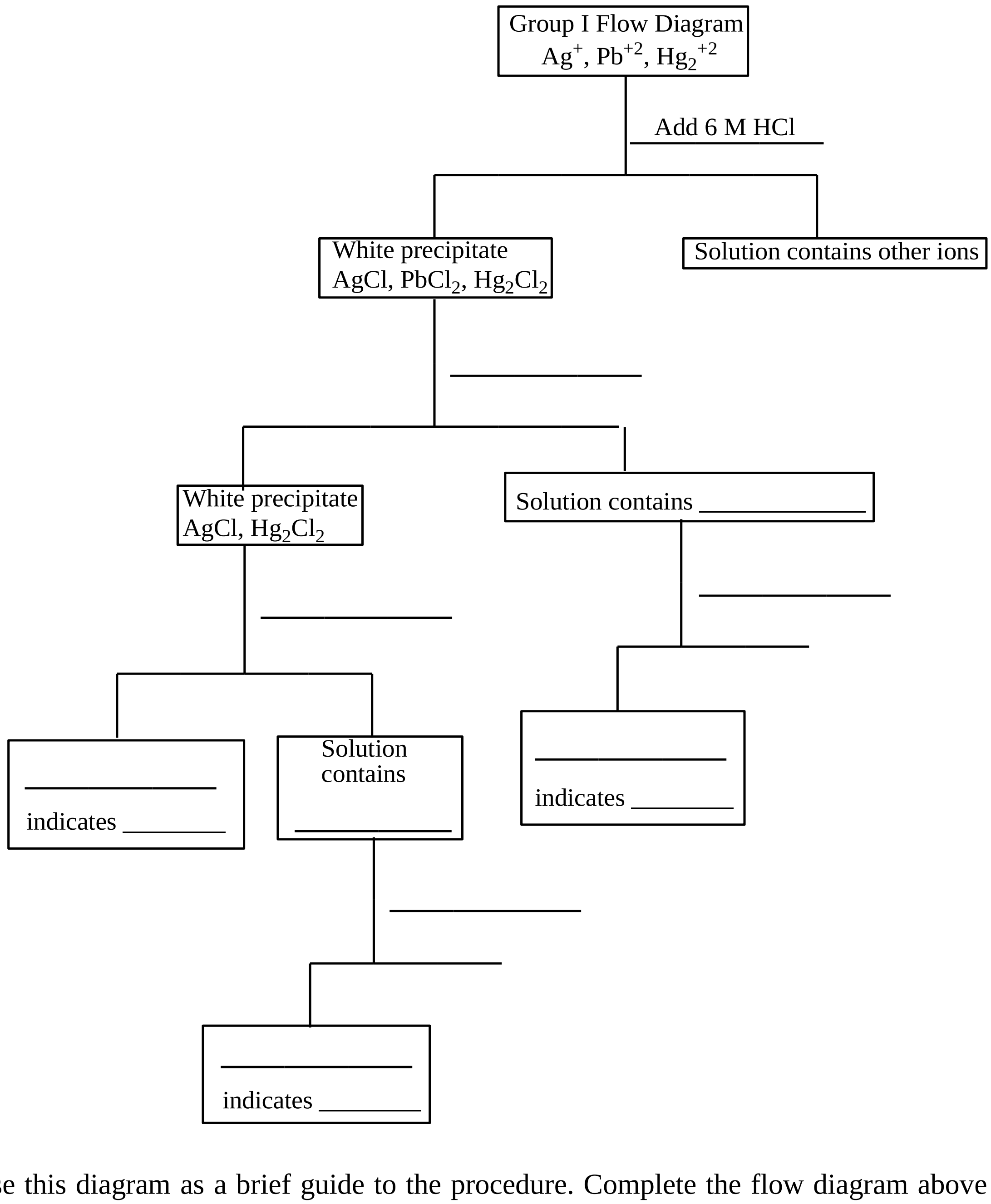
It is possible to summarize the directions for analysis of the Group I cations in what is called a flow diagram. In the diagram, vertical lines link successive steps in the procedure. Reactant cations or reactant substances containing the ions are at the top end of each line and products formed are at the bottom end. On the product end, a horizontal line separates the solid products on the left and the solution products on the right. Reagents and conditions used to carry out each step are placed alongside the lines. A partially completed flow diagram for the Group I ions follows:



Use this diagram as a brief guide to the procedure. Complete the flow diagram above by directly recording your observations on your known (in the boxes) and unknown (beside the boxes), perhaps using different colored markers.

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Experiment Results:

UNKNOWN NUMBER ________ IONS PRESENT _________________________

Post-Lab Questions: Group I Cations

1. A solution may contain Ag^+, Pb^{2+}, and Hg_2^{2+}. A white precipitate forms on addition of 6 M HCl. The precipitate is partially soluble in hot water. The solid remaining after treatment with hot water turns black on addition of 6 M NH_3. Which of the ions are present, which are absent, and which remain undetermined? State your reasoning below. NOTE: simply listing ions below without the appropriate reasoning will NOT earn you any credit!

Present ______________________________________

Absent ______________________________________

In Doubt ____________________________________