EXPERIMENT 11

Group I Cations: The Silver Group

Introduction

The Group I cations, Ag^+, Pb^{2+}, and Hg_2^{2+} are the only common cations that form insoluble chlorides in dilute hydrochloric acid. This allows the Group I cations to be separated from other cations in solution by addition of HCI. The net-ionic equations for the precipitation are:

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)} \quad \textbf{(EQ 11.1)}$$

$$Hg_2^{2+} + 2C1^- \rightarrow Hg_2Cl_{2(s)} \quad \textbf{(EQ 11.2)}$$

$$Pb^{2+} + 2C1^- \rightarrow PbCl_{2(s)} \quad \textbf{(EQ 11.3)}$$

Table 11.1 gives the solubility product and molar solubility values for these chloride salts. Note that the $PbCl_2$ is significantly more soluble. The solubility of $PbCl_2$ increases significantly with increase in temperature. This increase in solubility on heating is the basis of separating $PbCl_2$ from the AgCl and Hg_2Cl_2.

$$PbC1_2 + H_2O + \text{heat} \rightarrow Pb^{2+}_{(aq)} + Cl^-_{(aq)} \quad \textbf{(EQ 11.4)}$$

TABLE 11.1 Solubilities of Group I Chlorides at 25°C

Salt	K_{sp}	Molar Solubility, *M*
Hg_2C1_2	1.1×10^{-18}	6.5×10^{-7}
AgCl	1.8×10^{-10}	1.3×10^{-5}
$PbC1_2$	1.7×10^{-5}	1.6×10^{-2}

Lead ion is confirmed by adding K_2CrO_4 to the test solution which precipitates yellow lead chromate.

$$Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4 \quad \textbf{(EQ 11.5)}$$

Aqueous ammonia is used to separate AgCl and Hg_2Cl_2 solids. Silver chloride dissolves in aqueous ammonia, forming a complex ion.

$$AgCl + 2NH_3 \rightarrow Ag(NH_3)_2Cl \quad \textbf{(EQ 11.6)}$$

By contrast, Hg_2Cl_2 undergoes auto-oxidation-reduction in aqueous ammonia, forming metallic mercury, a black precipitate, and $HgNH_2C1$, an insoluble white salt.

$$Hg_2Cl_2 + 2NH_3 \rightarrow Hg_{(l)} + HgNH_2Cl_{(s)} + NH_4^+ + Cl^- \quad \textbf{(EQ 11.7)}$$

The formation of a black precipitate on addition of aqueous ammonia confirms mercury.

Silver ion is confirmed by acidifying the aqueous ammonia extract with nitric acid. The acid destroys the silver ammine complex, causing the silver chloride to re-precipitate.

$$Ag(NH_3)_2^+ + 2H^+ + Cl^- \rightarrow AgCl + 2NH_4^+ \quad \textbf{(EQ 11.8)}$$

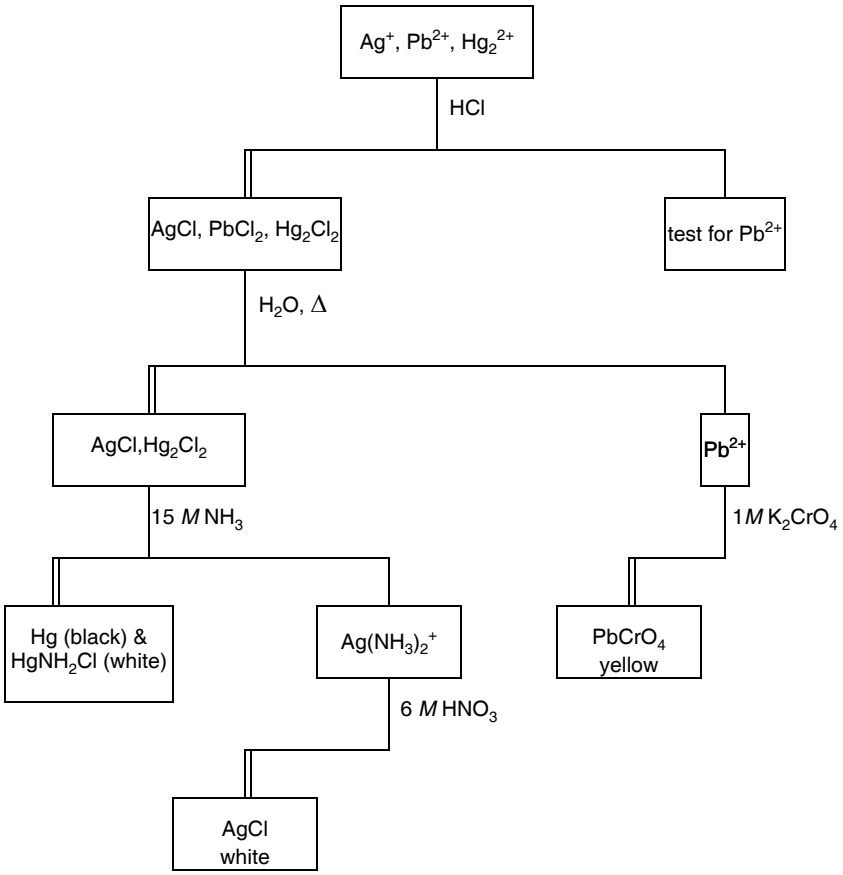
The formation of a whitish precipitate on addition of aqueous ammonia occurs when $PbCl_2$ is not completely removed by the hot water extraction. Any $PbCl_2$ remaining with the Hg_2Cl_2 and AgCl reacts with NH_3 according to the equation.

$$2PbCl_{2(s)} + 3NH_3 + 3H_2O \rightarrow Pb(OH)Cl_{(s)} + Pb(OH)_{2(s)} + 3NH_4^+ + 3Cl^- \quad \textbf{(EQ 11.9)}$$

The equation is written this way because varying amounts of white insoluble products are formed.

Experimental Procedure: Analytical Group I

FIGURE 11.1 Flow Chart for Group I: The Silver Group



Test a known solution simultaneously with your unknown.

Step 1: Precipitation of Group 1. To 10 drops of the solution to be analyzed add 2 drops 6 *M* HCI. Stir well. Cfg and decant the solution (S 1) from the ppt (P1). Treat the ppt P1 according to Step 2.

STEP 2: Dissolving Lead Chloride. Boil about 10 mL of DI water in a small beaker. Add 10 drops of the hot DI H_2O to P1 and heat in a water bath for 2-3 minutes Stir. Immediately cfg. and decant the solution (S2) while still hot. Repeat this extraction on any remaining ppt (P2). Test S2 according to Step 3. Treat the P2 as in Step 4.

STEP 3: Test for Lead. To solution S 1 or S2 add 2 drops 1 *M* K_2CrO_4. Formation of a yellow ppt of $PbCrO_4$ confirms lead.

STEP 4: Separation of Silver and Test for Mercury. To ppt P2 add 4 drops 15 *M* NH_3. Stir, Cfg, and decant solution (S3). Repeat with another 4 drops 15 *M* NH_3, combining both solutions. A black ppt formed on the addition of the NH_3 confirms mercury. Test solution S3 as in Step 5.

STEP 5: Test for Silver. To solution S3 add 6 *M* HNO_3 until acidic to litmus; add 1 more drop. Formation of a white ppt of AgCl confirms silver.

Data and Calculations

1. Write a flow chart for your unknown analysis in your lab notebook. You should include formulas of all reagents added, colors of all solutions and ppts, and conclusions made from these observations. For example, your original solution is colorless, you add HCl forming a white ppt and a colorless solution. At this point you do not know what the formula of the white ppt is, so do not write one.
2. What cation is present in your unknown?

Questions

1. Write net-ionic equations for all the reactions occurring in the Group I analysis for each cation in the group. Write all the reactions for lead, then all those for mercury, then all those for silver.
2. Calculate the $[Ag^+]$ that would remain in solution under the conditions of the group precipitation, i.e., 1.0 *M* HCl and 0.10 M Ag^+ at time of mixing.
3. Using a single reagent, how could you distinguish between the following pairs of substances contained in separate test tubes? Give the net-ionic equation for each test.
    a. AgCl and $ZnCl_2$ (solids)
    b. $PbCl_2$ and Hg_2Cl_2 (solids)
    c. $Cd(NO_3)_2$ and $AgNO_3$ (solutions)
    d. HCl and HNO_3 (solutions)
    e. $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ (solutions)