Directions: Answer the following questions. For numerical answers a) show all work to support your final numerical answer(s), b) include correct units and significant figures, and c) circle your final numerical answer. Answer non-numerical questions by a) answering the question, b) fully explaining, and c) using complete sentences.

1. During the qualitative analysis scheme, preliminary separation of cations into five different groups via addition of four different group reagents is based upon what factor?

   Based upon differences in Ksp value.

2. An aqueous solution of a salt (one cation and one anion) is thought to contain the metal cation Ba\(^{2+}\). To test this hypothesis, a student added (NH₄)₂CO₃ in NH₃/NH₄Cl buffer to 1 mL of the salt solution and obtained a precipitate. The student then concluded that the aqueous solution contained a Group IV metal cation.

   a. What is wrong with this student's reasoning?

   b. To what groups could the cation belong?

   c. What is the proper procedure for testing for the presence of a Group IV metal cation?

3. An aqueous solution was tested for the presence of cations belonging to Groups I-V as outlined in Experiment 8. The first group reagent was added to 1 mL of the aqueous solution and any precipitate was separated from the supernatant liquid. The second group reagent was added to the supernatant liquid and any precipitate was separated, etc. In this way, the four group reagents were sequentially added to the supernatant liquid obtained from the previous separation step. The experimental results are listed below. Cations from which groups are or may be present in this solution? Explain.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:  dilute HCl</td>
<td>no precipitate</td>
</tr>
<tr>
<td>2:  H₂S in 0.3 M HCl</td>
<td>precipitate</td>
</tr>
<tr>
<td>3:  H₂S in NH₃/NH₄Cl</td>
<td>precipitate</td>
</tr>
<tr>
<td>4:  (NH₄)₂CO₃ in NH₃/NH₄Cl</td>
<td>no precipitate</td>
</tr>
</tbody>
</table>

Cations from Groups II and III are present and cations from Groups IV may be present.
4. To prove the statement...PbCl₂ is more soluble than AgCl...found on page 91 of Experiment 8, calculate the solubilities (in g/100 mL) of AgCl and PbCl₂ in pure water. The equilibria are:

\[
\begin{align*}
\text{AgCl(s)} & \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) & K_{sp} &= 1.8 \times 10^{-10} \\
\text{PbCl}_2(s) & \rightleftharpoons \text{Pb}^{2+}(aq) + 2 \text{Cl}^-(aq) & K_{sp} &= 1.2 \times 10^{-5}
\end{align*}
\]

\[K_{sp} = x^2\
\]
\[x = 0.30 M\]
\[\text{AgCl}(s) \rightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)\]  
\[\text{PbCl}_2(s) \rightarrow \text{Pb}^{2+}(aq) + 2 \text{Cl}^-(aq)\]

A solution is 0.00030 M in each of the cations, Ag⁺, Hg₂⁺, and Pb²⁺. The K_{sp} values for AgCl, Hg₂Cl₂, and PbCl₂ are 1.8 \times 10^{-10}, 1.4 \times 10^{-18}, and 1.2 \times 10^{-5}, respectively.

a. (1) Calculate the concentration of Cl⁻ needed to begin the precipitation of each cation.

\[\text{Need CCl} > \text{M}\]

b. (2) As dilute HCl is added and the concentration of Cl⁻ is steadily increased, which chloride salt precipitates first? Which last?

c. (1) What concentration of Cl⁻ is needed to precipitate as much Hg₂Cl₂ as possible without precipitating the Ag⁺ or Pb²⁺?

d. (1) What concentration of Cl⁻ is needed to precipitate as much Ag⁺ and Hg₂⁺ as possible without precipitating the Pb²⁺?

e. (1) Enough HCl is added so that the equilibrium concentration of Cl⁻ is 0.20 M. Calculate the concentration of Ag⁺ and Pb²⁺ which remain in solution when [Cl⁻]_{eq} = 0.20 M.

f. (2) At this concentration of Cl⁻, which one of the cations (Ag⁺ or Pb²⁺) still remains in solution to a significant extent? Remember, the original solution was 0.00030 M in each cation. Explain. Only the Pb²⁺ still remains in solution to a significant extent at this conc. Cl⁻. Most of the Ag⁺ is precipitated at this conc. Cl⁻.
Chemistry 116: Laboratory Homework
Experiment 9 & 10: Groups II-III Qualitative Analysis

Student Name: [Name] Lab Room No. [Room No.]
Lab Day [Day] Lab Start Time [Time] Date [Date]

Directions: Answer the following questions. For numerical answers a) show all work to support your final numerical answer(s), b) include correct units and significant figures, and c) circle your final numerical answer. Answer non-numerical questions by a) answering the question, b) fully explaining, and c) using complete sentences.

1. A solution is saturated with H₂S at a concentration of 0.10 M and is 4.0 × 10⁻⁵ M in each of the metal cations Co²⁺, Fe⁺⁺, Mn²⁺, Ni²⁺, and Zn²⁺. At a pH of 4.0, which of the metal cations will precipitate as the sulfide? Explain. (HINT: Calculate IP.)

   \[
   \begin{align*}
   \text{Metal Sulfide} & \quad K_{sp} \\
   \text{ZnS} & \quad 3 \times 10^{-2} \\
   \text{NiS} & \quad 0.80 \\
   \text{CoS} & \quad 3 \\
   \text{FeS} & \quad 6 \times 10^{-2} \\
   \text{MnS} & \quad 3 \times 10^{-6}
   \end{align*}
   \]

   \[
   K_{sp} = \frac{[\text{M}^{2+}] [\text{S}^{2-}]}{[\text{MS}]} \]

   \[
   \text{H}_2\text{S} + \text{M}^{2+} \rightarrow \text{M}^{2+} + \text{H}_2\text{S} \text{(aq)}
   \]

   \[
   K_{sp} \text{ (CoS)} = \frac{[\text{Co}^{2+}] [\text{S}^{2-}]}{[\text{CoS}]} = \frac{(4.0 \times 10^{-5}) (0.10)}{(1 \times 10^{-4})^2} = 4 \times 10^{-2}
   \]

   Zn²⁺, Ni²⁺, Co²⁺, and Mn²⁺ will precipitate as the sulfides since their products are greater than the solubility product constants.

2. Under the conditions given in the preceding question, what pH is needed to precipitate as much of the Zn²⁺ and Ni²⁺ as possible without precipitating the Co²⁺, Fe⁺⁺ and Mn²⁺?

   \[
   \begin{align*}
   \text{As steadily raise pH, Co}^{2+} \text{ will ppt before Fe}^{2+} + \text{Mn}^{2+} \\
   \text{CoS} + 2\text{H}^+ \rightarrow \text{Co}^{2+} + \text{HS}^- + \text{H}_2\text{O} \\
   K_{sp} = \frac{[\text{Co}^{2+}] [\text{HS}^-]}{[\text{CoS}]} = \frac{(4.0 \times 10^{-5}) (0.10)}{(1 \times 10^{-4})^2} = 1.5 \times 10^{-3}
   \end{align*}
   \]

   \[
   \text{pH} = 2.9
   \]

3. Under the conditions given in the first question, at what pH will the Fe⁺⁺ first begin to precipitate from solution?

   \[
   \begin{align*}
   K_{sp} = \frac{[\text{Fe}^{2+}] [\text{CH}_3\text{S}]}{[\text{CH}_3\text{O}J]} \\
   \text{CH}_3\text{O}J = \left(\frac{4.0 \times 10^{-5} (0.10)}{K_{sp}}\right)^{\frac{1}{2}} = 8.16 \times 10^{-3}
   \]

   \[
   \text{pH} = \log 8.16 \times 10^{-5}
   \]

   At pH > 4.1, Fe⁺⁺ will first begin to precipitate from solution.
Experiments 9 & 10: Groups II & III Qualitative Analysis

4. An aqueous solution contains the metal cations Hg$^{2+}$ and Mn$^{2+}$ belonging to Groups II and III, respectively. Thioacetamide, which produces H$_2$S, is added, and the solution is buffered to a pH of 8 by addition of NH$_3$/NH$_4$Cl.

a. Under these Group III conditions, what compounds will precipitate from solution?

HgS and MnS will both precipitate.

b. If Group II conditions are imposed by lowering the solution pH to 1, what compound(s) (if any) will remain precipitated?

HgS will remain precipitated. The MnS will no longer be precipitated at this pH.

5. A solution is 0.0016 M in each of the metal cations Mn$^{2+}$ and Cu$^{2+}$. (MnS: $K_{spA} = 3 \times 10^{-10}$, CuS: $K_{spA} = 6 \times 10^{-16}$)

a. Enough thioacetamide and HCl are added to give the following equilibrium concentrations: [H$_2$S]$_{eq} = 0.1$ M and [H$_3$O$^+$] = 6 M. Calculate the concentrations of Mn$^{2+}$ and Cu$^{2+}$ which remain in solution under these Group II conditions.

\[
\frac{\text{Mn}^{2+}}{\text{K}_{spA} = \frac{\text{C}_{\text{Mn}^{2+}} \cdot \text{C}_{\text{Cu}^{2+}}}{\text{C}_{\text{H}_2\text{S}}}} = \frac{3 \times 10^{-10} \times (6 \times 10^{-6})^2}{0.1} = 1 \times 10^{-7} M
\]

\[
\frac{\text{Cu}^{2+}}{\text{K}_{spA} = \frac{\text{C}_{\text{Mn}^{2+}} \cdot \text{C}_{\text{Cu}^{2+}}}{\text{C}_{\text{H}_2\text{S}}}} = \frac{6 \times 10^{-16} \times (6 \times 10^{-6})^2}{0.1} = 3 \times 10^{-25} M
\]

b. Under these Group II conditions, have the cations (Mn$^{2+}$ or Cu$^{2+}$) been almost totally removed from solution by precipitation? Explain.

Yes, both Mn$^{2+}$ and Cu$^{2+}$ have been almost totally removed from solution.

4. Enough NH$_3$/NH$_4$Cl buffer is added to give the following equilibrium conditions: [NH$_3$] = 2.0 M, [NH$_4$Cl]$_{eq}$ = 0.10 M, and [H$_2$S]$_{eq}$ = 0.016 M. Calculate the concentrations of Cu$^{2+}$ and Mn$^{2+}$ which remain in solution under these Group III conditions.

\[
\text{[NH}_3\text{]} = 2.0 M, \quad \text{[NH}_4\text{Cl]} = 0.10 M, \quad \text{[H}_2\text{S]} = 0.016 M
\]

\[
\text{pH} = 9.24 + \log \left( \frac{\text{Cu}^{2+}}{\text{K}_{spA}} \right) = 9.24 + \log \left( \frac{1 \times 10^{-7}}{3 \times 10^{-25}} \right) = 9.24 + 25.50 = 34.74
\]

\[
\text{Cu}^{2+} = \frac{1 \times 10^{-7}}{3 \times 10^{-25}} M
\]

\[
\text{Mn}^{2+} = \frac{0.10}{3 \times 10^{-25}} M
\]

d. Under these Group III conditions, have the cations (Mn$^{2+}$ or Cu$^{2+}$) been almost totally removed from solution by precipitation? Explain.

Yes, both Mn$^{2+}$ and Cu$^{2+}$ have been almost totally removed from solution.