Chem 116 Make-up Experiment

Group Separations in Qualitative Analysis

Objective:

To become familiar with the qualitative analysis scheme for the metallic cations and to learn the procedure for separating cations into five different groups with the addition of four different group reagents.

Introduction:

Qualitative Analysis Scheme: *Qualitative analysis* concerns the methods and principles involved in determining what constituents are present in a given material. Qualitative analysis schemes, such as the one to be studied in this course, are rarely used today for actual analytical work. Analyses today are completed much more quickly by physical methods, by spot tests with a variety of selective organic reagents, or by instrumental methods. Today, qualitative analysis is used primarily to provide a convenient way to study the chemistry of the metals and to illustrate the principles which govern chemical reactions in solutions.

In this course, the qualitative analysis of solutions of metallic cations will be studied. The scheme of analysis is based upon the fact that successive groups of cations can be precipitated, leaving other cations in solution. The precipitating reagents (or *group reagents*) are chosen so that the one precipitating the smallest number of elements is used first. *Preliminary separation of the cations into Groups I through V is based upon relative K_{sp} values.* The scheme for preliminary separation of the cations into five different groups via the addition of four different group reagents is shown in outline form in Figure 1 (next page).

The cations in Group I are those that precipitate as chlorides upon addition of the first group reagent, cold dilute HCl. Precipitation of these three cations occurs because, under Group I conditions, the *ion product (IP)* exceeds the K_{sp} value only for the chlorides of Ag^+, Hg_2^{+2}, and Pb^{+2}. Remember, precipitation will occur only when IP > K_{sp}. If IP ≤ K_{sp}, precipitation will not occur. Pb^{+2} is not completely precipitated in Group I because $PbCl_2$ is considerably more soluble (i.e. has a higher K_{sp} value) than the chlorides of Ag^+ and Hg_2^{+2}.

The cations in Group II are those that precipitate as sulfides upon addition of the second group reagent, H_2S in 0.3 M HCl (acidic solution). Precipitation of these four cations occurs because, under Group II conditions, the ion product (IP) exceeds the K_{sp} value only for the sulfides of Pb^{+2}, Hg^{+2}, Bi^{+3} and Cu^{+2}. The Group II sulfides, PbS, HgS, Bi_2S_3, and CuS, are referred to as the *acid insoluble sulfides*. These four sulfides have such low K_{sp} values and are so insoluble they will precipitate even in acidic solutions (as well as neutral and basic solutions).

The cations in Group III are those that precipitate as sulfides (or hydroxide in the case of Al^{+3}) upon addition of the third group reagent, H_2S in NH_3/NH_4Cl (basic solution). Precipitation of these four cations occurs because, under Group III conditions, the ion product (IP) exceeds the K_{sp} value only for the sulfides (or for aluminum the hydroxide) of Ni^{+2}, Mn^{+2}, Fe^{+2} and Al^{+3}. The Group III sulfides, NiS, MnS, and FeS, are referred to as the

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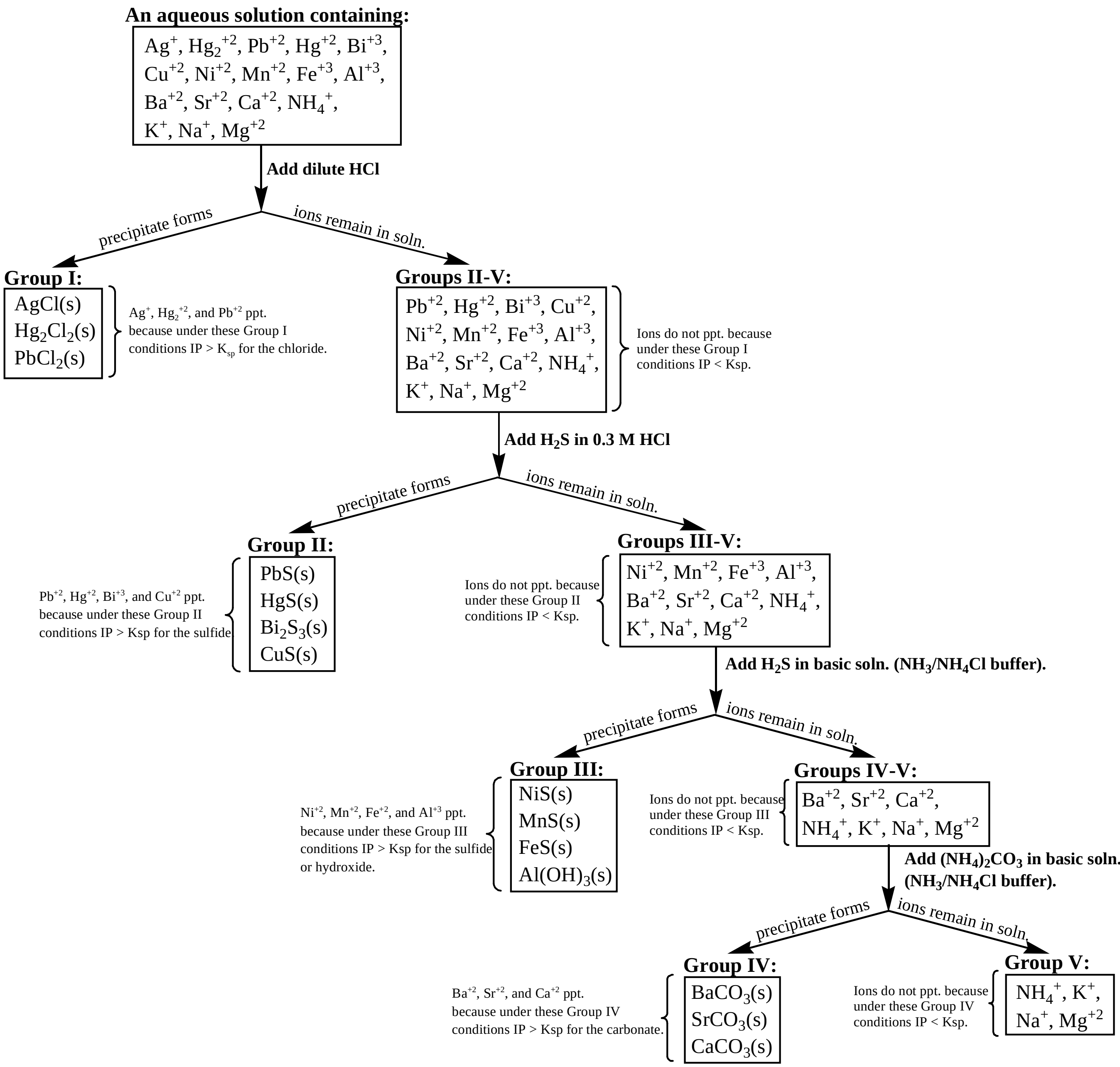

Figure 1.
Qualitative Analysis Scheme: Separation into Groups I-V

base insoluble sulfides. These three sulfides have significantly higher K_{sp} values than the Group II sulfides and are soluble in very acidic solutions. Therefore, a basic solution is required for precipitation of the Group III sulfides. Adjustment of the acidity before precipitation of Group II is one of the most important steps in the entire scheme of cation analysis. If the acidity is too high, the Group II sulfides will not precipitate. If the acidity is too low, Group III will precipitate along with Group II.

The cations in Group IV are those that precipitate as carbonates upon addition of the fourth group reagent, $(NH_4)_2CO_3$ in NH_3/NH_4Cl buffer (basic solution). Precipitation of these three cations occurs because, under Group IV conditions, the ion product (IP) exceeds the K_{sp} value only for the carbonates of Ba^{+2}, Sr^{+2}, and Ca^{+2}. The cations which remain after precipitation of Groups I, II, III, and IV comprise Group V.

When analyzing for the cation in a general unknown, the four group reagents must be added in the sequential order: 1) cold dilute HCl, 2) H_2S in 0.3 M HCl, 3) H_2S in NH_3/NH_4Cl buffer, and 4) $(NH_4)_2CO_3$ in NH_3/NH_4Cl buffer. For instance, a Group I cation will precipitate on addition of the first group reagent (dilute HCl) as well as with addition of the other three group reagents. Therefore, the absence of a Group I cation must be established prior to testing for the presence of a Group II cation. A Group II cation will precipitate on addition of the second group reagent (H_2S in 0.3 M HCl) as well as with addition of the third and fourth group reagents. Therefore, the absence of a Group II cation must be established prior to testing for the presence of a Group III cation.

The ions within each group are separated from each other by suitable chemical reactions and then appropriate reagents are added which give distinctive confirmatory tests for the presence or absence of an ion. Separation and identification procedures within a group are based upon relative K_{sp} values, acid-base properties, complex ion formation, and oxidation-reduction.

Pre-laboratory Questions:

1. During qualitative analysis, what factor is used for the preliminary separation of metallic cations into groups by addition of four different group reagents?

2. An aqueous solution of a salt (one cation and one anion) is thought to contain the Group IV metal cation Ca^{+2}. To test this hypothesis, a student added $(NH_4)_2CO_3$ in NH_3/NH_4Cl 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 this experiment. 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.

	Reagent	Result
1:	dilute HCl	no precipitate
2:	H_2S in 0.3 M HCl	precipitate
3:	H_2S in NH_3/NH_4Cl	precipitate
4:	$(NH_4)_2CO_3$ in NH_3/NH_4Cl	no precipitate

4. To prove the statement....*Pb^{+2} is not completely precipitated in Group I because $PbCl_2$ is considerably more soluble (i.e. has a higher K_{sp} value) than the chlorides of Ag^+ and Hg_2^{+2}*.....found on page 1 of this experiment, calculate (a) the molar solubility of $PbCl_2$ ($K_{sp} = 1.7\times10^{-5}$) in pure water and (b) the concentration of Pb^{+2} in a saturated solution. Based upon this concentration of Pb^{+2} in a saturated solution, prove that precipitation of PbS ($K_{spA} = 3\times10^{-7}$) will occur under Group II conditions (pH=0.6 and 0.10 M H_2S) by (c) calculating IP and comparing it to K_{spA}.

Safety Precautions:	•	Safety goggles and apron must be worn at all times.
	•	Acid and base solutions are corrosive. Immediately wash all spills with excess cool water and inform the teaching assistant.
	•	Carry out reactions under the student hood to minimize exposure to noxious fumes. Make sure the student hood is firmly seated against the rubber gasket.
	•	Lead and mercury are toxic if ingested. Thoroughly wash hands with soap and water before leaving the laboratory.

Procedure:

A. Precipitation of Group I (Ag^+, Hg_2^{+2}, and Pb^{+2}).

1. Place a 1 mL portion of the Group I-V known sample in a small test tube. The known sample contains cations from all five groups. Add dilute HCl dropwise with stirring until the solution is acid to litmus. Add one drop of excess HCl. Formation of a white precipitate indicates the presence of one or more Group I cations. The reactions are shown below.

$$AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$$
$$Hg_2(NO_3)_2(aq) + 2\ HCl(aq) \rightarrow Hg_2Cl_2(s) + 2\ HNO_3(aq)$$
$$Pb(NO_3)_2(aq) + 2\ HCl(aq) \rightarrow PbCl_2(s) + 2\ HNO_3(aq)$$

2. If the reaction mixture is warm after the addition of HCl, run cold water over the outside of the test tube before separating out the precipitate. Centrifuge to separate the precipitate from the supernatant liquid. **CAUTION: The centrifuge must be balanced. Place a test tube containing an equal volume of liquid opposite your test tube. An unbalanced centrifuge is dangerous because it may wobble and fall from the bench top.** Transfer the supernatant liquid to another test tube. ***Keep the supernatant liquid!*** The supernatant liquid contains cations in Groups II-V. Wash the precipitate with 1 mL of distilled water, centrifuge, and combine the washings with the supernatant liquid. Discard the precipitate.

B. Analysis of Group II (Pb^{+2}, Hg^{+2}, Bi^{+3}, and Cu^{+2}).

1. To the supernatant liquid from the precipitation of Group I add dilute NH_3 dropwise with stirring until the solution is just basic to litmus. Make the solution just acidic by dropwise addition of dilute HCl (1 drop may be sufficient), then add 1 drop excess. Any precipitates which appear on addition of aqueous NH_3 will be converted to sulfides in the next step.

2. Add 10 drops of thioacetamide ($CH_3C(S)NH_2$) and place the test tube in a 100 mL beaker of boiling water for 5 minutes. **CAUTION: Be sure to carry out this heating process under the student hood. Highly toxic $H_2S(g)$ is**

generated from the hydrolysis of thioacetamide. Add 1 mL of distilled water and an additional 10 drops of thioacetamide and place the test tube in boiling water for an additional 5 minutes. It is essential to complete both stages of the thioacetamide precipitation even though a precipitate may have been obtained after the first stage. The formation of a dark-colored precipitate indicates the presence of one or more Group II cations. The reactions are shown below.

$$Pb(NO_3)_2(aq) + H_2S(aq) \rightarrow PbS(s) + 2\ HNO_3(aq)$$

$$Hg(NO_3)_2(aq) + H_2S(aq) \rightarrow HgS(s) + 2\ HNO_3(aq)$$

$$2\ Bi(NO_3)_3(aq) + 3\ H_2S(aq) \rightarrow Bi_2S_3(s) + 6\ HNO_3(aq)$$

$$Cu(NO_3)_2(aq) + H_2S(aq) \rightarrow CuS(s) + 2\ HNO_3(aq)$$

3. Centrifuge the precipitate and transfer the supernatant liquid to another test tube. ***Keep the supernatant liquid!*** The supernatant liquid contains cations in Groups III-V. Wash the precipitate with 1 mL of distilled water, centrifuge, and combine the washings with the supernatant liquid. Discard the precipitate. Transfer the liquid to an evaporating dish. Evaporate to a volume of about 1 mL.

C. Analysis of Group III (Ni^{+2}, Mn^{+2}, Fe^{+3}, and Al^{+3}).

1. Transfer the supernatant liquid to a small test tube. Add 5 drops $NH_4Cl(aq)$, 10 drops dilute NH_3, and 10 drops thioacetamide. Place test tube in a 100 mL beaker of boiling water for 5 minutes. **CAUTION: Again and due to the formation of $H_2S(g)$, carry out this heating process under the student hood.** The formation of a precipitate indicates that one or more Group III cations are present. The reactions are shown below.

$$Ni(NO_3)_2(aq) + (NH_4)_2S(aq) \rightarrow NiS(s) + 2\ NH_4NO_3(aq)$$

$$Mn(NO_3)_2(aq) + (NH_4)_2S(aq) \rightarrow MnS(s) + 2\ NH_4NO_3(aq)$$

$$2\ \overset{+3}{Fe}(NO_3)_3(aq) + 3\ (NH_4)_2\overset{-2}{S}(aq) \rightarrow 2\ \overset{+2}{Fe}S(s) + \overset{0}{S}(s) + 6\ NH_4NO_3(aq)$$

$$Al(NO_3)_3(aq) + 3\ NH_3(aq) + 3\ H_2O(l) \rightarrow Al(OH)_3(s) + 3\ NH_4NO_3(aq)$$

2. Centrifuge the precipitate and transfer the supernatant liquid to another test

tube. ***Keep the supernatant liquid!*** The supernatant liquid contains cations in Groups IV-V. Wash the precipitate with 1 mL of distilled water, centrifuge, and combine the washings with the supernatant liquid. Discard the precipitate. Acidify the supernatant liquid with HCl and place the test tube in boiling water for 10 minutes to boil off the H_2S. Centrifuge and discard any precipitate which forms.

D. Analysis of Group IV (Ca^{+2}, Sr^{+2}, and Ba^{+2}).

1. To the supernatant liquid from the precipitation of Group III, add 10 drops of NH_4Cl. Add dilute NH_3 dropwise with stirring until the solution is just basic to litmus. Add 10 drops of $(NH_4)_2CO_3$. Stir and place the test tube in a beaker of boiling water for 5 minutes. The formation of a white precipitate indicates the presence of Group IV. The reactions are shown below.

$$Ca(NO_3)_2(aq) + (NH_4)_2CO_3(aq) \rightarrow CaCO_3(s) + 2\ NH_4NO_3(aq)$$

$$Sr(NO_3)_2(aq) + (NH_4)_2CO_3(aq) \rightarrow SrCO_3(s) + 2\ NH_4NO_3(aq)$$

$$Ba(NO_3)_2(aq) + (NH_4)_2CO_3(aq) \rightarrow BaCO_3(s) + 2\ NH_4NO_3(aq)$$

2. At this point the supernatant liquid would contain cations from Group V. This group of cations is often referred to as the *soluble cation group*, since the cations in this group do not react or precipitate with any of the four group reagents.

E. Analysis of Unknown (contains cations from Groups I-IV).

1. To determine which groups are present in your unknown, repeat the precipitation and analysis procedures (outlined in A-D) on your unknown. Not all groups will be present in your unknown. If a group is absent, proceed immediately to the next group analysis. Centrifuging is not necessary unless a precipitate is obtained.

   If a given group is present, you should obtain about the same amount of precipitate for it as you obtained from the known solution. Small amounts of precipitates in Groups II and III may result from improper separations of previous groups or from the formation of sulfur (resulting from oxidation of H_2S). A milky Group II precipitate is undoubtedly sulfur and should not be reported as Group II.

   Fill in the attached unknown report sheet and turn it in to your laboratory teaching assistant.

Data:

E. Unknown

Reagent Added	Observations	Conclusions

Groups present in unknown? ______________________

Unknown Report Sheet

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Chemistry 116 **Fall 2011 Make-up Experiment**

Group Separations in Qualitative Analysis

Lab Room No.: __________ Desk No.: __________ Lab Day: __________ Time: AM or PM
(Circle)

Student Name: ________________________________

E. Unknown.

Groups present in unknown? ______________________

On the reverse side of this unknown report sheet, briefly explain your conclusions as to which ions were present or absent from the unknown.
