

Experiment # 8

Qualitative Analysis of Cations

Objectives

Part I: Separate a mixture of known cations: Pb^{2+} , Fe^{3+} , Al^{3+} , Cu^{2+} , and Ca^{2+} into individual ions. Perform a series of tests to become familiar with reactions characteristic of each cation.

Part II: Separate and identify individual cations in an unknown solution containing a mixture of up to five cations. Use information gathered in part I to identify the cations.

Introduction

Qualitative analysis is a general name for the process of determining the identity rather than the amount of chemical species. The qualitative process utilizes reaction(s) characteristic of a given chemical species and interprets the obtained results using a deductive thought process. Qualitative analysis of cations requires an extensive knowledge of various aspects of chemistry including acid-base equilibria, complex ion equilibria, solubility, etc. However, in the deductive process, common sense and logic can be as helpful as a knowledge of the chemistry involved.

In this lab you will be working with a solution containing a mixture of cations. Before individual components of the mixture can be successfully identified, they have to be separated. The individual cations, once separated, can then be identified in ensuing confirmatory reactions (see the flowchart below). Knowing the actual results of the reactions characteristic for a given cation (or a group of cations) makes it easier to identify the ion in an unknown sample. Therefore, it is useful to perform all of the characteristic reactions first on a mixture of ions of known identity, and then proceed to the unknown sample.

Reactions Characteristic for Pb^{+2}

Separation of Pb^{+2} from Fe^{+3} , Al^{+3} , Cu^{+2} , and Ca^{+2}

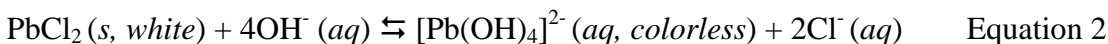
Out the five cations in the mixture, only lead ion will precipitate, as PbCl_2 , when hydrochloric acid is added to the solution.



The solid PbCl_2 is separated from the solution containing the other four ions by centrifuging the reaction mixture.

Confirmation for Pb^{+2}

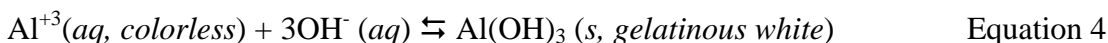
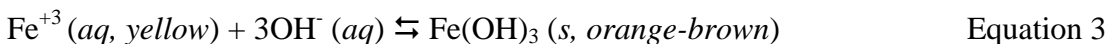
If the separated solid dissolves to form a colorless solution of a lead(II) complex when treated with NaOH, the presence of Pb^{+2} in the mixture is confirmed:



Reactions Characteristic for Fe^{+3} and Al^{+3}

Separation of Fe^{+3} and Al^{+3} from Cu^{+2} and Ca^{+2}

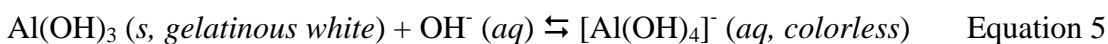
The supernatant solution from the previous test now contains only four ions. Iron(III) ions and aluminum ions are precipitated together as hydroxides upon addition of aqueous ammonia:



Remember that aqueous ammonia is a weak base that is only partially ionized by water to form OH^{-} ions and NH_4^{+} ions. A strong hydroxide such as NaOH would precipitate copper(II) hydroxide while keeping aluminum ions in solution as a complex ion (equation 5).

Separation of Fe^{+3} and Al^{+3}

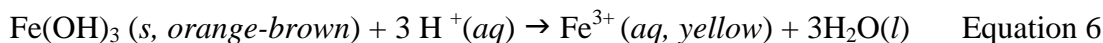
Before each ion can be identified, the Fe^{+3} and Al^{+3} must be separated from each other. This is achieved by adding a strong base, NaOH. Because aluminum ion is amphoteric, $\text{Al}(\text{OH})_3$ will dissolve in a strong base while $\text{Fe}(\text{OH})_3$ will not:



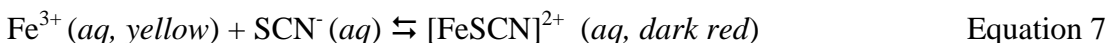
The orange solid, $\text{Fe}(\text{OH})_3$, is separated by centrifugation from the colorless supernatant solution containing $[\text{Al}(\text{OH})_4]^{-}$ ions and the pellet is washed with water to ensure that any adhering $\text{Al}(\text{OH})_3$ is washed away.

Confirmation of Fe^{+3}

Since Fe^{+3} ion is in a solid at this point it has to be dissolved by hydrochloric acid before it can undergo a confirmation reaction. The resulting solution contains aqueous iron (III) chloride.

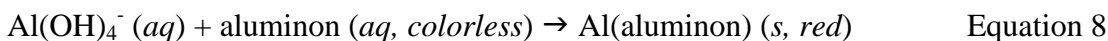


The confirmation reaction for Fe^{+3} ions involves addition of aqueous potassium thiocyanate, KSCN, to form dark red FeSCN^{+2} .



Confirmation of Al^{+3}

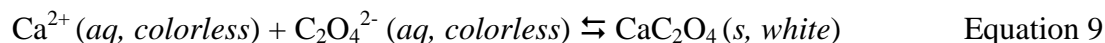
Aluminum ion is confirmed by the formation of a light-red, gelatinous, almost transparent solid upon addition of a solution of an organic compound, aluminon, in a moderately basic environment.



Reactions Characteristic for Cu^{+2} and Ca^{+2}

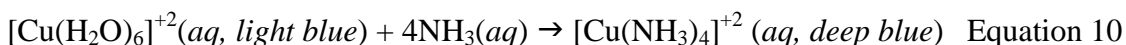
Separation and Confirmation of Ca^{+2}

The reaction used to separate the Ca^{2+} ion, at the same time provides the confirmation for the presence of that ion. A precipitate of calcium oxalate is formed after the supernatant remaining after separating iron (III) and aluminum ions is treated with ammonium oxalate solution. This precipitate is separated from the solution containing copper(II) ion by centrifuging, rinsing, and verifying that the precipitate is white.



Confirmation of Cu^{+2}

The deep blue color of the remaining supernatant solution confirms the presence of Cu^{2+} ion in the form of the copper(II) tetraammine complex ion, $[\text{Cu}(\text{NH}_3)_4]^{+2}$.



Strategy for identifying the unknown

To identify the cations (up to five) in the unknown sample, one has to separate the ions first. Therefore, the unknown is subject to the same separation procedures as the known. The logic followed here, however, is slightly different than for the known. You have to make decisions as you go, and should not blindly follow the procedure outlined for the known mixture. For example, let's say that upon addition of HCl to the unknown solution, there was no white precipitate observed. Would you still do the centrifuging step since there is no solid to remove? In the second step, what if addition of ammonia yields a white, gelatinous precipitate rather than a red-brown precipitate? Will it be necessary to separate and identify both iron and aluminum ions? Do you need to add 6 M NaOH? What does it mean when the addition of ammonia in the second step yields a colorless solution rather than a deep-blue solution? Do you still need to test for the presence of calcium?

Report

Your report should clearly identify the results seen with each reaction for your known solution and state the identity of all cations present in the unknown. Clearly state the reasoning behind your identification of the unknown cations. Use a flowchart format if needed to provide evidence for the presence of the identified cations.

PROCEDURE

General notes:

1. Solutions must be mixed well after addition of each reagent this can be done by tapping the bottom of the tube with your finger while securely holding the top of the tube, or by tapping the tube on the bench top.
2. Precipitates must be separated from the supernatant solution by centrifugation.
3. The supernatant solution is separated from the precipitate by decanting (pouring) the liquid into another tube. Make sure that the solid stays behind in the original tube.
4. All precipitates, after they have been separated from the supernatant solution, must be rinsed thoroughly with distilled water before proceeding to the identification of the cation present. To rinse a supernatant you should add one mL of water to the tube containing the solid pellet, mix well, centrifuge, and then decant the water into a waste beaker. Repeat

this step 1-2 times.

5. Carefully checking the pH is crucial in obtaining good results in this experiment.

6. 1 M NaOH and 6M acetic acid (weak acid) may be used to fine tune the pH if a small change of pH needed.

Terms and techniques used in this experiment

Centrifugation

The process of separating more dense solid particles from less dense liquid (solution) is done by spinning the solution at high velocity. The apparatus used is called a centrifuge. It must be balanced and the lid must be closed tightly to function properly. Balancing is done by putting the centrifuge tube containing the tightly capped reaction mixture in a centrifuge slot, then placing a centrifuge tube with an equal volume of tap water in a slot across from the first tube. You can also balance the solution against that of another student if the two solutions are of the same volume. Make sure you note the centrifuge slot of your solution.

Decanting

After centrifugation, the two phases can be separated by carefully decanting or pouring the supernatant liquid out of the tube leaving the solid behind.

Rinsing precipitates

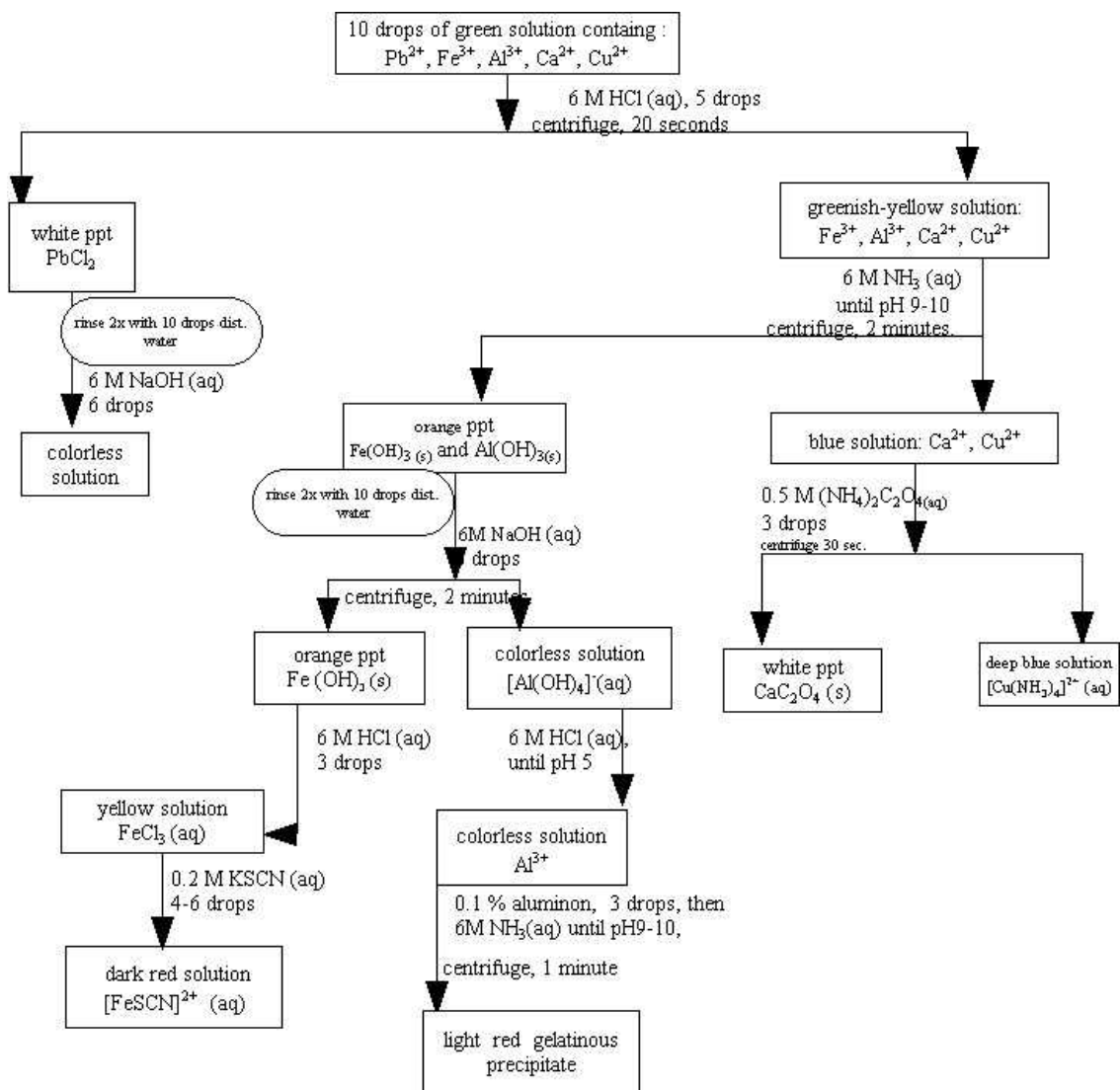
Precipitates must be rinsed to remove any cations that are present in the supernatant solution but that are adhering to the solid. The presence of these ions may cause confusing results in the process of further identification or separation. The solid remaining after the supernatant solution has been removed is mixed with one mL of distilled water and the tube is tapped to thoroughly mix the contents. The tube is then centrifuged, the rinse water is decanted, and the process repeated one to two more times.

Testing pH

Never test the pH by dropping the pH paper into the solution. Instead, wash a watch-glass and rinse it well with tap water, then with distilled water. Leave it wet, but not excessively wet. Place several small pieces of pH paper around the perimeter of the watch glass (they will soak up some of the distilled water). Have a clean, dry glass stirring rod handy. After addition of acid or base to the solution whose pH is being adjusted, shake the tube to mix then dip the end of the stirring rod in the solution being tested and touch it to one the pieces of pH paper. Compare the color of the paper with the color chart on the pH paper box.

Procedure

Follow the procedure on the flow chart below.



Discussion:

Chemistry 1225 experiment 8 **Prelab Questions** Name _____

1. Why is it important to mix the solutions after adding the reagents? How is mixing done in this experiment?

2. What is the reason for rinsing the precipitates before further testing?

3. What two things are extremely important to remember when centrifuging?

4. Why is it possible to separate Cu^{+2} from Al^{+3} and Fe^{+3} with NH_4OH but not with NaOH ? (Hint, consider solubility properties.)

Chemistry 1225 experiment 8 **Post Lab Questions** Name _____

1. A student analyzing an unknown mixture of cations obtained the results listed in the table below. For each test draw a conclusion concerning what ions were proven present or possibly present and what ions were proven absent.

Test	Result	Cation proven present or possibly present (if any)	Cation proven absent (if any)
A) 5 drops of 6M HCl are added to the mixture	No precipitate forms		
B) The solution from (A) is adjusted to pH 9.5 with 6 M NH ₃ (aq)	cloudy, orange-brown mixture is formed		
C) The solution from (B) is centrifuged and the colorless supernatant liquid is decanted. The precipitate is rinsed and 6 M NaOH added.	An orange precipitate and colorless supernatant solution results		
D)The precipitate from (C) is rinsed and dissolved in 6 M HCl (aq), then 6 drops 0.2 M KSCN is added	Dark red solution		
E) 0.5 M (NH ₄) ₂ C ₂ O ₄ (aq) is added to supernatant liquid from (C)	a clear, colorless solution		