Qualitative Analysis

Lab 10

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Pre-Lab

- Page 402
- Complete all pre-lab questions

- Quiz 6 –Next week
  - Factors Affecting Reaction Rates

Introduction to Qualitative Analysis

- The purpose of this experiment is to study the reactions of 6 cations. You will use your observations to identify the ions in samples of unknown composition.
- Qualitative analysis is used to separate and detect cations and anions in a sample substance.
- Qualitative analysis is the procedure by which one can determine the nature, but not the amount of species in a mixture. This experiment deals with tests isolated for specific ions in solution.

Description of Lab

- Knowledge of chemical reactivity to identify 6 metal cations
- Written substantiation of the method used to identify each solid such as a qualitative analysis flow chart

Experimental Procedure

- You will be provided with 2 test-tubes.
- One will contain all six of the cations to be detected. This is your reference solution
- The other test-tube will contain a number of unknown cations that you will need to identify by experimental observations.

- Make careful notes of your observations.
- Look closely for gases, and note colors of precipitates

- Types of reactions encountered in qualitative analysis include
  - precipitation
  - complex ion formation
  - redox reactions
  - acid-base reactions

- Some means of identifying ions by qualitative analysis are:
  - color changes,
  - evolution of gas,
  - change in pH (acidity or basicity)
  - or ability to redissolve a precipitate by addition of a complexing ligand.

Common grouping of cations

- Group I: Ag^+, Hg_2^{2+}, Pb^{2+}
  Precipitated in 1 M HCl

- Group II: Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, (Pb^{2+}), Sb^{3+} and Sb^{5+}, Sn^{2+} and Sn^{4+}
  Precipitated in 0.1 M H_2S solution at pH 0.5

Common grouping of cations

- Group III: Al^{3+}, (Cd^{2+}), Co^{2+}, Cr^{3+}, Fe^{2+} and Fe^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}
  Precipitated in 0.1 M H_2S solution at pH 9

- Group IV: Ba^{2+}, Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+
  Ba^{2+}, Ca^{2+}, and Mg^{2+} are precipitated in 0.2 M $(NH_4)_2CO_3$ solution at pH 10; the other ions are soluble

Common Qualitative Analysis Reagents

- Many reagents are used in qualitative analysis, but only a few are involved in nearly every group procedure.
- The four most commonly used reagents are HCl, HNO_3, NaOH and NH_3.
- Understanding the uses of the reagents is helpful when planning an analysis.

Reagent	Effect
HCl	**Increases [H^+] Increases [Cl^-]** **Decreases [OH^-]** **Dissolves insoluble carbonates, chromates, hydroxides, some sulfates** **Destroys hydroxo and NH_3 complexes** **Precipitates insoluble chlorides**
HNO_3	**Increases [H^+] Decreases [OH^-]** **Dissolves insoluble carbonates, chromates, and hydroxides** **Dissolves insoluble sulfides by oxidizing sulfide ion** **Destroys hydroxo and ammonia complexes** **Good oxidizing agent.**

NaOH	Increases [OH^-] Decreases [H^+] Forms hydroxo complexes Precipitates insoluble hydroxides
NH_3	Increases [NH_3] Increases [OH^-] Decreases [H^+] Precipitates insoluble hydroxides Forms NH_3 complexes Forms a basic buffer with NH_4^+

Process for Salt Identification

- Appearance of compound
- Heating effect
- Flame test
- Solubility in water
- Reaction with nitric acid
- The remaining tests must be performed on a solution of the compound.

Reactions to be performed on a solution of the solid:

- Reaction with sodium hydroxide
- Reaction with ammonia
- Reaction with hydrochloric acid
- Reaction with sulfuric acid
- Reaction with silver nitrate
- Reaction with barium nitrate

Appearance of Compounds

- The compound will most likely be in solid form.
- Note the color and shape of the crystals.
- Ionic compounds formed from the representative elements tend to be white or colorless
- Ions of transition elements tend to be colored.

Ion	**Color**
Co^{2+}	**rose**
Co^{3+}	**violet**
Cr^{3+}	**violet**
Cu^{2+}	**blue**
Fe^{2+}	**pale green, pale violet**
Fe^{3+}	**yellow-brown**
Mn^{2+}	**pale pink**
Ni^{2+}	**blue-green**

Heating Effect

- Heating a compound can cause a liquid to condense on the inside of the test tube.
- This is probably water, indicating that the compound is a hydrate.
- Hydrated salts tend to be sparkly, and have well defined crystalline facets.
- $CuSO_4 \cdot xH_2O$ blue → $CuSO_4$ (white)

- If a gas is given off, note the color and odor of the gas.
- The nitrate, carbonate, and sulfite ions may decompose, as illustrated by the reactions:
  - 2 $Pb(NO_3)_2(s)$ + heat --> 2 $PbO(s)$ + $O_2(g)$ + 4 NO_2(g, brown)
  - $CaCO_3(s)$ + heat --> $CaO(s)$ + CO_2(g, colorless, odorless)
  - $CaSO_3(s)$ + heat --> $CaO(s)$ + SO_2(g, colorless, pungent)
- Some bromides and iodides decompose to give Br_2(g, orange-brown) and I_2(g, purple).

Flame Tests

- Solutions of ions, when mixed with concentrated HCl and heated on a nickel/chromium wire in a flame, cause the flame to change to a color characteristic of the atom.

- A flame test can be used as a confirmatory test.

- One problem, is that sodium is often an impurity so will almost always see a yellow flame. Therefore careful observations need to be recorded.

Sodium	**Bright yellow (intense, persistant)**
Potassium	**Pale violet (slight, fleeting)**
Calcium	**Brick red (medium, fleeting)**
Strontium	**Crimson (medium)**
Barium	**Light green**
Lead	**Pale bluish (slight, fleeting)**
Copper	**Green or blue (medium, persistant)**

Solubility

- Place one small spatula of the compound in 1 mL of water.
- If the compound is soluble this amount will dissolve after considerable stirring.
- If the compound is moderately soluble, some of this amount will dissolve.
- If the compound is insoluble, even a very small amount will not dissolve

Solubility Guidelines

1. All nitrates are soluble.
2. Practically all sodium, potassium, and ammonium salts are soluble.
3. All chlorides, bromides, and iodides are soluble except those of silver, mercury(I), and lead(II).
4. All sulfates are soluble except those of strontium, barium, and lead(II), which are insoluble, and those of calcium and silver which are moderately soluble.
5. All carbonates, sulfites, and phosphates are insoluble except those of sodium, potassium, and ammonium.

All sulfides are insoluble except those of the alkali metals, the alkaline earth metals, and ammonium.

All hydroxides are insoluble except those of the alkali metals.

The hydroxides of calcium, strontium, and barium are moderately soluble.

Ammonium hydroxide does not exist; ammonium hydroxide is a misnomer for aqueous ammonia, $NH_3(aq)$.

- The remaining tests must be performed on a solution of the compound, usually in water. If the compound is not water soluble, use nitric acid.

Reaction with NaOH

- Add NaOH dropwise to the solution, stir or shake the solution, and observe any reaction (if the compound was dissolved in nitric acid, the first several drops will neutralize the acid so be sure to check the pH with litmus paper).
- Look for a precipitate (refer to the solubility rules for hydroxides). If a precipitate forms, continue adding NaOH.
- Some metal hydroxides are amphoteric and will form a complex ion and redissolve.

Amphoteric Ions

- Having the characteristics of an acid and a base and capable of reacting chemically either as an acid or a base.
- Whether an amphoteric chemical acts as an acid or a base depends on what other chemicals happen to be around.

- If a base (like NH_3) is present, **water can act as an acid** and react by donating a proton to that base. In doing so, water is changed into its conjugate base, hydroxide ion.

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

- If an acid (like HCl) is present, **water can act as a base** and react by accepting a proton from that acid. In doing so, water is changed into its conjugate acid, hydronium ion.

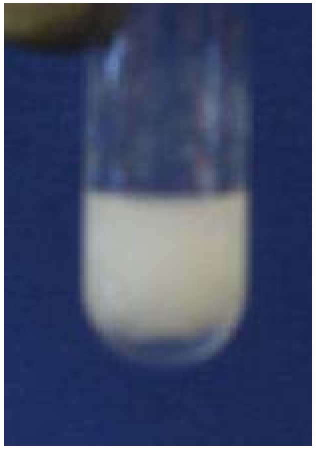
$$H_2O + HCl \rightarrow Cl^- + H_3O^+$$

Amphoteric Ions

Species	Acidic Solution	Slightly Basic Solution	Basic Solution
Al^{3+}	$Al^{3+}(aq)$	$Al(OH)_3(s)$	$Al(OH)_4^-(aq)$
Cr^{3+}	$Cr^{3+}(aq)$	$Cr(OH)_3(s)$	$Cr(OH)_4^-(aq)$
Pb^{2+}	$Pb^{2+}(s)$	$Pb(OH)_2(s)$	$Pb(OH)_4^{2-}(aq)$
Zn^{2+}	$Zn^{2+}(aq)$	$Zn(OH)_2(s)$	$Zn(OH)_4^{2-}(aq)$
Sn^{4+}	$Sn^{4+}(aq)$	$Sn(OH)_4(s)$	$Sn(OH)_6^{2-}(aq)$

$Al(NO_3)_3$ in solution

Excess NaOH is added the precipitate redissolves as the $Al(OH)_4^-$ complex ion is formed.



$Al(OH)_3$ precipitates with the addition of NaOH.

The remaining tests must be performed on a solution of the compound, usually in water. If compound is not water soluble, use nitric acid.

Reaction with NaOH

- Add NaOH dropwise to the solution, stir or shake the solution, and observe any reaction (if the compound was dissolved in nitric acid, the first several drops will neutralize the acid so be sure to check the pH with litmus paper).
- Look for a precipitate (refer to the solubility rules for hydroxides). If a precipitate forms, continue adding NaOH.
- Some metal hydroxides are amphoteric and will form a complex ion and redissolve.

Reaction with ammonia

- Add NH_3 dropwise to the solution, stir or shake the solution.
- Observe any reaction.
- If a metal hydroxide precipitate forms, continue adding ammonia.
- Some metal hydroxides form a complex ion and redissolve.

Complexes with Ammonia

Acid Solution	Basic Solution	Solution with Excess NH_3	Color of Complex
$Ni^{2+}(aq)$	$Ni(OH)_2(s)$	$Ni(NH_3)_6^{2+}(aq)$	violet
$Cu^{2+}(aq)$	$Cu(OH)_2(s)$	$Cu(NH_3)_4^{2+}(aq)$	blue
$Zn^{2+}(aq)$	$Zn(OH)_2(s)$	$Zn(NH_3)_4^{2+}(aq)$	colorless
$Ag^{+}(aq)$	$Ag_2O(s)$	$Ag(NH_3)_2^{+}(aq)$	colorless
$Cd^{2+}(aq)$	$Cd(OH)_2(s)$	$Cd(NH_3)_4^{2+}(aq)$	colorless

Reaction with HCl or H_2SO_4

- Add HCl dropwise until solution tests acidic to litmus paper and observe any reaction.
- A precipitate will form with any cation that forms an insoluble chloride (refer to the solubility rules).

$$Pb^{2+} + 2Cl^{-} \text{-->} PbCl_2(s)$$

- Add H_2SO_4 dropwise until solution is acidic and observe any reaction. A precipitate will form with any cation that forms an insoluble sulfate

$$Ba^{2+} + SO_4^{2-} \text{-->} BaSO_4(s)$$

Reaction with silver nitrate

- Add HNO_3 dropwise until solution is acidic (unless of course it was dissolved in nitric acid)
- then add a few drops of $AgNO_3$ and observe any reaction.
- A precipitate will form with certain cations that form insoluble silver compounds, but because of the acidic environment, some insoluble silver salts (e.g. salts containing CO_3^{2-}, S^{2-}, and PO_4^{3-} ions) are "destroyed."
- Cl^-, Br^-, and I^- form insoluble compounds

$$Ag^+ + Cl^- \text{-->} AgCl(s)$$

- SO_4^{2-} forms a moderately insoluble compound.

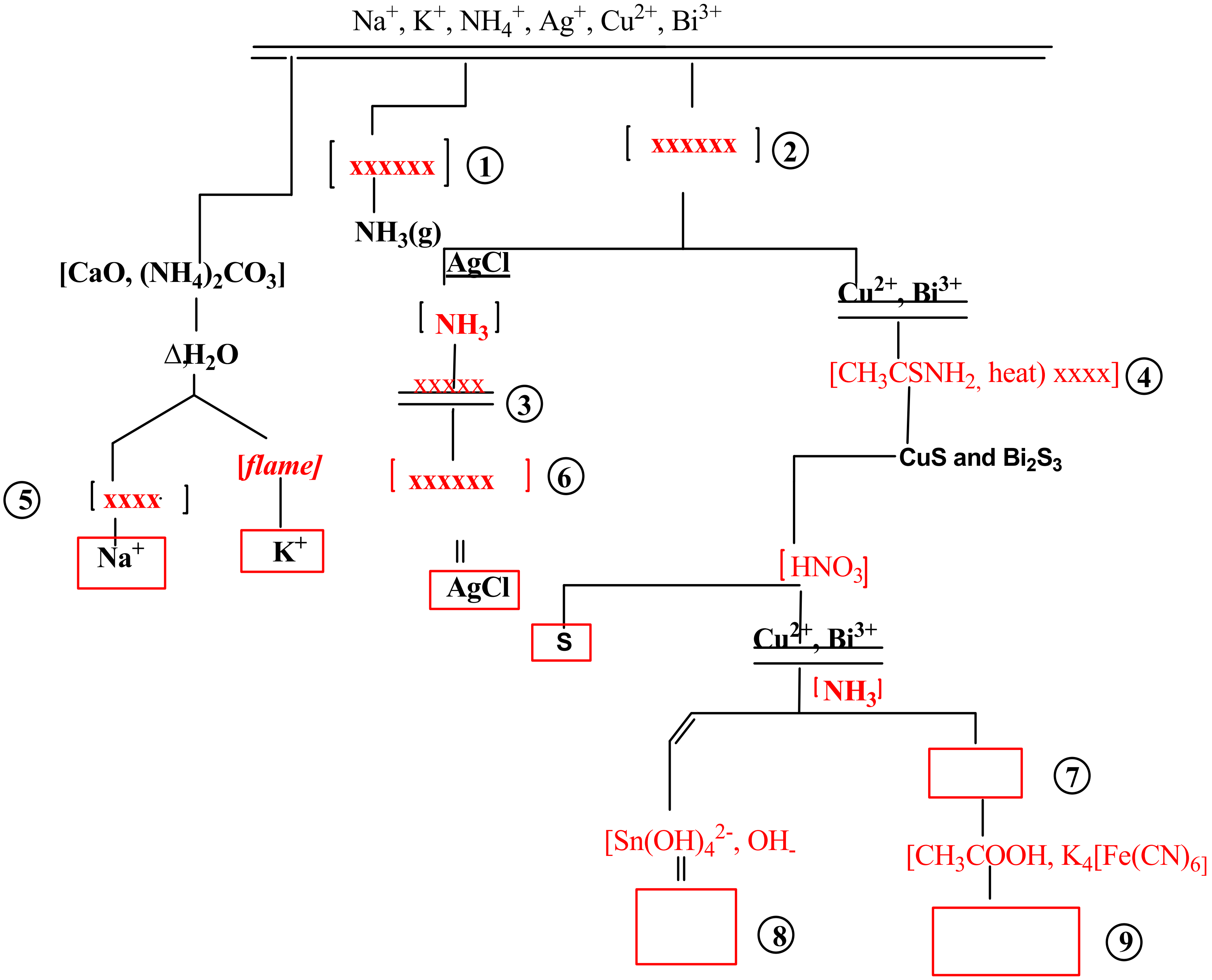
Reaction with nitric acid

- Add nitric acid to the compound and observe any reaction that occurs.
- If the compound dissolved in water, it should dissolve in nitric acid.
- If it did not dissolve in water, but appears to be dissolving in nitric acid, it is undergoing a chemical reaction.
- In general, compounds that contain anions that are the conjugate bases of weak acids (e.g. CH_3COOH and H_2S are acidic, conjugate bases are CH_3COO^- and HS^- . These will generally react (unless the compounds are very insoluble).

Recap: Conjugate pairs of acids and bases.

- When an acid gives up its proton, what remains is called the conjugate base of that acid. When a base accepts a proton, the resulting chemical is called the conjugate acid of that original base. HF and F^- are a conjugate acid-base pair. H_2O and H_3O^+ are a conjugate pair, where H_3O^+ is the acid and H_2O is the base.

- For example:
  - $CaCO_3$(s) + 2 H^+(aq) --> Ca^{2+}(aq) + H_2O(l) + CO_2(g, colorless, odorless)
  - NiS(s) + 2 H^+(aq) --> Ni^{2+}(aq) + H_2S(g, colorless, rotten egg smell)
  - $Ca_3(PO_4)_2$(s) + 6 H^+(aq) --> 3 Ca^{2+}(aq) + 2 H_3PO_4(aq)



Na^+, K^+, NH_4^+, Ag^+, Cu^{2+}, Bi^{3+}

[xxxxxx] ①

NH_3(g)

[xxxxxx] ②

$[CaO, (NH_4)_2CO_3]$

ΔH$_2$O

⑤ [xxxx]

Na^+

[*flame*]

K^+

AgCl

[NH_3]

xxxxx ③

[xxxxxx] ⑥

||

AgCl

Cu^{2+}, Bi^{3+}

$[CH_3CSNH_2$, heat) xxxx] ④

CuS and Bi_2S_3

$[HNO_3]$

S

Cu^{2+}, Bi^{3+}

$[NH_3]$

⑦

$[Sn(OH)_4^{2-}$, OH_-

||

⑧

$[CH_3COOH, K_4[Fe(CN)_6]$

⑨

- From the ions on the top line, you need to perform chemical tests, that will allow you the identification of each metal ion.

- You will not need to memorize the flow chart but in a quiz or exam will need to be able to put reagents and products into an incomplete flow-chart.

Completing the flow chart:

1. The first product isolated is NH_3 (g). Looking at the cations, what could we add that would give us NH_3(g)
2. Calcium oxide (basic anhydride) and ammonium chloride are reacted with the cations to precipitate all cations as the hydroxide except Na^+, K^+ and NH_4^+.

- One more reagent needs to be added to the initial solution (2). This needs to form AgCl. What would react with Ag^+ to give AgCl. Fill in space 2.

- Product 3 = The reaction of AgCl + NH_3

- Product 4: 2 reagents are added. H_2S is an acidic anhydride and will form and acidic solution. Metal II Sulfides: (Metal has oxidation state of +2; for example, M = Cu^{2+}, Fe^{2+})
- $MS(s) \rightarrow M^{2+}(aq) + S^{2-}(aq)$

  $S^{2-}(s) + H_2O(l) \rightarrow HS^{-}(aq) + OH^{-}(aq)$
- The S^{2-} ion is a strong base and will react immediately to form HS^{-} and a hydroxide ion. The concentration of S^{2-} in solution is negligible
- $MS(s) + H_2O(l) \rightarrow M^{2+}(aq) + HS^{-}(aq) + OH^{-}$.
- K_{sp} for the dissolution of a metal II sulphide is :
  - » $K_{sp} = [M^{2+}][HS^{-}][OH^{-}]$

- The addition of acid will use up OH^- and hence, shift the summed equilibrium to the right thus dissolving more of the salt (MS).

- Since the Solubility is higher in acid solution and quite low in base solution, it is often more convenient (and conventional) to rewrite the equation for the dissolution in an acidic solution.

- As the pH is lowered (higher H_3O^+ concentration) the solubility of the metal sulfide increases.

- Product 5: Potassium has been identified by a positive flame test. What technique could be used to confirm the Na^+ presence?

- Reactant 6: Needs to be something that will precipitate out the product AgCl after the earlier reaction of silver + (aq) ammonia. The initial reaction was performed to separate out Ag from the other heavier cations.

- Product 7: Bi^{3+} / Cu^{2+} + $NH_3(aq) \rightarrow$? Consider, will one of the products be soluble or insoluble . (This reaction was performed in the metathesis lab, look back at the extra sheet of questions)

- Product 8: The Bi^{3+} in the bismuth hydroxide is reduced, and the tin hydroxide compound is the reducing agent, therefore oxidized itself to $[Sn(OH)_6]^{2-}$

- Product 9: Potassium hexacyanoferrate = $K_4[Fe(CN)_6]$ is used a confirmatory test for Cu, forming a reddish brown ppt. (see page 396 Beran).