Qualitative Analysis

Pre-lab: Pages 230 – 231
No Post-Lab Questions
Pre-lab and Lab report 50%

Introduction to Qualitative Analysis

- 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.

Experimental Aims

- To observe the chemical properties of ten cations: Na^{+},NH_4^{+}, Ag^{+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}
- To perform a series of tests that isolates then confirms each of these ions.
- Identification of an unknown solution of cations.

Note

- Part II: Separation of anions will not be performed.

- Read pages 241 – 242, experimental techniques.

Lab Techniques

- Ensure all glassware is clean, but it does not need to be dry.
- Use distilled water at all times
- Label test tubes to avoid confusion
- Mix solutions by flicking the test tube
- Estimate volumes by assuming 20 drops by pipette ≈ 1ml

Example of an interfering ion

- The formation of a yellow precipitate upon addition of aqueous S^{2-} confirms the presence of Cd^{2+} in a solution.
- The color of this compound, however, will be hidden if any Pb^{2+} or Cu^{2+} are present in solution since they will form a black precipitate with added S^{2-}.
- In order to test for cadmium, then, any interfering ions must first be removed.

Experimental Procedure

- You will be provided with 2 samples.
- One will contain all 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 solutions and precipitates.
- Recap on your solubility rules

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.

Types of reactions

- Precipitation
- Complex ion formation
- Redox reactions
- Acid-base reactions

Some means of identifying ions by qualitative analysis are:

- Color changes or color of the solution.
- Evolution of gas
- Change in pH (acidity or basicity)
- Or ability to redissolve a precipitate by addition of a complexing ligand.

- 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:
  - $2\ Pb(NO_3)_2(s) + heat \rightarrow 2\ PbO(s) + O_2(g) + 4\ NO_2(g, brown)$
  - $CaCO_3(s) + heat \rightarrow CaO(s) + CO_2(g, colorless, odorless)$
  - $CaSO_3(s) + heat \rightarrow CaO(s) + SO_2(g, colorless, pungent)$
- Some bromides and iodides decompose to give Br_2(g, orange-brown) and I_2(g, purple).

Common ways to test for ions

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

- 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

- 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

- 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^+

Step 1: Testing for Na^+ and NH_4^+

Test for sodium ions using a flame test.

Test for ammonium ions by addition of base.

Flame Tests

- Heat the solution to a moist residue, use the evaporating dish and a bunsen flame.
- 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.

- Sodium is often an impurity so will almost always see a yellow flame. Therefore careful observations need to be recorded.

- A brilliant yellow persistent flame indicates the presence of sodium.

Test for Silver ions

- All chloride salts are water soluble except those of silver, mercury and lead.

- Of the ten cations, only Ag forms an insoluble chloride.

Test for Silver ions

- Take your solution and add HCl
- Observe what happens.
- A precipitate of AgCl should form if Ag^+ is present.
- Add a slight excess of HCl to ensure complete precipitation (equilbrium).

Confirmatory Test: Reaction with ammonia

- Add NH_3 drop wise to the precipitate, stir or shake the solution.

- Observe any reaction ~ silver forms a complex ion with ammonia, lead and mercury do not behave in the way.

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

Fe^{3+}, Ni^{2+} and Cr^{3+} detection

- Transition elements are usually highly colored.
- Of the 10 cations, three are transition elements and these have distinct colors.
- Iron (III): Rust colored, Ni(II) green and Cr(III) blue-green.

Fe^{3+}, Ni^{2+} and Cr^{3+} detection

- A colorless unknown solution should inform you of the absence of these ions.

- A colored solution can hint at the transition metal cations present.

Fe^{3+}, Al^{3+} and Cr^{3+} detection

- These ions are separated from the others by precipitating them as their hydroxides.

- The pH must be carefully controlled. If the pH is too high (basic), $Mg(OH)_2$ will also precipitate.

Controlling pH

- An alkaline buffer of NH_3 and NH_4Cl provides enough OH to precipitate the Fe, Al and Cr cations and leaves the Mg^{2+} in solution.

What is a buffer?

- **A Buffer** is a chemical species which resists change in pH upon addition of small amounts of acid or base.

- A buffer consists of a solution of a weak acid and the corresponding conjugate base. One can also state it consists of a solution of a weak base and its conjugate acid. These two statements say the same thing. A buffer may be prepared from either a weak acid or a weak base. Both species must be present in solution at reasonable concentrations.

- Two species are required in a buffer solution. One is capable of reacting with OH^- and the other will react with H_3O^+. The two species must not react with each other.

Confirming Iron, Chromium and Aluminum

- To the three hydroxides add NaOH (a strong base) and H_2O_2 (an oxidizing agent)
- $Fe(OH)_3$ does not react
- $Al(OH)_3$ is amphoteric and dissolves – and is colorless
- Cr forms CrO_4^{2-} - yellow
- Fe is confirmed by addition of $K_4[Fe(CN)_6]$

Separation and detection of Ca^{2+}

- 4 cations remain in solution: calcium, magnesium, nickel and zinc
- Addition of oxalate precipitates calcium and or magnesium.
- Calcium can be confirmed by a flame test.

Zinc and Nickel

- Zinc can be separated from nickel and magnesium.
- Zinc hydroxide is amphoteric and can be precipitated from acidic solution by addition of $K_4[Fe(CN)_6]$, precipitating a gray-blue solid of $Zn_3K_2[F(CN)_6]_2$

Nickel

- Identification of nickel is from the soluble complex ion hexaamminenickel(II), $[Ni(NH_3)_6]^{2+}$
- Addition of dimethylgloxime to this, forms a strawberry red solid, $Ni(C_4H_7N_2O_2)_2$

Magnesium

- Magnesium is confirmed by the addition of a magnesium reagent to a solution of Mg^{2+} .
- Mg reagent: 0.1g p-nitrobenzeneazorescorcinal + 1.0g NaOH per liter.
- This results in a blue colored oil (lake).