Qualitative Analysis

Page 139 – 156
Pre-lab, pages 143-144, AND 153-154
Post Lab, page 156, all questions
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: Na\(^+\), K\(^+\), NH\(_4\)\(^+\), Cu\(^{2+}\) and Bi\(^{3+}\)

• To perform a series of tests that isolate each of these ions.
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 my flicking the test tube
• Estimate volumes by assuming 20 drops by pipette $\approx 1$ ml
Experimental Procedure

• You will be provided with 2 test-tubes.
• 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.

• Part E will be omitted, no other ions other than those listed will be present.

• 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,
- 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:
  • \(2 \text{Pb(NO}_3\text{)}_2(s) + \text{heat} \rightarrow 2 \text{PbO}(s) + \text{O}_2(g) + 4 \text{NO}_2(g, \text{brown})\)
  • \(\text{CaCO}_3(s) + \text{heat} \rightarrow \text{CaO}(s) + \text{CO}_2(g, \text{colorless, odorless})\)
  • \(\text{CaSO}_3(s) + \text{heat} \rightarrow \text{CaO}(s) + \text{SO}_2(g, \text{colorless, pungent})\)
  • Some bromides and iodides decompose to give \(\text{Br}_2(g, \text{orange-brown})\) and \(\text{I}_2(g, \text{purple})\).
Common ways to test for ions

• Group I: $\text{Ag}^+$, $\text{Hg}_2^{2+}$, $\text{Pb}^{2+}$
  Precipitated in 1 M HCl

• Group II: $\text{Bi}^{3+}$, $\text{Cd}^{2+}$, $\text{Cu}^{2+}$, $\text{Hg}^{2+}$, ($\text{Pb}^{2+}$), $\text{Sb}^{3+}$ and $\text{Sb}^{5+}$, $\text{Sn}^{2+}$ and $\text{Sn}^{4+}$
  Precipitated in 0.1 M H$_2$S solution at pH 0.5
Common grouping of cations

- **Group III**: $\text{Al}^{3+}$, $(\text{Cd}^{2+})$, $\text{Co}^{2+}$, $\text{Cr}^{3+}$, $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$, $\text{Mn}^{2+}$, $\text{Ni}^{2+}$, $\text{Zn}^{2+}$
  Precipitated in 0.1 M $\text{H}_2\text{S}$ solution at pH 9

- **Group IV**: $\text{Ba}^{2+}$, $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{Na}^+$, $\text{NH}_4^+$
  $\text{Ba}^{2+}$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ are precipitated in 0.2 M $\text{(NH}_4\text{)}_2\text{CO}_3$ 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, HNO₃, NaOH and NH₃.
- Understanding the uses of the reagents is helpful when planning an analysis.
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Increases $[H^+]$ Increases $[Cl^-]$ Decreases $[OH^-]$ Dissolves insoluble carbonates, chromates, hydroxides, some sulfates Destroys hydroxo and NH$_3$ complexes Precipitates insoluble chlorides</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>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.</td>
</tr>
<tr>
<td></td>
<td>Effects</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>NaOH</td>
<td>Increases $[\text{OH}^-]$ Decreases $[\text{H}^+]$</td>
</tr>
<tr>
<td></td>
<td>Forms hydroxo complexes</td>
</tr>
<tr>
<td></td>
<td>Precipitates insoluble hydroxides</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Increases $[\text{NH}_3]$ Increases $[\text{OH}^-]$ Decreases $[\text{H}^+]$</td>
</tr>
<tr>
<td></td>
<td>Precipitates insoluble hydroxides</td>
</tr>
<tr>
<td></td>
<td>Forms $\text{NH}_3$ complexes</td>
</tr>
<tr>
<td></td>
<td>Forms a basic buffer with $\text{NH}_4^+$</td>
</tr>
</tbody>
</table>
Step 1: Testing for Na\(^+\) and K\(^+\)

- Take your reference and unknown solution and add solid calcium oxide (CaO) or Ca(OH)\(_2\).

- This is to remove the interfering ions.

- An interfering ion is one that will give a false positive result.
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.
Why add CaO / Ca(OH)\(_2\)?

- \(\text{Na}^+\), \(\text{K}^+\), \(\text{NH}_4^+\), \(\text{Cu}^{2+}\) and \(\text{Bi}^{3+}\) are the ions present
- \(\text{Cu(OH)}_2\), \(\text{Bi(OH)}_3\) are insoluble salts and will precipitate out
- \(\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}\)
- Test the solution, using a flame test for \(\text{Na}^+\) and \(\text{K}^+\) ions
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.

• A pale violet flame indicates the presence of potassium (best viewed through blue cobalt glass)
<table>
<thead>
<tr>
<th>Element</th>
<th>Color Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Bright yellow (intense, persistant)</td>
</tr>
<tr>
<td>Potassium</td>
<td>Pale violet (slight, fleeting)</td>
</tr>
<tr>
<td>Calcium</td>
<td>Brick red (medium, fleeting)</td>
</tr>
<tr>
<td>Strontium</td>
<td>Crimson (medium)</td>
</tr>
<tr>
<td>Barium</td>
<td>Light green</td>
</tr>
<tr>
<td>Lead</td>
<td>Pale bluish (slight, fleeting)</td>
</tr>
<tr>
<td>Copper</td>
<td>Green or blue (medium, persistant)</td>
</tr>
</tbody>
</table>
Test for NH$_4^+$

- Take 5 mls of your reference solution and place in a clean small beaker
- Take 5 mls of your unknown solution and place in a clean small beaker
- Heat the solution gently until a residue begins to form
- Once the residue forms cover the beaker with a watch glass, with a piece of red litmus paper attached
• Observe whether there is a pH change
• To confirm whether you have NH$_4^+$ present, add 1-2 mls of NaOH.
• Gently warm the solution (with your hands should be ok, if not gently heat)
• Test the vapor with litmus paper (or carefully smell the solution for NH$_3$ presence)
Test for Silver ions

- Take your solution and add HCl
- Observe what happens.
- A precipitate of AgCl should form if Ag⁺ is present.
- Ensure complete mixing of the solution, by agitating with a stirring rod.
- Centrifuge the solution and check for complete precipitation
Confirmatory Test: Reaction with ammonia

- Add NH$_3$ dropwise to the precipitate, stir or shake the solution.

- Observe any reaction.

- Keep the supernatant for the next part of the experiment.
## Complexes with Ammonia

<table>
<thead>
<tr>
<th>Acid Solution</th>
<th>Basic Solution</th>
<th>Solution with Excess NH(_3)</th>
<th>Color of Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(^{2+})(aq)</td>
<td>Ni(OH)(_2)(s)</td>
<td>Ni(NH(_3))(_6)^{2+}(aq)</td>
<td>violet</td>
</tr>
<tr>
<td>Cu(^{2+})(aq)</td>
<td>Cu(OH)(_2)(s)</td>
<td>Cu(NH(_3))(_4)^{2+}(aq)</td>
<td>blue</td>
</tr>
<tr>
<td>Zn(^{2+})(aq)</td>
<td>Zn(OH)(_2)(s)</td>
<td>Zn(NH(_3))(_4)^{2+}(aq)</td>
<td>colorless</td>
</tr>
<tr>
<td>Ag(^{+})(aq)</td>
<td>Ag(_2)O(s)</td>
<td>Ag(NH(_3))(_2)^+(aq)</td>
<td>colorless</td>
</tr>
<tr>
<td>Cd(^{2+})(aq)</td>
<td>Cd(OH)(_2)(s)</td>
<td>Cd(NH(_3))(_4)^{2+}(aq)</td>
<td>colorless</td>
</tr>
</tbody>
</table>
Copper Ion Test

- From the supernatant from testing for the silver ion, add a solution of ammonia.
- A deep blue solution of Cu(NH$_3$)$_4^{2+}$, indicates the presence of a Cu$^{2+}$ ion.
- Centrifuge and save the precipitate Bi(OH)$_3$.
- Perform the confirmatory test.
Confirmatory Test for Cu $^{2+}$

- Acidify the supernatant (after centrifuging) with 6M $\text{CH}_3\text{COOH}$.
- Add $\text{K}_4[\text{Fe(CN)}_6]$, potassium hexacyanoferrate (II)
- This forms a red brown precipitate of $\text{Cu}_2[\text{Fe(CN)}_6]$
Finally.. Test for Bi$^{3+}$

- Sodium stannite will be prepared for you.
- To the precipitate from the copper test, add the sodium stannite.
- Observation of a black precipitate of Bi(s) is indicative of the presence of Bismuth ions.
- This is a redox reaction.
• 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$_2$S 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$^{2+}$)

• $\text{MS(s)} \rightarrow \text{M}^{2+} \text{(aq)} + \text{S}^{2-} \text{(aq)}$

• $\text{S}^{2-}(s) + \text{H}_2\text{O(l)} \rightarrow \text{HS}^{-}(\text{aq}) + \text{OH}^{-}(\text{aq})$

• 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

• $\text{MS(s)} + \text{H}_2\text{O(l)} \rightarrow \text{M}^{2+} \text{(aq)} + \text{HS}^{-}(\text{aq}) + \text{OH}^{-}$.

• $K_{sp}$ for the dissolution of a metal II sulphide is:

$$K_{sp} = [\text{M}^{2+}][\text{HS}^{-}][\text{OH}^{-}]$$
• 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\(_3\)O\(^+\) 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: $\text{Bi}^{3+}/\text{Cu}^{2+} + \text{NH}_3(\text{aq}) \rightarrow ?$ 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 $\text{Bi}^{3+}$ in the bismuth hydroxide is reduced, and the tin hydroxide compound is the reducing agent, therefore oxidized itself to $[\text{Sn(OH)}_6]^{2-}$

• Product 9: Potassium hexacyanoferrate = $\text{K}_4[\text{Fe(CN)}_6]$ is used a confirmatory test for Cu, forming a reddish brown ppt. (see page 396 Beran).