

## Experiment #7 Qualitative Analysis of Anions

### Objective

Part I: Identify the presence of each of the following anions:  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{NO}_3^-$ , using qualitative analysis.

Part II: Identify the anions in an unknown sample of ionic salts utilizing the information gathered in Part I.

### Introduction

Qualitative analysis is a general name for the determination of the presence or absence of a particular chemical compound or element. Quantitative analysis determines the amount of that compound present in a sample. The qualitative process utilizes reactions characteristic of a given chemical species and interprets the obtained results using a deductive thought process.

Qualitative analysis often requires an extensive knowledge of various aspects of chemistry including acid-base equilibrium, redox reactions, solubility, etc. However, in the deductive process of identifying the presence of a compound, common sense and logic may be as helpful as a knowledge of the chemistry involved. In modern chemistry, wet methods of qualitative analysis have for the most part been replaced by various spectroscopic techniques that can not only identify but also quantify the compounds present in a very small sample. However, qualitative analysis is still useful in illustrating chemical principles, in teaching general laboratory techniques, and in quickly identifying specific anions or cations present in a solution.

To facilitate the analysis process, it is often useful to put ions that react in similar ways and follow similar chemical reaction patterns into groups. For example, it may be useful to group ions based on their solubility properties. Some anions such as halides and sulfates are insoluble in lead containing solutions while remaining soluble in iron or copper containing solutions. Therefore, anions can be roughly classified into groups according to their solubility in a particular solution. The reactions used to form groups of anions are referred to in this lab protocol as classification reactions. The individual anions in each group are then separated and identified using different reactions often referred to as confirmatory reactions.

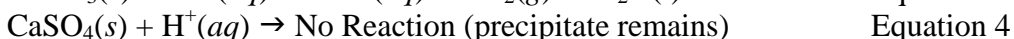
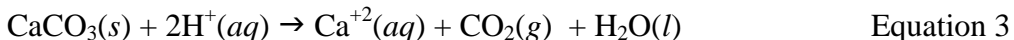
In this laboratory experiment we will use our knowledge of the solubility of anions to separate anions into groups and then to further separate the groups into individual anions that can be identified in confirmatory reactions. Knowing the actual results of the reactions characteristic for a given anion makes it easier to identify this anion in an unknown sample. We will, therefore, perform all the characteristic reactions on a known solution containing all the ions in question and then proceed to an unknown sample containing just one or two anions.

### Group I: Formation of insoluble calcium salts (sulfate and carbonate ions)

The first group of anions to be separated will be those that precipitate in the presence of calcium ions,  $\text{Ca}^{+2}$ . Sulfate ions,  $\text{SO}_4^{-2}$ , and carbonate ions,  $\text{CO}_3^{-2}$ , precipitate, that is they form a solid, when mixed with an aqueous solution containing  $\text{Ca}^{2+}$  ions. The net ionic equations representing the reactions occurring are shown below

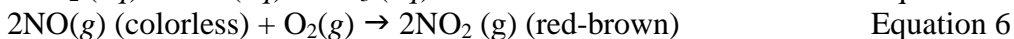


A confirmatory reaction that distinguishes between sulfate ion and carbonate ion utilizes the fact that calcium carbonate will undergo a reaction with a strong acid to form carbon dioxide gas and water while calcium sulfate will not (see equations 3 and 4).



### Group II: Gas forming anions (nitrite)

When mixed with dilute sulfuric acid, and heated, the nitrite ion,  $\text{NO}_2^-$ , forms red-brown nitrogen dioxide gas and nitrate ion. This is a confirmatory reaction, since only one ion is involved.



Equation 5 is a simplified representation of a multi-step process involving hydrolysis and auto-redox reactions of nitrite ion (that is,  $\text{NO}_2^-$  is acting as both the oxidizing agent and the reducing agent).

Note that carbonate ion could also be listed in this group (gas forming anions), since it does produce a gas, carbon dioxide, in its reaction with acid. However, the presence of carbonate ion was confirmed earlier in Group I.

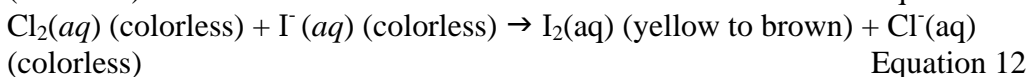
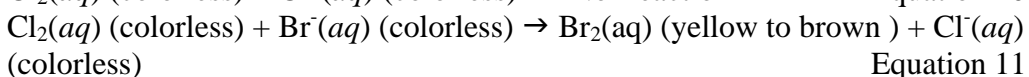
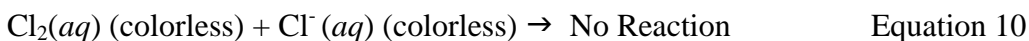
### Group III: Formation of insoluble silver salts (halide ions)

Precipitation is also the main reaction type in the classification of halides, but with a different precipitating agent than for Group I above.  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions, when mixed with an aqueous solution containing  $\text{Ag}^+$  ion, form precipitates that are insoluble in water. As opposed to other solid silver salts, silver halides are also insoluble in strong acid (nitric acid will be used here). Therefore, once the precipitate is formed, it will not dissolve on addition of acid. The  $\text{Ag}^+$  ion solution used in this experiment is aqueous silver nitrate solution, the only silver salt that is soluble in water.

Net ionic equations:



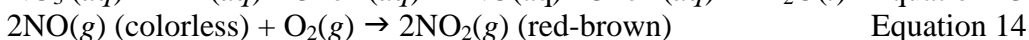
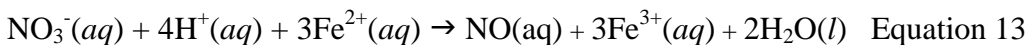
Confirmatory reactions that distinguish between the three halide ions and identify each are based on a redox process. All three halides can act as reducing agents and in the process are oxidized to their diatomic elemental forms. Their relative reducing strength is as follows:  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ . When coupled with a strong oxidizing agent such as aqueous  $\text{Cl}_2$  (chlorine water), bromide and iodide ions will undergo oxidation. If chloride reacts with chlorine it will produce chloride and chlorine. While this may happen, it is easier to say that no reaction occurs.



If  $\text{Cl}^-$  ion is present in the solution, without any other halide, the chlorine water will remain colorless. Therefore, this test verifies the presence of  $\text{Cl}^-$  ion only if the classification test produced a silver precipitate that did not dissolve in acid. After addition of colorless chlorine water to a colorless solution of either bromide or iodide, the solution will change color to yellow-brown, since elemental iodine and bromine impart such color to water. This test, however, does not distinguish between the two ions. One more step is necessary. It is not a reaction, but a physical process of *extraction* with hexane of the solution obtained upon addition of chlorine water. A small volume of hexane is added to the yellow-brown halide solution. A pink or purple hexane layer (the top layer) after extraction indicates that the initial solution contained  $\text{I}^-$  ion. A yellow to brown-orange hexane layer indicates that the initial solution contained  $\text{Br}^-$  ion. The actual shade of the hexane layer depends on the concentration of the halogen (a higher concentration of the halogen produces a darker shade).

#### **Group IV: Nitrate ion**

Nitrate ion does not directly produce any precipitates (remember the solubility rules?) nor does it produce any gaseous products in an acidic environment. However, upon reduction by  $\text{Fe}^{2+}$  ion it forms a characteristic brown gas, nitrogen dioxide. As with nitrite, the reaction is considered a confirmatory one. The equations for the reactions involved are as follows:



#### **Known anion testing strategy**

Our purpose in testing the salts of known anions is to help you become familiar with the physical results of the reactions so that when you encounter them in an unknown sample you can easily identify the anion.

#### **Unknown anion testing strategy**

The best strategy in determining the identity of the unknown anion is to start by classifying the unknown into a group. Then, one needs to prove the "suspicion" by confirming the identity of the ion. Start with the test for group I anions. If this test is negative (no ppt formed), you do not have any of the group I anions. Proceed to the group II test. If this test is negative (no red-brown gas formed), you do not have group II anions. Perform the classification test for group III. If this test is negative (no precipitate formed), you do not have any of the group III anions. If at this point none of the classification tests have been positive, you probably have nitrate ion. Note that you still need to confirm this.

After you have obtained a positive result in a classification test you do not have to proceed with the other classification tests. But you do need to perform the necessary confirmatory tests within a group. In other words, you do not need to continue testing for group II, III, and IV ions if you obtain a white precipitate with calcium chloride since you already know your anion belongs to group I. However, you do need to verify whether it is a carbonate or sulfate ion.

It may be useful for you to prepare a flowchart outlining the steps needed for complete analysis of the known anions. The example above may be helpful in developing such flowchart. It is important to remember that group III tests should not be done before group I and II, as the silver salt precipitates may be obtained with anions other than the halides. These solids, however, will dissolve in nitric acid.

## **PROCEDURE**

1. Use a small amount (an amount that fits on the corner tip of the square end of a spatula) of solid salt for each test. (The sulfate test requires a little more).
2. Make sure that a new sample of salt is used for each new test (unless you are checking for the acid solubility of a precipitate formed in a classification reaction).
3. Always shake the tube to mix the contents after adding a reagent.
4. After adding a reagent, always record your observations.
5. Any bubbling or fizzing indicates formation of gas
6. Any turbidity, milkiness, etc., formed upon addition of a reagent to a previously clear solution means that a precipitate (ppt) was formed.

## **PART I: KNOWN ANIONS**

### **Group I**

Classification test for carbonate ion.

1. In a labeled test tube, dissolve a small amount of sodium carbonate in 5 drops of distilled water.
2. Add 1 drop of 1.0 M  $\text{CaCl}_2$  solution to the test tube. Record your observations.

Confirmation test for carbonate ion.

3. To the precipitate resulting from step 2, add 4 drops of 3.0 M nitric acid,  $\text{HNO}_3$ . Record your observations.

Classification test for sulfate ion.

4. Repeat steps 1-3 using sodium sulfate (use twice as much sulfate as you did carbonate and in step 2, add 10 drops of 1.0 M  $\text{CaCl}_2$ ). Calcium sulfate precipitate is not produced instantaneously, it will take several seconds of shaking the tube before it forms. The precipitate should not dissolve in acid

### **Group II.**

Classification and confirmation

1. In a labeled test tube, dissolve a small amount of sodium nitrite, in 5 drops of distilled water.

2. Add 5 drops of 3.0 M  $\text{H}_2\text{SO}_4$ .
3. If nothing can be observed, gently heat the test tube and its contents in a hot water bath in the fume hood.

NOTE: Do not remove the test tube from the fume hood, until after the brown gas dissipates from the tube

### **Group III**

Classification test for bromide ion

1. In a labeled test tube, dissolve a small amount of sodium bromide in 5 drops of distilled water.
2. Add 2 drops of 0.1 M  $\text{AgNO}_3$ . Record what happens.
3. Add 3 drops of 3.0 M  $\text{HNO}_3$ . Record what happens.

Confirmation test for bromide ion.

1. In a labeled test tube, dissolve a new portion of sodium bromide in 5 drops of distilled water.
2. Add 5 drops of fresh chlorine water (make sure that you quickly recap the bottle of chlorine water).
3. Add about 1 ml of hexane (enough to produce two distinct layers).
4. Shake the tube vigorously until the top (hexane) layer changes color. Record the color of top layer.

Classification and confirmation tests for iodide and chloride ions.

1. Repeat steps 1-3 in the classification process for bromide ion and steps 1-4 in the confirmation of bromide ion using sodium iodide, then sodium chloride (the hexane layer will remain colorless for chloride ion). Record all observations.

### **Group IV**

1. In a labeled test tube, dissolve a small amount of sodium nitrate in 5 drops of a 1.0 M solution of acidic  $\text{FeSO}_4$ .
2. In a fume hood, Add 3 drops of concentrated sulfuric acid (not the 3.0 M acid solution used previously).
3. If the red-brown  $\text{NO}_2$  gas is not produced spontaneously, heat the test tube and its contents in a hot water bath (in the fume hood).

## **PART II: UNKNOWN ANIONS**

Obtain one unknown to identify. Record the code letter or number of the unknown.

Use the procedure outlined above for the known ions with the unknown salt.

Follow the proper strategy and perform only the tests necessary to identify your unknown.

## REPORT

The report for this experiment consists of data sheet and a discussion of results in which the following elements are included:

- code letter or number of unknown
- identity of anion present in the unknown.
- justification (stepwise deductive process) for your decision concerning the identity of the unknown (see the example above).
- net ionic equations for all reactions leading to the identification of your unknown.
- a flowchart prepared for your known anions including observations of each reaction.

1. List all the anions in this lab that are identified using:

A. precipitation reactions

B. redox reactions

C. acid-base reactions

D. gas-forming reactions

2. Write a balanced chemical equation for the reaction of one anion in each of the categories in question 1.

A. a precipitation reaction

B. a redox reaction

C. an acid-base reaction

D. a gas-forming reaction

1. What does the term qualitative analysis mean?
2. The confirmatory reactions that identify nitrate and nitrite both produce brown  $\text{NO}_2$  gas. What criterion will you use to determine which anion produced the gas?
3. The confirmation reaction for the halides involves the addition of chlorine water. Describe how you will know which, if any, of the anions is present.
4. A student added calcium ion,  $\text{Ca}^{+2}$  to an aqueous solution and observed formation of a precipitate. Addition of  $\text{HNO}_3$  had no effect on the precipitate. What anion was present in the original solution? Explain your answer.