10 Qualitative Analysis IV: Anions II

Version: December 1, 2004

- **Apply acid-base, solubility, oxidation-reduction, and complex ion equilibrium principles to the identification of anions in solution.**
- **Learn some descriptive chemistry of common anions.**

DISCUSSION

This experiment is a continuation of the identification of anions in solution begun in Experiment 9. The ions to be studied are the halides (F^-, Cl^-, Br^-, and I^-). These ions are colorless in solution, are neutral to litmus, and do not form precipitates with barium (see Experiment 9).

You will identify I^- and Br^- by oxidizing them to I_2 and Br_2 with sodium hypochlorite, NaClO. The oxidizing strength of the solution depends upon its acidity, as the following half reactions and standard potentials illustrate:

$$I_2(s) + 2\,e^- \rightarrow 2\,I^-$$
$$E^o = 0.535\text{ V}$$

$$ClO^- + H_2O + 2\,e \rightarrow Cl^- + 2\,OH^-$$
$$E^o = 0.89\text{ V}$$

$$Br_2(\ell) + 2\,e^- \rightarrow 2\,Br-$$
$$E^o = 1.08\text{ V}$$

$$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2(s) + 6H_2O(\ell)$$
$$E^o = 1.20\text{ V}$$

$$2HClO(aq) + 2H^+ + 2e^- \rightarrow Cl_2(g) + 2H_2O$$
$$E^o = 1.63\text{ V}$$

In neutral or basic solutions, ClO^- is present. It will oxidize I^- but not Br^-. When the solution is acidified, however, the stronger oxidizing agent HClO is formed, and it will oxidize *both* I^- and Br^-.

Bromine and iodine are detected by their colors in hexane. A positive test is given by the gold color of bromine (which may vary from light yellow to dark reddish brown, depending on concentration), or the purple color of iodine, in the hexane layer.

If I^- and Br^- both are present in an unknown, the intense iodine color will mask the color of bromine. Fortunately, HClO is a sufficiently strong oxidizing agent to oxidize I_2 to colorless IO_3^-, thus allowing you to see the bromine color. However, adding too much HClO and acid can also oxidize Br_2 to BrO_3^-, so avoid adding a large excess of bleach and acid.

You will identify fluoride by forming insoluble CaF_2. This precipitate is white but under the conditions of the experiment is so finely divided that it often remains suspended, giving a milky appearance to the solution. You will have to observe very carefully to see it. The precipitate does not interfere with succeeding tests, so it is not necessary to centrifuge and remove it from the solution.

You will identify chloride by forming insoluble white AgCl. This test is easy when bromide and iodide are both absent, but if they are present they will form off-white AgBr*(s)* and yellow AgI*(s)*. (AgF is soluble, so fluoride will not interfere). To identify chloride in the presence of bromide or iodide, you will take advantage of the fact that, in ammonia, AgCl is much more soluble than either AgBr or AgI. After dissolving AgCl in ammonia, you will separate it from the AgBr and AgI, and you will then acidify the solution to precipitate AgCl.

PROCEDURE

1. Preliminary Observations

6. Place 2 mL samples of 0.1 *M* solutions of F^-, Cl^-, Br^-, and I^- in separate small test tubes. Use sodium or potassium salts here and in Step 8. To each tube add ½ mL of hexane and 1 drop of 5% NaClO*(aq)* (household bleach). Gently shake the test tubes to increase the contact between the hexane and the aqueous solution. Observe the color of the hexane layer, and record your observations on the report.

7. Next add 2 drops of 6 *M* $HNO_3(aq)$ and 2 more drops of NaClO*(aq)*. Shake the tubes well. If necessary, add more $HNO_3(aq)$ and NaClO*(aq)*, a little at a time, and continue to shake the tube until the iodine color disappears from the hexane layer. Solid iodine may form in the aqueous layer but will gradually react with HClO in the acidic solution to form iodate.

Now mix 1 mL of solution containing I^- with 1 mL of solution containing Br-. Repeat Steps 6 and 7, noting the appearance in the hexane first of the iodine color, then its disappearance and the appearance of the bromine color. *Dispose of the contents of these test tubes in the organic waste container.*

8. Obtain new 2 mL samples of the halide ions in separate test tubes. To each test tube add 5 drops of 1 *M* $Ca(NO_3)_2$*(aq)*. Mix well and look closely for a white cloudiness in one test tube. Record your observations on the report.

9. Next add 2 drops of 6 *M* HNO_3*(aq)*, then 2 mL of 0.1 *M* $AgNO_3$*(aq)* to each test tube. Mix well, and centrifuge if a precipitate forms. If the solution is still very cloudy after being centrifuged, precipitation is not complete. Not enough $AgNO_3$*(aq)* was added, and the halide ions are still in excess. The cloudiness comes because these ions are adsorbed onto the precipitate, giving it a negative charge and preventing it from forming particles large enough to settle. Add a little more $AgNO_3$*(aq)*, mix well, and centrifuge again. Observe carefully the subtle differences in the colors of the precipitates, and record your observations on the report. Discard the solution (in the container provided for waste silver), wash each precipitate with 2 mL of water, centrifuge again and discard the water.

10. To each test tube add 3 mL of water, 1 mL of 1 *M* NH_3*(aq)*, and ½ mL of 0.1 *M* $AgNO_3$*(aq)*. Measure these quantities carefully. Stir well, then centrifuge. Transfer the solutions to clean test tubes. If they are cloudy, centrifuge again. Now acidify the solutions with 6 *M* HNO_3*(aq)*. A white precipitate should form only in the solution containing chloride. Record your observations on the report. Dispose of solutions and precipitates containing silver in the containers provided for that purpose.

2. Preparation of the Flowchart

Before starting the analysis of the unknowns, fill out the flowchart on page 2 of the report by referring to your preliminary observations and by studying the procedures below. When the flowchart is filled out, have it initialed by the lab instructor before proceeding.

3. Analysis of the Unknowns

Exchange two of your clean test tubes for unknown solutions at the stockroom window. Mix each unknown well and record your unknown numbers on the report.

6. To a 2 mL sample of each unknown, add 1 drop of 5 % NaClO(aq) and ½ mL of hexane. *(Refer to the preliminary observations for important cautions)*. Gently shake the test tubes and observe the color of the hexane layer.

7. Add 2 drops of 6 *M* HNO_3 *(aq)* and 2 more drops of NaClO*(aq)*. If I^- is present, add more HNO_3*(aq)* and NaClO*(aq)*, a little at a time, and gently shake the test tube until the purple color disappears from the hexane layer. Observe the color that remains. *Remember to discard the contents of these test tubes in the organic waste container.*

8. To a new 2 mL sample of each unknown add 5 drops of 1 *M* $Ca(NO_3)_2$*(aq)*. Mix well and look closely for a precipitate.

9. Next add 2 drops of 6 *M* HNO_3*(aq)* and 2 drops of 0.1 *M* $AgNO_3$*(aq)*. If Br^- and I^- are absent (as determined in steps 6 and 7), you do not need to finish step 9 or do step 10. A white precipitate proves chloride is present, and no precipitate proves it is absent. If you do have Br^- or I^-, add 1 mL of $AgNO_3$*(aq)* and centrifuge. Test for completeness of precipitation, and add more $AgNO_3$*(aq)* if necessary until no more precipitate forms. Discard the solution, wash the precipitate, and discard the water.

10. Add 3 mL of water, 1 mL of 1 *M* NH_3*(aq),* and ½ mL of 0.1 *M* $AgNO_3$*(aq)* to the precipitate and stir well. Centrifuge and discard the precipitate. Add 6 *M* HNO_3*(aq)* to the solution until it is acidic to litmus and watch for a white precipitate. *Discard all solutions and precipitates containing silver in the waste silver container.*

4. Confirming the Analysis

As before, it is recommended that you confirm your identification of ions in your unknown by preparing a known solution to match its composition.

10 Qual Analysis IV: Anions II

Name ______________________________
Section __________________Locker ____
Instructor ___________________________

1. Preliminary Observations

Steps 6 and 7. In the boxes below, describe the appearance of the solutions, and, *if the halide ion has reacted*, write the formula of the principal products in the boxes.

Step 6

	Water	**Hexane**
F^-		
Cl^-		
Br^-		
I^-		
Br^- and I^-		

Step 7

	Water	**Hexane**
F^-		
Cl^-		
Br^-		
I^-		
Br^- and I^-		

Step 8. What is the formula of the precipitate formed when calcium nitrate was added? Write a net ionic equation for the reaction:

Step 9. Describe the color of each precipitate.

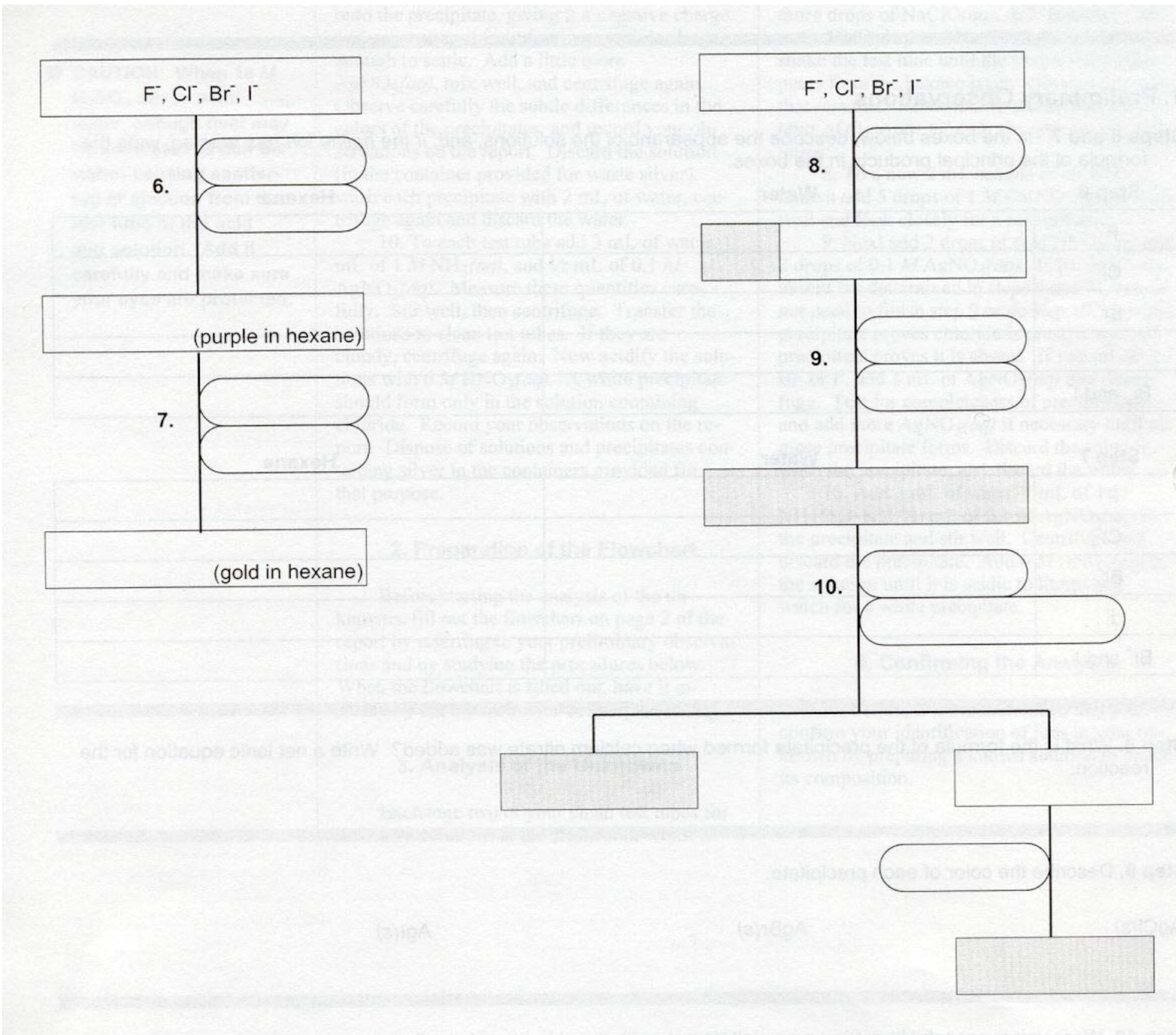
AgCl*(s)* AgBr*(s)* AgI*(s)*

Step 10. Were you successful in getting a precipitate only with the chloride solution?

Write net ionic equations for the two reactions in this step, one starting with AgCl*(s)* and one ending with AgCl*(s)*.

2. Preparation of the Flowchart

As before, the shaded boxes should contain the formulas of precipitates, the open boxes should contain formulas of substances in solution, and the rounded boxes should contain the formulas of reagents. Bold face numbers indicate the steps in the procedure.



3. Analysis of the Unknowns

Complete the following table for your unknowns:

Unknown	Step	Observations	Conclusion

Summarize your analysis in the following table:

Unknown Number	Ions Found

4. Confirming the Analysis

Describe below what you did to confirm that your analysis is correct.

APPLICATION OF PRINCIPLES

1. Write the net ionic equation for the reaction between ClO^- and I^-.

2. Write the net ionic equation for the reaction between HClO*(aq)* and I_2*(s)* to form IO_3- in acidic solution.