

# 9 Qualitative Analysis III: Anions I

Version: November 18, 2004

## DISCUSSION

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

Most of the common anions are colorless in solution, which prevents their identification by direct observation. You can identify them, however, by taking advantage of differences in their chemical behavior. In Experiment 6, you used acid-base, solubility and complex ion equilibria to separate and identify five colorless cations. You will use the same principles, along with oxidation-reduction equilibria, to identify several common anions in Experiment 9 and Experiment 10.

The anions studied in these experiments are listed in the table below, which gives the pH of 0.1 M solutions of their sodium salts. The first step in the procedure will be to test the unknowns with litmus paper. This will give you valuable information about the anions that may or may not be present.

### Reaction of Common Anions with Litmus

*pH of 0.1 M solutions of their sodium salts*

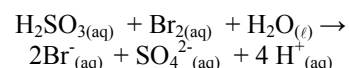
| Anion                         | ACIDIC<br><i>Turns<br/>litmus red</i> | NEUTRAL<br><i>No effect on<br/>litmus</i> | BASIC<br><i>Turns<br/>litmus<br/>blue</i> |
|-------------------------------|---------------------------------------|---|---|
| SO <sub>4</sub> <sup>2-</sup> |                                       | 7.5                                       |   |
| SO <sub>3</sub> <sup>2-</sup> |                                       |   | 10.1                                      |
| CO <sub>3</sub> <sup>2-</sup> |                                       |   | 11.7                                      |
| PO <sub>4</sub> <sup>3-</sup> |                                       |   | 12.6                                      |
| F <sup>-</sup>                |                                       | 8.1                                       |   |
| Cl <sup>-</sup>               |                                       | 7.0                                       |   |
| Br <sup>-</sup>               |                                       | 7.0                                       |   |
| I <sup>-</sup>                |                                       | 7.0                                       |   |

The last four ions listed in the table are studied in Experiment 10. When you do Experiment 11 (the general unknown), you will need to combine the procedures of Experiment 9 and Experiment 10 to identify the anions present.

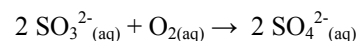
After testing the pH of the solution, you will add barium nitrate to precipitate all of the anions except the halides and nitrate, which are studied

in Experiment 10. After the barium salts are precipitated, you will add HCl(aq). If a precipitate remains, sulfate is indicated since BaSO<sub>4</sub>(s) will not dissolve in HCl(aq). If BaCO<sub>3</sub>(s) is present, it will effervesce (bubble) vigorously as CO<sub>2</sub>(g) is liberated, proving carbonate present in the unknown. BaSO<sub>3</sub> and Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> are salts of the weak acids H<sub>2</sub>SO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> and will be dissolved by the strong acid HCl(aq). You will then test the solution for the presence of these acids.

The test for sulfite involves the oxidation of sulfurous acid to sulfate by bromine, which is reduced to bromide.



Since barium is already present in the solution, barium sulfate will precipitate, proving the presence of sulfite. Sulfite is also oxidized by oxygen in the air over a period of a few days:



Thus, if you have sulfite in your unknown, you probably will get a positive test for sulfate also unless your unknown is prepared immediately before testing.

The test for phosphate is the re-precipitation of barium phosphate from the other weak acid, H<sub>3</sub>PO<sub>4</sub>, when the solution is made alkaline. If carbonate is present, BaCO<sub>3</sub> will also precipitate in alkaline solution. Therefore, it must be removed by boiling before testing for phosphate.

## PROCEDURE

### 1. Preliminary Observations

- **CAUTION: remember that barium compounds are toxic. Avoid contact with any solutions containing barium, and wash thoroughly if any such solutions contact your skin.**
- **CAUTION: bromine is highly volatile and very toxic. Use care when handling it.**

1. Obtain one 3 mL sample each of 0.1 M  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ , and obtain two 3 mL samples of 0.1 M  $\text{CO}_3^{2-}$ . Use sodium salts. Test the solutions with litmus paper. Record your observations on the report.

2. Add to each sample 1 mL of saturated barium nitrate solution. Mix well. Centrifuge and discard the solutions. Record your observations on the report.

3. To each of the 5 precipitates add 1 mL of 6 M  $\text{HCl}(aq)$  and 2 mL of water, and stir well with a stirring rod. Record your observations on the report. Does the precipitate dissolve? Is there effervescence? Where a precipitate remains, centrifuge and discard the precipitate.

4. To each of the 5 solutions add 3 drops of bromine water and mix. The bromine water should be used only under the hood. Observe the color of the solutions and whether any precipitate forms. If the solution is not colored, add 1 mL of bromine water and mix again. If necessary, continue adding until the color of bromine remains in solution (but avoid a large excess). Centrifuge and discard the precipitate.

5. Heat one of the  $\text{CO}_3^{2-}$  solutions nearly to boiling, and drive off the resulting  $\text{CO}_2$ . Do not splatter the solution out of the test tube by overheating it. Add to each of the 5 test tubes  $\frac{1}{2}$  mL of 6 M  $\text{NaOH}(aq)$ . In which test tube(s) does a precipitate reappear? Does a precipitate appear both in the heated and unheated carbonate solutions?

### 2. Preparation of the Flowchart

On the second page of the report is a flowchart which summarizes the procedures to be followed in analyzing an unknown solution. Before starting the analysis of the unknowns, fill out the flowchart by referring to your preliminary observations and by studying the discussion and the procedures below. When the flowchart is filled out, have it initialed by the lab instructor before proceeding.

### 3. Analysis of the Unknowns

As in previous experiments, exchange two of your clean test tubes for unknown solutions at the stockroom window. Mix each unknown

well and record the unknown numbers on the report.

1. Start with a 3 mL sample of each unknown in a small test tube. Test each solution with litmus paper. Consult the table in the discussion and draw whatever conclusions you can about which ions may or may not be present.

2. Add 1 mL of saturated  $\text{Ba}(\text{NO}_3)_2$  solution to each sample. Centrifuge, then test for completeness of precipitation by adding another drop to the clear solution. If more precipitate forms, add another  $\frac{1}{2}$  mL of the  $\text{Ba}(\text{NO}_3)_2$  solution and centrifuge again. Repeat this if necessary until precipitation is complete. Centrifuge and discard the solution. (If you are doing a general unknown—Experiment 11—save this solution for the procedures of Experiment 10).

3. To each precipitate add 1 mL of 6 M  $\text{HCl}(aq)$  and watch carefully for the effervescence that indicates the presence of carbonate. Then add 2 mL of water and stir well. A precipitate remaining under these conditions proves sulfate. Centrifuge and discard the precipitate.

4. Add to the solution 3 drops of bromine water and mix. If the color disappears and a white precipitate appears, sulfite is present in your unknown. If this is the case, add  $\frac{1}{2}$  mL more bromine water, and more if needed, until the yellow color remains in solution and precipitation is complete. Avoid a large excess of bromine, however. Centrifuge and discard any precipitate.

5. If carbonate was present, heat the solution *almost* to boiling, and drive off all the  $\text{CO}_2$ . (A full boil may cause the solution to splatter out of the test tube.) Add, drop-wise, 6 M  $\text{NaOH}(aq)$  until the solution is alkaline. A white precipitate proves the presence of phosphate in your unknown.

### 4. Confirming the Analysis

You may, if you desire, prepare known solutions matching the suspected composition of your unknowns, and test them along with other samples of your unknowns to confirm your analysis. This is optional, and no place is provided on the report for recording this work. Do as much as is necessary to have confidence in your report of the composition of the unknowns.

# 9 Qualitative Analysis III: Anions I

Name \_\_\_\_\_  
 Section \_\_\_\_\_ Locker \_\_\_\_\_  
 Instructor \_\_\_\_\_

## 1. Preliminary Observations

In the first column in the following table, indicate whether the solutions were acidic, basic, or neutral to litmus paper. In the second column, write the colors and the formulas of the precipitates formed when barium nitrate was added. In the third column, indicate if the precipitates dissolved when  $\text{HCl}(aq)$  was added and if a gas was produced. Write the formulas of the principal products formed. In the fourth column, write the formula of any precipitate that appears on addition of sodium hydroxide.

| Anion                       | Litmus | Barium Nitrate | Hydrochloric Acid | Sodium Hydroxide |
|-----------------------------|--------|----------------|-------------------|------------------|
| $\text{SO}_4^{2-}$          |        |                |                   |                  |
| $\text{SO}_3^{2-}$          |        |                |                   |                  |
| $\text{PO}_4^{3-}$          |        |                |                   |                  |
| $\text{CO}_3^{2-}$          |        |                |                   |                  |
| $\text{CO}_3^{2-}$ (heated) |        |                |                   |                  |

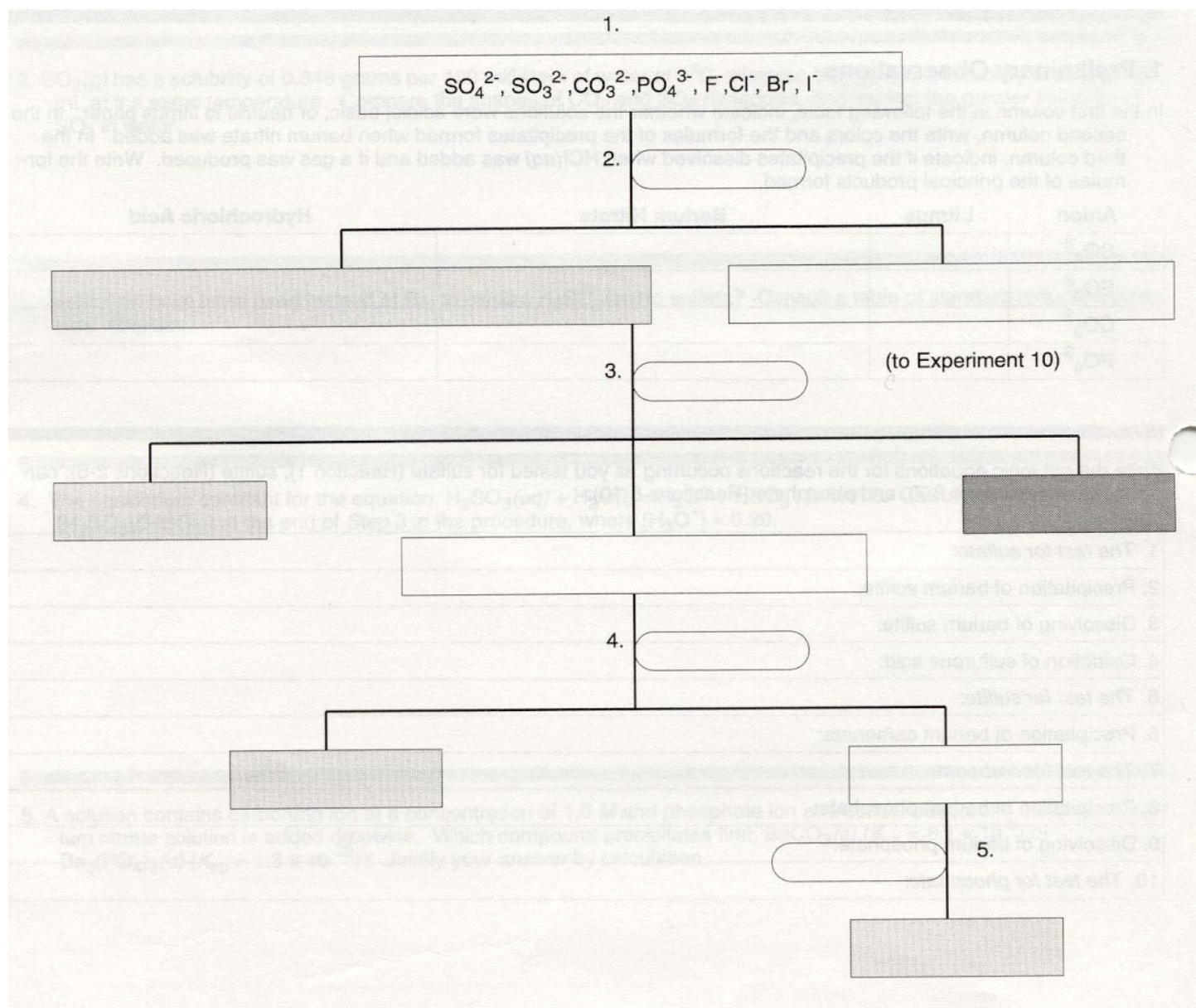
In Step 5 of the analysis, you will test for phosphate by adding  $\text{NaOH}$  to the solution (which contains barium ions). If phosphate is present (as  $\text{H}_3\text{PO}_4$ ), it will precipitate as white  $\text{Ba}_3(\text{PO}_4)_2$ . How will you be certain that the precipitate is indeed barium phosphate rather than the identical-appearing, white  $\text{BaCO}_3$ ?

Write the net ionic equations for the reactions occurring as you tested for sulfate (Reaction 1), sulfite (Reactions 2-5), carbonate (Reactions 6-7), and phosphate (Reactions 8-10):

|                                       |
|---------------------------------------|
| 1. <i>The test for sulfate:</i>       |
| 2. Precipitation of barium sulfite:   |
| 3. Dissolving of barium sulfite:      |
| 4. Oxidation of sulfurous acid:       |
| 5. <i>The test for sulfite:</i>       |
| 6. Precipitation of barium carbonate: |
| 7. <i>The test for carbonate</i>      |
| 8. Precipitation of barium phosphate: |
| 9. Dissolving of barium phosphate:    |
| 10. <i>The test for phosphate:</i>    |

## 2. Preparation of Flowchart

As in experiment 6, each branch indicates centrifuging and separation. The shaded boxes should contain the formulas of precipitates (except the one darker box where the formula of a gas belongs), and the open boxes should contain the formulas of substances in solution. Place the formulas of reagents in the rounded boxes. Numbers in bold type 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 |
|----------------|------------|
|                |            |
|                |            |
|                |            |

### 3. Confirming the Analysis

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

**APPLICATION OF PRINCIPLES**

1.  $\text{BaSO}_4$  and  $\text{BaSO}_3$  are both insoluble in water. Why does  $\text{BaSO}_3(s)$  dissolve, but  $\text{BaSO}_4(s)$  does not, when  $\text{HCl}(aq)$  is added?

2.  $\text{CO}_2(g)$  has a solubility of 0.348 grams per 100 milliliters of water at  $0^\circ\text{C}$ , whereas  $\text{SO}_2(g)$  has a solubility of 22.8 g/100 mL at the same temperature. Compare the shapes of  $\text{CO}_2$  and  $\text{SO}_2$  molecules, and explain the greater solubility of  $\text{SO}_2$  in water.

3. Could  $\text{I}_2(s)$  have been used instead of  $\text{Br}_2$  to oxidize  $\text{H}_2\text{SO}_3(aq)$  to sulfate? Consult a table of standard reduction potentials. Explain.

4. The equilibrium constant for the equation,  $\text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l) = \text{H}_3\text{O}^+ + \text{HSO}_3^-$ , is 0.012. Calculate the ratio  $[\text{H}_2\text{SO}_3]/[\text{HSO}_3^-]$  at the end of *Step 3* in the procedure, where  $[\text{H}_3\text{O}^+] = 0.20$ .

5. A solution contains carbonate ion at a concentration of 1.0 M and phosphate ion at a concentration of 0.0040 M. A barium nitrate solution is added drop-wise. Which compound precipitates first,  $\text{BaCO}_3(s)$  ( $K_{sp} = 8.1 \times 10^{-9}$ ) or  $\text{Ba}_3(\text{PO}_4)_2(s)$  ( $K_{sp} = 1.3 \times 10^{-29}$ )? Justify your answer by calculation.