EXPERIMENT **4**

"...THEREFORE THERE IS NOT ANYTHING WHICH RETURNS TO NOTHING, BUT ALL THINGS RETURN DISSOLVED INTO THEIR ELEMENTS..."

DETERMINATION OF THE SOLUBILITY PRODUCT OF $Fe(OH)_3$

Techniques

- Successive dilution
- graphing
- preparation of standards
- spectrophotometry

MSDS available for

- ferric chloride, $FeCl_3$
- sodium hydroxide, NaOH
- hydrochloric acid, HCl (aq)

Principles

- solubility, K_{sp}
- equilibrium
- Beer-Lambert law
- graphical extrapolation

Recommended Advanced Reading

- **Chapter 18 in Petrucci,Herring,Madura,Bissonnette's General Chemistry, 10th Ed**

INTRODUCTION

The beginning

In this experiment, you will perform a fairly simple experiment that will provide you with a lot of information. In today's session you will work with your partner to:

- Precipitate the maximum amount of $Fe(OH)_3$ possible from a mixture of $FeCl_3$ and NaOH solutions.
- Measure the pH of the resulting solution to determine the concentration of hydroxide ion remaining in solution.
- Use the technique of spectrophotometry to determine the absorbance of the ferric ion in the final solution and prepare a standard iron (III) ion solution to be used as part of a calibration plot to determine the absolute value of the concentration of iron (III) ion in the final solution.
- Calculate an experimental value for K_{sp} of $Fe(OH)_3$ and compare it to the literature value.

This is a general overview of what you will be accomplishing in this experiment.

EXPERIMENT 4: *Determination of the Solubility Product of $Fe(OH)_3$*

Introduction

"*Acidic mine drainage (AMD), while more localized than acid rain, is a pressing environmental concern….the precipitation of $Fe(OH)_3$ is characteristic of this process.*"

Dissolution of a Substance

When a substance is being dissolved in water, there are two main factors that determine to what extent dissolution will occur. The first is the strength of the bonds holding the substance together, and the second is the attraction of the substance to water. If the intermolecular interaction in the solid is larger than the interaction between the solid and water, the solid will most likely remain undissolved and is said to be ***insoluble***. If the interaction between the molecules of the solid and water is stronger than the interaction between the molecules of the solid, the solid will most likely dissolve and is said to be ***soluble***. There are many other factors that could have an effect on the dissolution of a substance, but these two play a very major role. Although the term insoluble is used widely, in truth all substances are soluble, although the extent of their solubility may be very small. Thus the term ***slightly soluble*** is preferred to the term insoluble.

Solubility and K_{sp}

Quantitatively then, how is solubility determined? It is possible to measure the mass of a solid that dissolves in a given volume of solvent if enough of the solid will dissolve. Thus for soluble substances, the solubility is usually stated as mass per volume (normally grams per 100 mL). This is not easily measured if the substance is only slightly soluble. In that case it is necessary to use a quantity called the ***solubility product constant*** or ***K_{sp}.***

When a solid is in the process of dissolving in a solvent, the dissolution process continues until the solvent is incapable of holding any more of the dissolved ***solute*** (the substance being dissolved). At this point, the solid does not simply stop dissolving. Instead, for every solute molecule that goes into solution, or ***dissolves***, one solute molecule comes out of solution, or ***precipitates***. Such a situation is known as ***equilibrium***. At equilibrium, two opposing processes are occurring at the same rate. Thus, the rate of dissolution equals the rate of precipitation and it appears as if no more solid is dissolving.

This equilibrium can be stated in mathematical form. For a solid, A_xB_y, the chemical reaction of dissolution is

$$A_xB_y\,(s) \rightleftharpoons x\,A^{y+}\,(aq) + y\,B^{x-}\,(aq) \qquad [1]$$

Note that the double arrow is used to indicate that both the forward and reverse reactions are taking place. For this solid, the solubility product constant can be written as

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y \qquad [2]$$

Thus, if the concentration of the ions in solution can be determined, then Equation [2] can be used to determine the K_{sp}.

Concept of the Experiment

In this experiment, you will add a solution of sodium hydroxide, NaOH, to a solution of ferric chloride, $FeCl_3$ until no more precipitate is formed. At this point, you will measure the pH of the solution and use the pH value to determine the concentration of the hydroxide ion in the ***supernatant solution***, or the solution above the precipitate. In order to determine the solubility product constant, or K_{sp} value, it is necessary to know the concentration of the iron (III) ion or the ferric ion in solution. While there are many methods that can be used to determine the ferric ion concentration, we will use the technique of spectrophotometry, which measures the amount of light absorbed by the ferric ion.

Spectrophotometry

Spectrophotometry is the study of the interaction of electromagnetic radiation with matter. The two most commonly used terms when making spectrophotometric measurements are ***transmittance*** and ***absorbance***.

Transmittance is defined as the ratio of the intensity of light after it passes through the medium being studied (I) to the intensity of light before it passes through the medium (I_o).

$$T = I / I_o \qquad [3]$$

On the spectrophotometer, percent transmittance is used rather than transmittance.

$$\%T = I / I_o \times 100\% \quad [4]$$

Absorbance is related to the transmittance as follows:

$$A = - \log T = - \log (I / I_o) \quad [5]$$

Note that in Equation [5] it is the transmittance and not the percent transmittance that is used. Since you will be reading percent transmittance, it is necessary to convert it back to transmittance before determining the absorbance. Although most spectrophotometers have a scale for both percent transmittance and absorbance, the former is preferred. Percent transmittance is linear whereas absorbance follows a logarithmic scale. Hence it is more difficult to read the absorbance accurately on the spectrophotometer.

Spectrophotometry is an extremely powerful analytical tool that can be used to determine the concentration of fairly dilute solutions, as long as there is a species present that absorbs substantial quantities of light at a particular wavelength. Many such substances will absorb light over a range of wavelengths, but will absorb most strongly at a particular wavelength. In this experiment, the wavelength of maximum absorption is 430 nm. How, then, is the absorbance related to the concentration of the solution? The relation between absorbance and concentration is called the ***Beer-Lambert law*** and the equation for this relation is given below:

$$A = \varepsilon b c \quad [6]$$

In this relation, A represents the absorbance, ε represents the molar absorptivity coefficient, b represents the path length and c represents the concentration of the absorbing species in the solution. For a given substance that absorbs light, the molar absorptivity coefficient is a constant. Since you will be using the same cuvette to make all the measurements, the path length will also remain constant. Hence, Equation [6] shows that the absorbance is directly proportional to the concentration. This means that a plot of absorbance as a function of the concentration of the absorbing species should be linear and should pass through the origin.

(TTD) Things to Do

- Complete the prelab exercises before coming to the laboratory.
- Precipitate the maximum amount of $Fe(OH)_3$ from a mixture of $FeCl_3$ in HCl and NaOH solutions. Filter the precipitate using a cotton plug.
- Measure the pH and percent transmittance of the supernatant solution.
- Prepare one of the standard solutions and measure its percent transmittance.
- Prepare a calibration curve of absorbance vs. concentration and determine the concentration of ferric ion in the supernatant solution. Use the pH to determine the concentration of the hydroxide ion in the supernatant.
- Calculate the K_{sp} of $Fe(OH)_3$ and compare to the literature value.
- Use safe laboratory procedures at all times.

Safety Precautions

1. **Wear approved eye protection at all times**.
2. Acids are **corrosive**. Be careful!!

PROCEDURE

Equipment and chemicals needed	*Chemicals*	*Equipment*
	$0.05\ M\ FeCl_3$ in HCl	2 – 50 mL beakers
	0.05 M HCl	2 - 25 mL burets
	0.1 M NaOH	cotton, filter funnel
	1.0 M HCl	10 mL graduated cylinders
		ruler, pencils, graph paper

Determination of the K_{sp} of $Fe(OH)_3$

Starting the experiment

Preparation of the precipitate

1. Using a 150 mL beaker, obtain approximately 50 mL of the $FeCl_3$ in HCl solution. Record the concentration of the solution.

2. Transfer enough of the $FeCl_3$ solution to a clean, labelled 25 mL buret (use a funnel if necessary). Remember to fill above the mark and drain through the tap. Record your initial volume of solution in the buret.

3. Using another 150 mL beaker, obtain approximately 20 mL of NaOH solution. Record its concentration.

4. Transfer the NaOH solution into a clean, labelled 25 mL buret (use a funnel if necessary). Remember to fill above the mark and drain through the tap. Record your initial volume of solution in the buret.

5. Transfer 10.00 mL of the $FeCl_3$ solution into a 50 mL beaker. Record the final volume on the buret and calculate the precise volume of solution you transferred.

6. Add the NaOH solution dropwise to the $FeCl_3$ solution. Note down your observations at all times.

7. After having added 13-14 mL of NaOH, allow the solution to settle for 10 minutes. Record the final volume on the

buret and calculate the precise volume of NaOH added (remember: a buret can be read to 2 digits after the decimal!).

8. While waiting, repeat Steps 5-7 with a second 10.00 mL portion of $FeCl_3$ solution in another 50 mL beaker. Remember to record ALL initial and final volume readings.

9. Using a filter funnel and a SMALL cotton plug, first decant, and then filter the solution in the beaker in Step 7. Use a stirring rod to gently press the cotton to drain as much of the solution as possible.

10. Repeat Step 9 with the contents of the beaker in Step 8.

11. Using the pH meter, measure and record the pH of the two individual supernatant solutions.

12. Add 1 ml of 1.0 M HCl to each beaker; allow solution to react for 10 minutes; record any observations.

13. Carefully transfer enough of each supernatant solution to a separate cuvette to fill it to just below the mark. Label the cuvettes.

Preparation of a Solution for the Calibration Plot

Moving Along!

14. Your TA will assign you the preparation of one of the standard solutions in Table 1 (end of the experiment).

15. Using an analytical balance, measure and record a mass as close as possible to the mass of $FeCl_3$ given in Table 1 for your standard solution. You are using $FeCl_3 \cdot 6\ H_2O$.

16. Use a beaker to obtain the HCl solution. Record its concentration.

17. Carefully transfer the $FeCl_3$ to the 10.00 mL volumetric flask. Add approximately 7-8 mL of the HCl solution and swirl the flask well until the $FeCl_3$ completely dissolves. Dilute to the mark (the line) with HCl. Cap the flask and mix the contents thoroughly.

Almost there!

18. Transfer enough solution from Step 17 to a clean cuvette to fill it just below the mark. Label the cuvette.

Finishing the Experiment

19. Insert your cuvette into the spectrophotometer and wait 30 seconds. Record the % Transmittance to 1 digit after the decimal. Give this value to your TA.

20. Repeat Step 19 for your two supernatant solutions in the other two cuvettes.

21. Obtain the % Transmittance values for the other standard solutions from your TA.

Cleaning Up!

22. Rinse and dry all glassware and return it to its proper place. All solutions may be rinsed down the drain, flushing with plenty of water.

23. Remember to get your raw data, written in PEN, signed by your TA and to attach this raw data to your report in order to receive a grade!

Calculations

1. Calculate the concentration of the hydroxide ion $[OH^-]$ using your pH and the fact that pH = - log $[OH^-]$.

2. Calculate the values of Absorbance, A, for each of the % Transmittance, %T, values of the standard solutions and your

two supernatant solutions using the fact that T = %T/100 and Equation [5].

3. Plot a graph of A as a function of [Fe^{3+}] for the standards.

4. Add the values of A for your two supernatant solutions to the plot.

5. Using the graph, determine the concentration of Fe^{3+} (aq) in your two supernatant solutions.

6. Use Equation [2] to calculate the K_{sp} of $Fe(OH)_3$. Remember:

$$Fe(OH)_3\ (s) \rightleftharpoons Fe^{3+}\ (aq) + 3\ OH^-\ (aq)$$

7. Calculate the percent error between the average experimental value of K_{sp} and the literature value of K_{sp} for $Fe(OH)_3$.

Points to Ponder

- Are your values for K_{sp} reasonable? Can you obtain literature values for these quantities?

- What factors in the lab can affect the value of K_{sp} that you obtain in the lab? Could you improve your result? If so, how?

- What are the sources of error inherent in the experiment? How does each source of error contribute to the result (ie. does it increase or decrease the value of the enthalpy?)

Lab Report

- *Refer to page iii in the FYI section and the lab report section in experiment 1.*

- All graphs should have titles, axes that are labelled, and clearly indicated scales and units. The graph should occupy as much of the page as possible and ***MUST BE ON MILLIMETRE X MILLIMETRE GRAPH PAPER!***

- Complete all the calculations, as outlined in the procedural section, and **don't forget to state all results with the correct number of significant figures!!**

Table 1. Masses of $FeCl_3$ (s) required for Different Standard Solutions

Concentration of $FeCl_3$ Solution (mol/L)	Mass of $FeCl_3$ salt required (g)
0.010	0.0271
0.015	0.0407
0.020	0.0542
0.025	0.0678
0.030	0.0813
0.035	0.0949
0.040	0.1084
0.045	0.1220
0.050	0.1355