Law of Multiple Proportions

Objectives: To determine the chloride content of two different compounds by volumetric analysis; to use the data collected to demonstrate the Law of Multiple Proportions.

Materials: Buret, buret clamp, analytical balance, 250-mL Erlenmeyer flask, standardized solution of approx. 0.05 M silver nitrate ($AgNO_3$); difluorescein indicator solution, samples of two iron compounds.

Safety: Wear safety goggles at all times in the laboratory. Note: Contact with the silver nitrate solution will cause black spots to occur on the skin within several hours. Take appropriate care when handling all solutions.

Waste Disposal: All solutions and solids containing silver should be collected as directed by your instructor.

INTRODUCTION

One of the postulates of Dalton's Atomic Theory is that atoms of different elements combine to form compounds in simple, whole number ratios (Law of Definite Proportion). An extension of this is the **Law of Multiple Proportions,** which states that if two elements form <u>more than one</u> compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will be ratios of small whole numbers.

As an example, consider two compounds consisting of carbon and oxygen: carbon monoxide (CO) and carbon dioxide (CO_2). Using the atomic masses for these compounds we can calculate the ratio of the mass of oxygen to carbon in each case:

$$\text{CO:}\quad \frac{\text{mass of O}}{\text{mass of C}} = \frac{16\text{ amu}}{12\text{ amu}} = 1.33 \qquad \text{CO}_2:\quad \frac{\text{mass of O}}{\text{mass of C}} = \frac{(16\text{ amu})\times 2}{12\text{ amu}} = 2.66$$

Comparing these mass ratios we see that the oxygen-to-carbon ratio in carbon dioxide is twice as big as the oxygen-to-carbon ratio in carbon monoxide (2.66/1.33 = 2).

In this experiment you will determine the amount of chloride in each of two different compounds containing iron, chloride and water, and use your data to demonstrate the Law of Multiple Proportions.

The method for determining the amount of chloride in each sample involves a **titration** in which the chloride reacts with silver to form silver chloride:

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

A titration is an example of a **volumetric** analysis because it requires the addition of carefully measured *volumes* of a reagent for complete reaction. In this experiment, the $AgNO_3$ solution is known as the **titrant** and is delivered to the reaction solution using a buret. The chloride in the unknown iron compounds is known as the **analyte**, or the substance to be determined by the analysis. The point at which the reaction between analyte and titrant is complete is called the **equivalence point**. Since it is not always obvious when a reaction is complete, an **indicator** is usually added to the reaction mixture. An indicator is a substance that undergoes a physical change (typically a color change) at or near the equivalence point in the titration. The point at which the color change occurs is called the **end point** of the titration.

To determine the amount of analyte in the unknown sample we must know three things:

1. The balanced chemical reaction between the analyte and the titrant.
2. The volume of titrant needed to reach the end point of the titration.
3. The *concentration* of the titrant, or the amount of titrant in a given volume of solution. The unit of concentration used in this case is **molarity (M)**, or moles of titrant per liter of solution (mol/L). A **mole** is the amount of a substance that has a mass in grams equal to the molecular weight of the substance in **atomic mass units**. For example,

$$\text{one molecule of CO: one C atom}\left(12\ \frac{\text{amu}}{\text{atom}}\right) + \text{one O atom}\left(16\ \frac{\text{amu}}{\text{atom}}\right) = 28\ \frac{\text{amu}}{\text{molecule}}$$

$$\text{one mole of CO: one mole of C atoms}\left(12\ \frac{\text{grams}}{\text{mole}}\right) + \text{one mole of O atoms}\left(16\ \frac{\text{grams}}{\text{mole}}\right) = 28\ \frac{\text{grams}}{\text{mole}}$$

Consider a typical analysis which required 23.48 mL of 0.0486 M $AgNO_3$ to reach the end point. The information necessary as indicated above is now:

1. The balanced chemical reaction indicates that one unit of Ag^{+} reacts with one unit of Cl^{-}, or $\left(\frac{1\text{ mole Cl}^{-}}{1\text{ mole Ag}^{+}}\right)$
2. The volume of titrant = 23.48 mL, or 0.02348 L $AgNO_3$
3. The concentration of titrant = 0.0486 M (moles $AgNO_3$/L)

The mass of chloride in the unknown sample can now be calculated using this information:

$$\left(0.02348\ \cancel{\text{liters AgNO}_3}\right)\left(\frac{0.0486\ \cancel{\text{mole Ag}^{+}}}{\cancel{\text{liter AgNO}_3}}\right)\left(\frac{1\ \cancel{\text{mole Cl}^{-}}}{1\ \cancel{\text{mole Ag}^{+}}}\right)\left(\frac{35.45\text{ grams Cl}^{-}}{\cancel{\text{mole Cl}^{-}}}\right) = 0.0405\text{ grams Cl}^{-}$$

Note that units cancel to yield the final answer in grams of Cl^{-}.

Pre-Lab Questions

1. Define the following terms:

   - Law of Multiple Proportions:

   - Titration:

   - Titrant:

   - Analyte:

2. What is the difference between the equivalence point and the end point in a titration?

3. To which set of compounds below would the Law of Multiple Proportions apply? Explain.

   (a) FeO and Fe_2O_3

   (b) CO_2 and NO_2

   (c) NO and NO_2

4. Identify the titrant and the analyte in the titration performed in this lab exercise.

PROCEDURE

1. Obtain about 200 mL of the standardized silver nitrate titrant solution to use during this experiment. Record the exact concentration of the titrant solution on your Data Sheet.

2. Prepare the titration assembly (buret, buret clamp, ring stand) as illustrated in Figure 1. Pour about 5 mL of titrant into the buret and rotate it so that the solution evenly coats the walls of the buret. Drain the extra solution from the buret through the stopcock. Repeat this procedure to ensure that the buret contains only silver nitrate solution at the given concentration.

3. Fill the buret to near the 0.00 mL mark. Record the initial volume of titrant in the buret to the nearest 0.01 mL on your data sheet. *Note:* It is not necessary that you start *exactly* at 0.00 mL, but it is essential that you record the exact initial volume. Remember to read the volume in the buret at the bottom of the meniscus when at eye level, as indicated in the expanded view of the buret in the upper left portion of Figure 1.

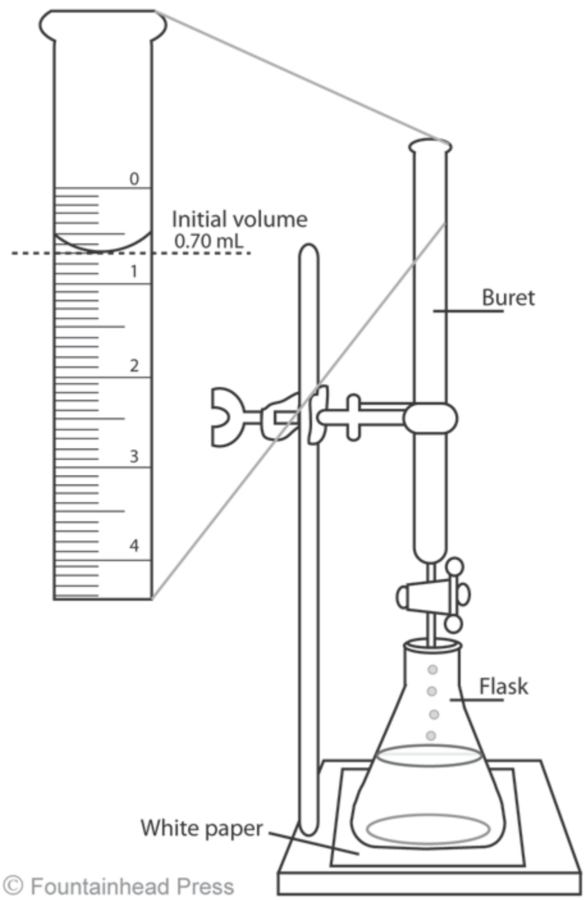

Figure 1. Titration set-up.

4. Using the analytical balance, weigh about 0.15 g of Unknown A into a 250-mL Erlenmeyer flask. Record the mass of the sample to the nearest 0.0001 g on your Data Sheet.

5. Add about 50 mL of distilled water to the flask and swirl to dissolve the sample. The exact volume of water is not critical, so it does not need to be measured precisely.

6. Add about 5–10 drops of indicator solution to the flask. The solution will be fluorescent yellow-green in color.

7. Slowly add titrant while stirring the solution. The $AgCl(s)$ will immediately precipitate and make the mixture appear cloudy. This is *not* the end point. As you approach the end point

you will observe a slight pink color appearing in solution as you add the titrant. Continue to add titrant slowly while swirling. When the pink color persists in solution after swirling you have reached the end point. Record the final volume of titrant in the buret to the nearest 0.01 mL on your Data Sheet.

8. Repeat the titration (steps 3 through 7) with two more samples of Unknown A.

9. Perform three more titrations with samples of Unknown B.

CALCULATIONS

I. Chloride Content

1. Calculate the total volume delivered in each of the three trials for each unknown as the difference between the final volume and the initial volume in the buret. Record the volume delivered on your Data Sheet.

2. Calculate the moles of Ag^+ delivered in each titration as:

$$\text{moles } Ag^+ = (\text{molarity of } AgNO_3) \times (\text{volume delivered, in L})$$

   Record the moles of Ag^+ delivered in each titration on your Data Sheet. Note that this is also equal to the number of moles of Cl^- in each sample titration.

3. Calculate the mass of Cl^- in each sample as:

$$\text{mass of } Cl^- = (\text{moles } Cl^-) \times \left(\frac{35.45 \text{ grams } Cl^-}{\text{mole } Cl^-} \right)$$

4. Record the mass of Cl^- in each sample on your Data Sheet.

II. Water Content

Since the iron compounds also contain water of hydration (i.e., water molecules that are incorporated in the compound crystal structure) we must correct for the mass of water in each sample before comparing the relative amounts of iron and chloride in each unknown.

5. Unknown A is 36.25% water by mass, and unknown B is 39.99% water by mass. We can calculate the amount of water in each sample as follows:

$$\text{Unknown A:} \quad \text{mass of water} = (\text{mass of sample}) \times 0.3625$$

$$\text{Unknown B:} \quad \text{mass of water} = (\text{mass of sample}) \times 0.3999$$

Calculate the mass of water in each sample and record this mass on your Data Sheet.

6. The unknown compounds contain only iron, chloride, and water. In other words,

mass of sample = mass of iron + mass of chloride + mass of water

We can rearrange this equation to find the mass of iron in each sample as:

mass of iron = mass of sample - (mass of chloride + mass of water)

Calculate the mass of iron in each sample and record this mass on your Data Sheet.

III. Composition

7. Calculate the mass of Cl per gram of iron in each sample and record this ratio on your Data Sheet.

8. Average the three ratios obtained for Unknowns A and B and record them on your Data Dheet.

10. Divide the ratio for Unknown B by the ratio for Unknown A and record it on your Data Sheet. What small whole number ratio does this represent?

Law of Multiple Proportions Data Sheet

Molarity of $AgNO_3$ = ________________ M

Unknown A	**Trial 1**	**Trial 2**	**Trial 3**
Weight of sample (g)	______________	______________	______________
Initial volume (mL)	______________	______________	______________
Final volume (mL)	______________	______________	______________
Volume delivered (mL)	______________	______________	______________
Moles Ag^+ = moles Cl^-	______________	______________	______________
Mass of Cl^- (g)	______________	______________	______________
Mass of water (g)	______________	______________	______________
Mass of iron (g)	______________	______________	______________
Grams Cl^-/grams iron	______________	______________	______________

Average $\left(\frac{\text{grams Cl}^-}{\text{grams iron}}\right)$ for Unknown A : ______________________

Unknown B	**Trial 1**	**Trial 2**	**Trial 3**
Weight of sample (g)	______________	______________	______________
Initial volume (mL)	______________	______________	______________
Final volume (mL)	______________	______________	______________
Volume delivered (mL)	______________	______________	______________
Moles Ag^{+} = moles Cl^{-}	______________	______________	______________
Mass of Cl^{-} (g)	______________	______________	______________
Mass of water (g)	______________	______________	______________
Mass of iron (g)	______________	______________	______________
Grams Cl^{-}/grams iron	______________	______________	______________

$$\text{Average}\left(\frac{\text{grams Cl}^{-}}{\text{grams iron}}\right) \text{ for Unknown B : } \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_$$

Results: $\dfrac{\text{Average for Unknown A}}{\text{Average for Unknown B}} = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_$

Small whole number ratio represented by result above = _________:__________

Post-Lab Questions

1. The mass of chloride per gram of iron calculated for the three samples of Unknown A should be in good agreement. Explain this result with regard to the Law of Constant Composition.

2. How does the calculation for the mass of iron in each sample represent the Law of Conservation of Mass? (See step 6 in the Calculations.)

3. If the molarity of silver nitrate used in the titration was lower than the recorded value, would the calculated mass of chloride be greater or less than the true value? (See steps 2 and 3 in the Calculations.)

4. Calculate the grams of oxygen per gram of nitrogen dioxide and nitrogen trioxide and use this data to illustrate the Law of Multiple Proportions.

5. In steps 5 and 6 of the calculations you were given the percent water in the unknown compounds to correct for the amount of water in each sample. Describe a simple procedure that might allow you to determine the percent water in an unknown compound.