

Stoichiometry in the Lab: Titrations and Gravimetric Analysis!

Titration

- Goal: to determine the unknown concentration!
- A substance in a solution of unknown concentration is reacted with another substance in a solution of known concentration
- Vocab
 - **Titrant** – solution of known concentration (usually in a buret)
 - **Analyte** – solution of unknown concentration (usually in flask or beaker)

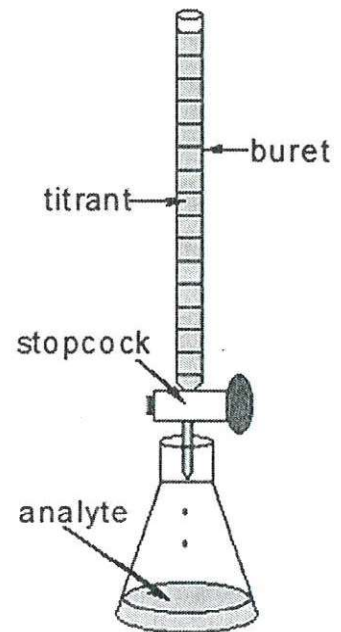
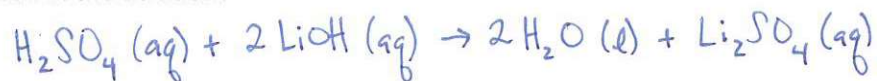


Figure 1: Titration Setup

- **Equivalence point** – acid and base have completely neutralized each other
 - Moles H⁺ = Moles OH⁻
- **End point** - indicator changes color

↳ if you chose the right indicator, this should be the same as eq. pt!

Example: By titration, 0.13 M aqueous sulfuric acid, H₂SO₄, neutralized 27.4 mL of 0.17 M LiOH solution. What was the volume of the acid solution used in the titration?



$$27.4 \text{ mL} \times 0.17 \text{ M} = 4.658 \text{ mmol LiOH} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol LiOH}} = 2.329 \text{ mmol H}_2\text{SO}_4$$

$$M = \frac{\text{mol}}{\text{L}} = \frac{\text{mmol}}{\text{mL}} \Rightarrow \# \text{ mL} = \frac{2.329 \text{ mmol}}{0.13 \text{ M}} = \boxed{18 \text{ mL H}_2\text{SO}_4}$$

or: moles of analyte + titrant are stoichiometrically equal

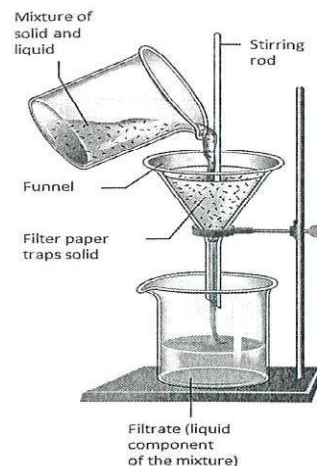
Gravimetric Analysis: a laboratory procedure in which an ion is precipitated out of a mixture in order to find the percent mass of that ion in an impure substance.

Method:

1. Reactant impure material with a known compound, to form a precipitate containing the ion of interest.
2. Filter and dry precipitate, then measure its mass.
3. Use stoichiometry calculations to determine the mass of the ion of interest, using the balanced reaction to work backwards from the mass of the precipitate measured in the lab.

Steps in Gravimetric Analysis (Lab Technique)

1. Dry and weigh impure sample.
2. Dissolve sample. (in H_2O)
3. Add precipitating reagent in excess.
4. Filter precipitate from solution.
5. Wash precipitate to remove impurities. \Rightarrow rinse with DI water ^{soluble}
6. Dry and weigh to constant mass (± 0.03 g)



Steps in Gravimetric Analysis (Math-y Math)

1. Write the balanced precipitation reaction.
2. Use stoichiometry to convert from the mass of your precipitate to the mass of the ion of interest.

3. Calculate % by mass: $\% \text{ mass of ion} = \frac{\text{mass of ion (calculated in step 2)}}{\text{mass of original sample}} \times 100$

Example: The following data were obtained when a sample of unknown alkali metal chloride was analyzed:

Mass of watch glass	8.2030 g
Mass of unknown chloride sample + watch glass	8.3014 g
Mass of $AgCl(s)$ + watch glass (after drying)	8.3922 g

- a. Calculate the mass of the precipitate.

$$8.3922 - 8.2030 = \boxed{0.1892 \text{ g } AgCl}$$

- b. Calculate the mass of chloride ions, Cl^- , in the original sample.

$$0.1892 \text{ g } AgCl \times \frac{1 \text{ mol } AgCl}{143.32 \text{ g } AgCl} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol } AgCl} \times \frac{35.45 \text{ g } Cl^-}{1 \text{ mol } Cl^-} = \boxed{0.04680 \text{ g } Cl^-}$$

- c. Calculate the percent mass of chloride ions, Cl^- , in the sample.

$$\text{Sample mass} = 8.3014 - 8.2030 = 0.0984 \text{ g} \quad \left. \vphantom{\text{Sample mass}} \right\} \% Cl^- = \frac{0.04680 \text{ g}}{0.0984 \text{ g}} \times 100 = \boxed{47.6\% Cl^-}$$

- d. Which of the following compounds is most likely to be the identity of your unknown alkali metal chloride: $LiCl$, $NaCl$, KCl , or $RbCl$? Justify with math.

$$\frac{35.45}{42.39} = 83.6\% Cl^-$$

$$\frac{35.45}{74.55} = 47.6\% Cl^-$$

$$\frac{35.45}{58.44} = 60.7\% Cl^-$$

$$\frac{35.45}{120.92} = 29.3\%$$

\Rightarrow Sample must be KCl, b/c same % Cl^- by mass

Common Lab Errors in Gravimetric Analysis

Error	Effect on Calculated % by Mass of Ion
Failure to add precipitating reagent in excess.	<ul style="list-style-type: none"> • Not all of the ion of interest will precipitate, thus some of the ion will be lost in the filtrate. • The calculated ion % will be <u>lower</u> than the actual ion % by mass.
Failure to wash the precipitate to remove soluble impurities.	<ul style="list-style-type: none"> • Some impurities will be left in the precipitate, so measured mass includes both the precipitate and these contaminants. • The calculated ion % will be <u>higher</u> than the actual ion % by mass.
The precipitate is excessively washed or washed with warm water.	<ul style="list-style-type: none"> • Although the precipitate is "insoluble", small amounts of precipitate will dissolve into the wash water and be carried into the filtrate. • The calculated ion % will be <u>lower</u> than the actual ion % by mass.
The precipitate is not dried to "constant mass".	<ul style="list-style-type: none"> • Not all of the water molecules will have been removed, so measured mass includes both the precipitate and remaining water molecules. • The calculated ion % will be <u>higher</u> than the actual ion % by mass.

Let's practice!

1. A 3.187 g impure sample containing sulfur and soluble inert material needed to be analyzed for sulfur content. As part of the procedure, the entire impure sample is dissolved in 350. mL of water, and the sulfur is converted to sulfate ion, SO_4^{2-} . Barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is added, which causes the sulfate to precipitate out as BaSO_4 . After being rinsed with distilled water and collected, the dried BaSO_4 has a mass of 2.005 g.

→ does not react ⇒ NOT in rxn!

- a. What mass of sulfur was in the original sample?

$$2.005 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.39 \text{ g BaSO}_4} \times \frac{1 \text{ mol S}}{1 \text{ mol BaSO}_4} \times \frac{32.06 \text{ g S}}{1 \text{ mol S}} = \boxed{0.2754 \text{ g S}}$$

- b. What is the percent of sulfur in the original ore?

$$\% \text{ S} = \frac{0.2754 \text{ g}}{3.187 \text{ g Sample}} \times 100 = \boxed{8.641\% \text{ S}}$$

- c. If a small amount of the BaSO_4 precipitate dissolved while being rinsed, what effect would this have on the calculated percent by mass of sulfur? Explain.

If some precipitate dissolved into the filtrate, it wouldn't be measured in the precipitate mass, so the calculated % by mass of S would be too low.

- d. If the original impure sample was instead dissolved into 500. mL of water, what effect would this have on the calculated percent by mass of sulfur? How do you know?

Adding extra water will have no effect on the amount of sulfur present, so this would not affect the calculated % by mass of S.



2. During a titration, 920. mL of a $\text{Sr}(\text{OH})_2$ solution is needed to neutralize 0.35 kg of HClO_4 . What is the molarity of the initial strontium hydroxide solution?

$$0.35 \text{ kg HClO}_4 \times \frac{1,000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol HClO}_4}{100.458 \text{ g HClO}_4} \times \frac{1 \text{ mol Sr}(\text{OH})_2}{2 \text{ mol HClO}_4} = 1.742 \text{ mol Sr}(\text{OH})_2$$

$$M = \frac{1.742 \text{ mol}}{0.920 \text{ L}} = \boxed{1.9 \text{ M Sr}(\text{OH})_2}$$

3. Suppose that 0.323 g of an unknown salt containing sulfate, SO_4^{2-} , is dissolved in 50 mL of water. The solution is acidified with 6 M HCl, heated, and an excess of aqueous BaCl_2 is slowly added to the mixture resulting in the formation of a white precipitate, BaSO_4 .

- a. Assuming that 0.433 g of precipitate is recovered, calculate the percent by mass of SO_4^{2-} in the unknown salt.

$$0.433 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.39 \text{ g BaSO}_4} \times \frac{1 \text{ mol SO}_4^{2-}}{1 \text{ mol BaSO}_4} \times \frac{96.06 \text{ g SO}_4^{2-}}{1 \text{ mol SO}_4^{2-}} = 0.17822 \text{ g SO}_4^{2-}$$

$$\% \text{SO}_4^{2-} = \frac{0.17822 \text{ g SO}_4^{2-}}{0.323 \text{ g Sample}} \times 100 = \boxed{55.2\%}$$

- b. If it is assumed that the salt is an alkali sulfate determine the identity of the alkali cation.

Potentials: Li_2SO_4 , Na_2SO_4 , $\boxed{\text{K}_2\text{SO}_4}$, Rb_2SO_4 (etc)

$$\frac{96.06}{109.94} = 87.4\% \quad \left. \begin{array}{l} \frac{96.06}{142.04} = 67.6\% \\ \frac{96.06}{174.26} = 55.1\% \end{array} \right\} \Rightarrow \text{must be } \text{K}_2\text{SO}_4 \quad \frac{96.06}{267} = 36.0\%$$

4. A 0.4500 g sample of impure potassium chloride, KCl, was dissolved in water and treated with an excess of silver nitrate, AgNO_3 . A 0.8402 g precipitate of AgCl was massed after reacting, collecting, washing and drying the precipitate. Calculate the percentage KCl in the original sample.

$$0.8402 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol AgCl}} \times \frac{1 \text{ mol KCl}}{1 \text{ mol Cl}^-} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = 0.437042 \text{ g KCl}$$

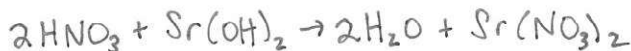
$$\% \text{KCl} = \frac{0.437042 \text{ g}}{0.4500 \text{ g}} = \boxed{97.12\%}$$

Multiple Choice Practice:

1. A sample of an unknown chloride compound was dissolved in water, and then titrated with excess $\text{Pb}(\text{NO}_3)_2$ to create a precipitate. After drying, it is determined there are 0.0050 mol of precipitate present. What mass of chloride is present in the original sample?

- a. 0.177 g **(b.)** 0.355 g c. 0.522 g d. 0.710 g

$$0.0050 \text{ mol PbCl}_2 \times \frac{2 \text{ Cl}^-}{1 \text{ PbCl}_2} \times \frac{35.45 \text{ g Cl}^-}{1 \text{ mol Cl}^-} = 0.3545 \text{ g}$$



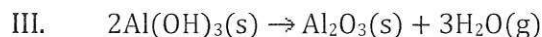
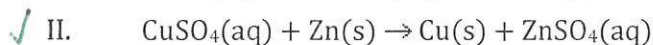
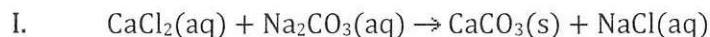
2. 0.60 M HNO_3 was used to neutralize 15 mL of 0.30 M $\text{Sr}(\text{OH})_2$. What volume of HNO_3 was needed?

- a. 7.5 mL **(b.)** 15.0 mL c. 22.5 mL d. 30.0 mL

$$15 \text{ mL} \times 0.30 \text{ M} = 4.5 \text{ mmol Sr}(\text{OH})_2 \times \frac{2 \text{ HNO}_3}{1 \text{ Sr}(\text{OH})_2} = 9.0 \text{ mmol HNO}_3$$

$$\left. \begin{array}{l} \\ \\ \\ \\ \\ \end{array} \right\} \frac{9.0 \text{ mmol}}{0.6 \text{ M}} = 15 \text{ mL}$$

3. Which of the chemical reactions described below is/are an example of a redox reaction(s)?



- a. I only **(b.)** II only c. II and III only d. I and III only

4. A student mixed equimolar amounts of $\text{Cu}(\text{NO}_3)_3(\text{aq})$ and $\text{LiOH}(\text{aq})$, and a blue precipitate formed. Which reaction below shows the correct net ionic equation for this reaction?

