## Chapter 4 - Aqueous Reactions and Solution Stoichiometry

## Section 5 - Solution Stoichiometry

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## Introduction

- In solution stoichiometry we presume that soluble ionic compounds dissociate completely in solution.
- Using balanced chemical equations, we can calculate the concentration of an unknown solution.
- There are two common types of stoichiometric calculations we will do in this section.
- Gravimetric Analysis: A quantitative analysis in which the amount of a substance is determined by converting the species to a product that can be isolated completely and weighed. This is generally used for precipitation reactions where a solid product is formed.
- Volumetric Analysis: A type of quantitative analysis based on titration of solutions.


## Gravimetric Analysis

In gravimetric analysis precipitation reactions are carried out.
After the reaction, the product is precipitated and collected in a crucible or filter paper.

The precipitate is weighed and then using mole ratios we can calculate the concentration of all species in original solution.

The precipitate is filtered. It can

The flask below shows the forming a precipitate.
then be dried and weighed. Then concentration of the desired ions can be calculated


## Volumetric Analysis - Titrations

Titration is an analytical technique used for determining the concentration of an unknown solution A (analyte) by adding a carefully measured volume with a known concentration of B (titrant) until the reaction of A and B is just complete. This can be for precipitation, neutralization or redox reactions.

Standardization is the determination of the exact concentration of a solution.
Equivalence point is when mole ratio of the two reactants is equal.
Endpoint is where the indicator changes colour. An indicator is used to signal the endpoint.


## Solved Problem: Calculating volume in gravimetric analysis

Zinc sulfide reacts with hydrochloric acid to produce hydrogen sulfide gas:

$$
\mathrm{ZnS}_{(\mathrm{s})}+2 \mathrm{HCl}_{(\mathrm{aq})} \rightarrow \mathrm{ZnCl}_{2(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{~S}_{(\mathrm{g})}
$$

How many milliliters of 0.0512 M HCl are required to react with 0.392 g ZnS ?

Make sure equation is balanced. Write the data.

| $\mathrm{ZnS}_{(\mathrm{s})}$ |  |
| :--- | :--- |
| 0.392 g | $+2 \mathrm{HCl}_{\text {(aq) }}$ |
|  | 0.0512 M <br> $\mathrm{ml} ?$ |$\rightarrow \mathrm{ZnCl}_{2(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{~S}_{(\mathrm{g})}$

Molar mass of $\mathrm{ZnS}=97.45 \mathrm{~g}$
Strategy: $\mathrm{g} \mathrm{ZnS} \rightarrow \mathrm{mol} \mathrm{ZnS} \rightarrow$ mol HCl (mol ratio from eq) $\rightarrow$ vol HCl (using Molarity)
$0.392 \mathrm{~g} \mathrm{ZnS} \times \frac{1 \mathrm{~mol} \mathrm{ZnS}}{97.45 \mathrm{~g} \mathrm{ZnS}} \times \frac{2 \mathrm{~mol} \mathrm{HCl}}{1 \mathrm{~mol} \mathrm{ZnS}} \times \frac{1 \mathrm{~L} \text { solution }}{0.0512 \mathrm{~mol} \mathrm{HCl}}=0.157 \mathrm{~L}=157 \mathrm{~mL} \mathrm{HCl}$ solution

## Solved Problem: Calculating mass in gravimetric titration

A dilute solution of hydrogen peroxide is sold in drugstores as a mild antiseptic. A typical solution was analyzed for the percentage of hydrogen peroxide by titrating it with potassium permanganate:
$5 \mathrm{H}_{2} \mathrm{O}_{2(\mathrm{aq})}+2 \mathrm{KMnO}_{4(\mathrm{aq)}}+6 \mathrm{H}^{+}{ }_{\text {(aq) }} \rightarrow 8 \mathrm{H}_{2} \mathrm{O}_{\text {(1) }}+5 \mathrm{O}_{2(\mathrm{~g})}+2 \mathrm{~K}^{+}{ }_{\text {(aq) }}+2 \mathrm{Mn}^{2+}{ }_{\text {(aq) }}$
What is the mass of $\mathrm{H}_{2} \underline{\mathrm{O}}_{2}$ in a solution if 57.5 g of solution required 38.9 mL of 0.534 $M \mathrm{KMnO}_{4}$ for its titration? Bonus: Calculate the mass percent of the solution.

Write the data.
$5 \mathrm{H}_{2} \mathrm{O}_{2(\mathrm{aq})}+2 \mathrm{KMnO}_{4(\mathrm{aq})}+6 \mathrm{H}^{+}{ }_{(\mathrm{aq})} \rightarrow 8 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+5 \mathrm{O}_{2(\mathrm{~g})}+2 \mathrm{~K}^{+}{ }_{(\mathrm{aq})}+2 \mathrm{Mn}^{2+}{ }_{\text {(aq) }}$
? g $\quad 38.9 \mathrm{~mL}$ of 0.534 M
Molar mass of $\mathrm{H}_{2} \mathrm{O}_{2}=34.01 \mathrm{~g}$

$$
\text { Strategy: mols } \mathrm{KMnO}_{4} \rightarrow \text { mols } \mathrm{H}_{2} \mathrm{O}_{2} \rightarrow \text { mass } \mathrm{H}_{2} \mathrm{O}_{2} \rightarrow \%_{2} \mathrm{H}_{2}
$$


$38.9 \times 10^{-3} \mathrm{~L} \times \frac{0.534 \mathrm{~mol} \mathrm{KMnO}_{4}}{1 \mathrm{~L}} \times \frac{5 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}_{2}}{2 \mathrm{~mol} \mathrm{KMnO}_{4}} \times \frac{34.01 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}_{2}}{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}_{2}}=1.77 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}_{2}$

$$
\text { Mass percent } \frac{1.77 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}_{2}}{57.5 \mathrm{~g} \mathrm{solution}} \times 100 \%=3.07 \mathrm{H}_{2} \mathrm{O}_{2}
$$

## Acid Base Titration

Acid base titrations are common in the lab to standardize solutions (meaning to confirm the concentration) or to find the concentration of an unknown acid or base.

- The unknown can be in the burette or in the flask.
- An indicator is added to the flask to know the end point, i.e. when the indicator changes color. (Equivalence point is when mols of acid are equal to mols of base)
- Standardization is done by using a chemical that has absolute weight and which does not absorb or release water.
- The formula for calculating molarity or volume in titrations where all chemicals are in solutions is given below. " $a$ " is for acid and " $b$ " is for base, " $n$ " is for the coefficient for the acid/base. You can see it is very similar to the dilution equation.

$$
\frac{M_{a} V_{a}}{n_{a}}=\frac{M_{b} V_{b}}{n_{b}}
$$

- Note: You can use this formula for any stoichiometric analysis provided all chemicals are in solution.


## Solved Problem: Calculating molarity in acid base titration

A student measured exactly 17.0 mL of an unknown monoprotic acidic solution and placed in an Erlenmeyer flask. An indicator was added to the flask. At the end of the titration the student had used 37.2 mL of a 0.110 M NaOH to neutralize the acid. Calculate the molarity of the acid.

## Strategy:

1) Write the equation first and balance it to find " $n$ " numbers. Write the data.

| NaOH | $+\mathrm{H}^{+}$ |
| :--- | :--- |
| 37.2 mL | 17 mL |
| 0.110 M | $? \mathrm{M}$ |

Mol ratio of acid to base is $1: 1$

1) Then you can use the formula to solve this problem since both acid and base are in solutions.
2) You can convert volumes to $L$ (in some cases you can work with mL also)

$$
\frac{M_{a} V_{a}}{n_{a}}=\frac{M_{b} V_{b}}{n_{b}} \quad \frac{M_{a} \times 0.017 L}{1}=\frac{0.110 M \times 0.0372 L}{1}
$$

$$
M a=\frac{0.110 \mathrm{M} \mathrm{x} 0.0372 \mathrm{~L} \mathrm{x} 1 \mathrm{~mol}}{1 \mathrm{molx} 0.017 \mathrm{~L}}=0.240705 M=0.241 \mathrm{M}
$$

## Solved Problem: Calculating molarity in acid base titration

Calculate the molarity of 25.0 mL of potassium hydroxide if it took 45.52 mL of 0.25 $M$ sulfuric acid to neutralize the base.

## Strategy:

1) Write the equation first and balance it to find " n " numbers. Write the data.

| 2 KOH |  |
| :--- | :--- |
| 20 mL |  |
| $? \mathbf{~ M}$ | $+\underset{2}{\mathrm{H}_{2} \mathrm{SO}_{4}} \rightarrow \mathrm{~K}_{2} \mathrm{SO}_{4}+2 \mathrm{H}_{2} \mathrm{O}$ |
|  | 0.25 mL |
|  |  |

1) Then you can use the formula to solve this problem since both acid and base are in solutions.
2) Make sure you convert volumes to L (in some cases you can work with mL also)


$$
M_{b}=\frac{0.25 \mathrm{M} \mathrm{x} 45.52 \mathrm{~L} \mathrm{x} 2 \mathrm{~mol}}{1 \mathrm{~mol} \mathrm{x} 25.0 \mathrm{~mL}}=0.9104 \mathrm{M}=0.910 \mathrm{M}
$$

## Solved Problem: Calculating molarity in acid base titration using solids

Calculate the molarity of 55.0 mL of sodium hydroxide if when 3.33 g of KHP is used to standardize the solution. KHP is a monoprotic acid (MW of KHP $=204.23 \mathrm{~g} / \mathrm{mol}$ )

## Strategy:

1) Mol ratio is given to be $1: 1$ so $\mathbf{n}$ is 1 for both acid and base. Write the data.

| NaOH | $+\mathrm{H}^{+}$ |  |
| :--- | :--- | :--- |
| 55.0 mL | 3.33 g |  |
| ?M |  |  |
|  |  |  |

1) Use gravimetric method to solve this problem as there is a solid here.
2) Make sure you convert volumes to L (here you need to find molarity, so it is important to have L)

Convert g KHP -> mol KHP -> mol ratio to NaOH -> divide by L of NaOH

$$
3.33 \mathrm{~g} \mathrm{KHP} \times \frac{1 \mathrm{~mol} \mathrm{KHP}}{204.23 \mathrm{~g} \mathrm{KHP}} \times \frac{1 \mathrm{~mol} \mathrm{KOH}}{\mathrm{i} \mathrm{~mol} \mathrm{KHP}} \times \frac{1}{0.055 \mathrm{~L}}=0.29645=0.296 \mathrm{M}
$$

## Redox Titration

- Redox titrations are used just like acid base titrations, i.e., find the concentration of an unknown solution.
- The unknown can be in the burette or in the flask.
- An indicator may or may not be used as some of these titrations are monitored by color changes also.
- The formula for calculating molarity or volume in titrations where all chemicals are in solutions is given below. It is the same as in acid base titration. Use the "a" and "b" for the chemicals you are working with in the equation. " n " is still the coefficient for balancing the equation. It is important to make sure you keep your numbers and chemicals together in the equation.

$$
\frac{M_{a} V_{a}}{n_{a}}=\frac{M_{b} V_{b}}{n_{b}}
$$

## Solved Problem: Calculating molarity in a redox titration

How many millilitres of a $0.1050 \mathrm{M} \mathrm{KMnO}_{4}$ are required to titerate 30.00 ml of $0.3252 \mathrm{M} \mathrm{Fe}^{2+}$ aqueous solution?

$$
5 \mathrm{Fe}^{2+}+\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+} \rightarrow 5 \mathrm{Fe}^{2+}+\mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}
$$

## Strategy:

1) Use the balance equation to get the coefficients and write the data.

$$
\begin{aligned}
& 5 \mathrm{Fe}^{2+} \\
& 30 \mathrm{~mL} \\
& 30 \\
& 0.3252 \mathrm{M} \\
& 0.0 .01050 \mathrm{MnO} \\
& \hline \mathrm{ML}
\end{aligned}
$$

1) Then you can use the formula given for acid base titration for this calculation since all values are given in molarity and volume.
2) Make sure you convert volumes to L (in some cases you can work with mL also)

$$
\begin{gathered}
\frac{M_{1} V_{1}}{n_{1}}=\frac{M_{2} V_{2}}{n_{2}} \begin{array}{c}
\text { Set } 1 \\
\frac{0.3252 \mathrm{M} \mathrm{x} 30.00 \mathrm{~mL}}{5 \mathrm{~mol} \mathrm{Fe}^{2+}}=\frac{0.1050 \mathrm{M} \mathrm{x} \mathrm{~V}_{2}}{1 \mathrm{~mol} \mathrm{MnO}_{4}^{-}} \\
\mathrm{V}_{2}=\frac{0.3252 \mathrm{M} \mathrm{x} 30.00 \mathrm{~mL} \times 1 \mathrm{~mol}}{5 \mathrm{~mol} \times 0.0105 \mathrm{M}}=185.828 \mathrm{~mL}=186 \mathrm{~mL}
\end{array}
\end{gathered}
$$

## Solved Problem: Calculating molarity in redox titration using solids

What is the molarity of $\mathrm{KMnO}_{4}$ if 567.4 mg sample of $\mathrm{KNO}_{2}$ required 31.61 mL KMnO 4 for titration. (MW of $\mathrm{KNO}_{2}=85.108 \mathrm{~g} / \mathrm{mol}$ ).

$$
5 \mathrm{NO}_{2}^{-}+2 \mathrm{MnO}_{4}^{-}+6 \mathrm{H}^{+} \rightarrow 5 \mathrm{NO}_{3}^{-}+2 \mathrm{Mn}^{2+}+3 \mathrm{H}_{2} \mathrm{O}
$$

## Strategy:

1) Equation and data:

$$
\begin{aligned}
& 5 \mathrm{NO}_{2}^{-} \\
& 567.4 \mathrm{mg}
\end{aligned}+\quad 2 \mathrm{MnO}_{4}^{-}+6 \mathrm{H}^{+} \rightarrow 5 \mathrm{NO}_{3}^{-}+2 \mathrm{Mn}^{2+}+3 \mathrm{H}_{2} \mathrm{O}
$$

? M

1) This will have to be calculated via dimensional analysis since we are given mg of sample.
2) Make sure you convert volumes to L (here you need to find molarity, so it is important to have L)
Convert $\mathrm{mg} \mathrm{KNO}->\mathrm{g} \mathrm{KNO}_{2}->$ mol $\mathrm{KNO}_{2}->$ mol ratio to $\mathrm{KMnO}_{4}->$ divide by L of $\mathrm{KMnO}_{4}$


$$
=0.08437 \mathrm{M}
$$

## Key Words/Concepts

- Solution stoichiometry
- Volumetric analysis (titration)
- End point
- Equivalence point
- Gravimetric analysis

