## Volumetric Analysis



Nigel Freestone
www.chemtextbook.com

## VOLUMETRIC ANALYSIS

A solution of accurately known concentration is called a standard solution. Standard solutions are used in volumetric (titrimetric) analysis, used to determine the unknown concentration of an identified chemical species (analyte). The volume of one solution that will react with a known volume of a standard solution (titrant) is determined. The point at which the exact amount of titrant added to just react with all the other reagent present is called the end point or equivalence point. Indicators, normally added to the solution of known volume, which change colour, are often used to determine the end point.
Volumetric analysis is widely used to determine the concentration of a broad range variety of parameters including basicity, acidity, total hardness and chloride levels.

Titrations can be categorised based on chemical reactions:
Acid-Base titrations are used to determine the concentration of an acid or base by exactly neutralising the acid or base with an acid or base of known concentration. This permits to quantitative analysis of the concentration of an unknown acid or base solution.

Redox titrations can be used to determine oxidizing or reducing agents in a solution. The reducing or oxidizing agent is used as the titrant against the other agent.

Back Titrations are used where analytes are either partially soluble or too slow to give a reaction. A known amount of excess reagent is used. The remaining excess reagent is then titrated with another second reagent to determine how much of the excess reagent was used in the first titration, allowing the original analyte's concentration to be determined.

Example 1: Chloride concentrations in water can be determined by titration against standardised silver nitrate solutions. A $50 \mathrm{~cm}^{3}$ water sample was titrated against 0.05 M silver nitrate solution, using potassium chromate as the indicator. This indicator changes colour when all the chloride has been precipitated out of solution as silver chloride. This colour change occurred after the addition of $10.9 \mathrm{~cm}^{3}$ of 0.05 M silver nitrate. What is the concentration of chloride ions in the water sample?

Step 1: Write the balanced chemical equation, insert the information given in the question and identify what you are trying to calculate

|  | $\mathrm{Cl}_{\text {-(aq) }}$ | + | $\mathrm{AgNO}_{3(\text { aq })}$ | $\rightarrow$ | $\mathrm{AgCl}_{(\mathrm{s})}+\mathrm{NO}_{3}{ }^{-}(\mathrm{aq})$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Volume $\left(\mathrm{cm}^{3}\right)$ | 50 |  | 10.9 |  |  |
| Moles |  |  | 0.05 |  |  |
| Concentration (M) | $?$ |  | 0.0 |  |  |
| Reaction coefficients | 1 | $:$ | 1 |  |  |

Please note volumetric analysis (titrations) are predominantly concerned with the reaction coefficient (stoichiometric) relationship between the reactants. The products are included in the above table for the sake of completeness.

Step 2: If two pieces of information from volume, number of moles, and concentration are known for a given species, the third can be calculated using:

## Concentration $(M)=$ Number of Moles / Volume of solution (L)

$$
c=n / v
$$

OR

Number of Moles = Concentration (M) x Volume of Solution (L)
$\mathbf{n}=\mathbf{c x} \mathbf{v}$

OR
Volume of Solution (L) = Number of Moles / Concentration (M)

$$
v=n / c
$$

| Volume ( $\mathrm{cm}^{3}$ ) | $\mathrm{Cl}^{-}(\mathrm{aq})$ | + | $\mathrm{AgNO}_{3(\mathrm{aq})}$ | $\longrightarrow$ | $\mathrm{AgCl}_{(\mathrm{s})}$ | $+\mathrm{NO}_{3}^{-}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 50 |  | 10.9 |  |  |  |
|  | (0.05 L) |  |  |  |  |  |
| Moles |  |  | $10.9 \times 0.05 / 1000$ |  |  |  |
|  |  |  | $=5.45 \times 10^{-4}$ |  |  |  |
| Concentration (M) | ? |  | 0.05 |  |  |  |
| Reaction coefficien | 1 | : | 1 |  |  |  |

Step 4: At the end point the amount of each species present is in accordance with the reaction coefficient (stoichiometric) relationship of the balanced chemical equation for the reaction. In this example the number of moles of Cl - in $50 \mathrm{~cm}^{3}=$ the number of moles Ag+ in $10.89 \mathrm{~cm}^{3}$

|  | $\mathrm{Cl}^{-}$(aq) | + | $\mathrm{AgNO}_{3(\text { aq) }}$ | $\rightarrow$ | $\mathrm{AgCl}_{(s)}$ | $+\mathrm{NO}_{3}{ }^{-}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Volume ( $\mathrm{cm}^{3}$ ) | $\begin{gathered} 50 \\ (0.05 \mathrm{~L}) \end{gathered}$ |  | 10.9 |  |  |  |
| Moles | $5.45 \times 10^{-4}$ |  | $10.9 \times 0.05 / 1000$ |  |  |  |
|  |  |  | $=5.45 \times 10^{-4}$ |  |  |  |
| Concentration (M) | ? |  | 0.05 |  |  |  |
| Reaction coefficients | 1 | : | 1 |  |  |  |

Step 4: Since we know both the number of moles of Cl - and its volume, we can calculate its concentration.
$\mathrm{Cl}_{(a q)}^{-}+\mathrm{AgNO}_{3(\mathrm{aq})} \quad \rightarrow \quad \mathrm{AgCl}_{(\mathrm{s})}+\mathrm{NO}_{3^{-(a q)}}^{-}$


Answer: Concentration of Cl- in tap water $=\mathbf{0 . 0 1 0 9} \mathbf{~ M}$

Example 2: A standard solution was prepared by dissolving 2.6061 g of anhydrous sodium carbonate in distilled water and making up to $250 \mathrm{~cm}^{3}$. A $25 \mathrm{~cm}^{3}$ portion of this solution was titrated against hydrochloric acid, using methyl orange as an indicator. This indicator changes colour when all the sodium carbonate has been converted into sodium chloride. $18.7 \mathrm{~cm}^{3}$ of the acid were required for neutralisation. What is the concentration of the acid?

Step 1: Fill in the information given in the question

|  | $\mathrm{Na}_{2} \mathrm{CO}_{3 \text { (aq) }}$ | + | $2 \mathrm{HCl}_{\text {(aq) }}$ | $\rightarrow$ |
| :--- | :---: | :---: | :---: | :---: |
| Volume $\left(\mathrm{cm}^{3}\right)$ | 25 |  | $2 \mathrm{NaCl}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$ |  |
| No. of moles |  |  | $?$ |  |
| Concentration (M) |  | $:$ | 1 |  |

Step 2: You need to know two pieces of information (volume, number of moles or concentration) about one of the species and one piece of information about another to solve volumetric (titrimetric) problems. If this information is not given directly in the question, then it can be calculated from the information provided- in this example the concentration of $\mathrm{Na}_{2} \mathrm{CO}_{3}$.
$\mathrm{Mr}_{\mathrm{r}}\left[\mathrm{Na}_{2} \mathrm{CO}_{3}\right]=106$
Number of moles of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ in $2.6061 \mathrm{~g}=\mathrm{mass} / \mathrm{M}_{\mathrm{r}}=2.6061 / 106=0.0246$
Therefore, the number of moles of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ in $250 \mathrm{~cm}^{3}(0.25 \mathrm{~L})=0.0246$
$25 \mathrm{~cm}^{3}$ of the $\mathrm{Na}_{2} \mathrm{CO}_{3}$ solution contains $0.0246 \times 25 / 250=2.46 \times 10^{-3}$ moles of $\mathrm{Na}_{2} \mathrm{CO}_{3}$
Concentration (ie number if moles in $1000 \mathrm{~cm}^{3}$ ) $=$ number of moles $/$ volume $=0.0246 / 0.25$
$=0.098 \mathrm{M}$

|  | $\mathrm{Na}_{2} \mathrm{CO}_{3}$ | + | $2 \mathrm{HCl}_{\text {(aq) }}$ | $\rightarrow$ |
| :--- | :---: | :---: | :---: | :---: |
| Volume $\left(\mathrm{cm}^{3}\right)$ | 25 |  | $2 \mathrm{NaCl}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$ |  |
| Moles | 0.098 |  |  |  |
| Concentration $(\mathrm{M}$ | $2.46 \times 10^{-3}$ |  | $?$ |  |
| Reaction coefficie | 2 | $:$ | 1 |  |

## Step 3:

At the end point (ie. when the indicator changes colour) there are 2 moles of HCl for every mole of $\mathrm{Na}_{2} \mathrm{CO}_{3}$.

Number of moles of HCl at the end point $=2 \times$ the number of moles of $\mathrm{Na}_{2} \mathrm{CO}_{3}$

$$
\begin{aligned}
& =2 \times 2.46 \times 10^{-3} \\
& =4.92 \times 10^{-3} \mathrm{moles}
\end{aligned}
$$

|  | $\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{aq})}$ | + | $2 \mathrm{HCl}_{(\mathrm{aq})}$ | $\rightarrow 2 \mathrm{NaCl}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$ |
| :--- | :---: | :---: | :---: | :---: |
| Volume $\left(\mathrm{cm}^{3}\right)$ | 25 |  | 18.7 |  |
| Moles | 0.0246 |  | $0.0246 \times 2=$ |  |
|  |  |  | $4.92 \times 10^{-3}$ |  |
| Concentration (M | 0.098 |  |  |  |
| Reaction coefficic | 2 | $:$ | 1 |  |

## Step 4:

Thus, the number of moles of HCl in $18.7 \mathrm{~cm}^{3}=4.92 \times 10^{-3}$ moles
Concentration is defined as the number of moles in 1 L i.e. = number of moles $/$ volume Convert volume from $\mathrm{cm}^{3}$ to $\mathrm{L}, 18.7 \mathrm{~cm}^{3}=18.7 / 1000=0.0187 \mathrm{~L}$
Therefore concentration of $\mathrm{HCl}=$ number of moles/volume $=4.92 \times 10^{-3} / 0.0187=0.263$ M

|  | $\mathrm{Na}_{2} \mathrm{CO}_{3(a q)}$ | + | $2 \mathrm{HCl}_{(\text {aq })}$ | $\rightarrow$ |
| :--- | :---: | :---: | :---: | :---: |
|  | 25 |  | $2 \mathrm{NaCl}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$ |  |
| Volume $\left(\mathrm{cm}^{3}\right)$ | 0.0246 |  | $4.92 \times 10^{-3}$ |  |
| Moles | $2.46 \times 10^{-3}$ |  | 0.263 |  |
| Concentration (M) | 2 | $:$ | 1 |  |

Answer: HCl concentration $\mathbf{= 0 . 2 6 3} \mathbf{~ M}$

Example 3: Magnesium oxide is not very soluble in water, and is difficult to titrate directly. Its purity can be determined by use of a 'back titration' method. 4.06 g of impure magnesium oxide was completely dissolved in $100 \mathrm{~cm}^{3}$ of hydrochloric acid, of concentration 2.0 M (in excess). The excess acid required $19.7 \mathrm{~cm}^{3}$ of sodium hydroxide $(0.20 \mathrm{M})$ for neutralisation. This second titration is called a 'back-titration', and is used to determine the unreacted acid.
a) write equations for the two neutralisation reactions.

## Answer:

$\mathrm{MgO}+2 \mathrm{HCl} \rightarrow \mathrm{MgCl}_{2}+2 \mathrm{HCl}$
$\mathrm{NaOH}+\mathrm{HCl} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$
b) calculate the moles of hydrochloric acid added to the magnesium oxide.

## Answer:

Number of moles of HCl in $100 \mathrm{~cm}^{3}$ of $2 \mathrm{M}=$ volume $\times$ concentration $=100 / 1000 \times 2=0.2$ moles
c) calculate the moles of excess hydrochloric acid titrated.

## Answer:

Number of moles in $19.7 \mathrm{~cm}^{3}(0.019 \mathrm{~L})$ of $0.2 \mathrm{M} \mathrm{HCl}=$ volume $\times$ concentration $=0.0197 \mathrm{x}$ $0.2=0.0197$ moles
(d) calculate the moles of hydrochloric acid reacting with the magnesium oxide.

## Answer:

Number of mole reacting with $\mathrm{MgO}=0.2-0.01986=0.1804$ moles
(e) calculate the moles and mass of magnesium oxide that reacted with the initial hydrochloric acid.

## Answer:

$\mathrm{M}_{\mathrm{r}}[\mathrm{MgO}]=40$
According to the reaction coefficients, 2 moles of HCl react with 1 mole of MgO
Therefore, the number of moles of $\mathrm{MgO}=0.1804=0.0902$
Mass of $\mathrm{MgO}=$ number of moles $\times \mathrm{M}_{\mathrm{r}}=0.0902 \times 40=3.608 \mathrm{~g}$
(f) hence the \% purity of the magnesium oxide.

## Answer:

$\%$ purity $=3.608 / 4.06 \times 100=88.9 \%$

Example 4: A sample of sodium hydrogencarbonate was tested for purity using the following method. 0.400 g of the solid was dissolved in $100.0 \mathrm{~cm}^{3}$ of water and titrated with 0.200 M hydrochloric acid using methyl orange indicator. $23.75 \mathrm{~cm}^{3}$ of acid was required for complete neutralisation. Determine the mass of sodium hydrogen carbonate titrated and hence the purity of the sample.

Answer:

|  | $\mathrm{NaHCO}_{3(\mathrm{aq})}$ | + | $\mathrm{HCl}_{(\text {aq) }}$ | $\rightarrow$ | $\mathrm{NaCl}+\mathrm{CO}_{2}+$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\mathrm{H}_{2} \mathrm{O}$ |
| Volume ( $\mathrm{cm}^{3}$ ) | 100 (0.1L) |  | 23.75 |  |  |
| Moles | $4.75 \times 10^{-3}$ |  | 23.75/1000 $\times 0.2=$ |  |  |
|  |  |  | $4.75 \times 10^{-3}$ |  |  |
| Concentration (M) | $4.76 \times 10^{-3}$ |  | 0.2 |  |  |
|  | /0.1 $=0.0476$ |  |  |  |  |
| Reaction coefficient | 1 | : | 1 |  |  |
| $\mathrm{Mr}_{\mathrm{r}}\left[\mathrm{NaHCO}_{3}\right]=84$ |  |  |  |  |  |
| Number of moles in $23.75 \mathrm{~cm}^{3} 0.2 \mathrm{M} \mathrm{HCl}=$ volume $\times$ concentration |  |  |  |  |  |



Example 5: The redox reaction between permanganate ions and iron(II) ions is:

$$
\mathrm{MnO}_{4}^{-}{ }_{(a q)}+8 \mathrm{H}^{+}{ }_{(\mathrm{aq)}}+5 \mathrm{Fe}^{2+}{ }_{(\mathrm{aq})} \rightarrow \mathrm{Mn}^{2}{ }_{(\mathrm{aq})}+5 \mathrm{Fe}^{3+}{ }_{(\mathrm{aq)}}+4 \mathrm{H}_{2} \mathrm{O}_{(1)}
$$

What volume (in $\mathrm{cm}^{3}$ ) of permanganate solution of concentration 0.04M would react exactly with $30 \mathrm{~cm}^{3}$ of a solution of iron(II) which has a concentration of 0.3 M ?

| Answer: |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Volume ( $\mathrm{cm}^{3}$ ) | $\mathrm{MnO}_{4}{ }^{-}$ | + | $8 \mathrm{H}^{+}$ | $+$ | $5 \mathrm{Fe}^{2+}$ | $\rightarrow$ | $\mathrm{Mn}^{2+}+5 \mathrm{Fe}^{3+}+4 \mathrm{H}_{2} \mathrm{O}$ |
|  | $1.8 \times 10^{-3}$ |  |  |  | 30 |  |  |
|  | $10.4 \times 1000$ |  |  |  |  |  |  |
|  | $=4.5$ |  |  |  |  |  |  |
| Moles | $1 / 5 \times 9 \times 10^{-3}$ |  |  |  | $30 / 1000 \times 0.3$ |  |  |
|  | $=1.8 \times 10^{-3}$ |  |  |  | $=9 \times 10^{-3}$ |  |  |
| Concentration (M) | 0.4 |  |  |  | 0.3 |  |  |
| Reaction Coefficient | 1 |  | 8 | : | 5 |  |  |

Number of moles in $30 \mathrm{~cm}^{3}, 0.3 \mathrm{M} \mathrm{Fe}^{2+}=$ volume $\times$ concentration $=30 / 1000 \times 0.3=9 \times 10^{-}$ 3

According to the reaction coefficients, at the end point number of moles of $\mathrm{MnO}_{4}^{-}=1 / 5$ $x$ number of moles of $\mathrm{Fe}^{2+}$

$$
\begin{aligned}
& =1 / 5 \times 9 \times 10^{-3} \\
& =1.8 \times 10^{-3}
\end{aligned}
$$

Volume of $\mathrm{KMnO}_{4}=$ number of moles $\times$ concentration $=1.8 \times 10^{-3} / 0.4 \times 1000=\mathbf{4 . 5} \mathbf{~ c m}^{\mathbf{3}}$

Example 6: Succinic acid has the formula $\left(\mathrm{CH}_{2}\right)_{n}(\mathrm{COOH})_{2}$ and reacts with dilute sodium hydroxide as follows:

$$
\left(\mathrm{CH}_{2}\right)_{n}(\mathrm{COOH})_{2(a \mathrm{q})}+2 \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow\left(\mathrm{CH}_{2}\right)_{n}(\mathrm{COONa})_{2(\mathrm{aq})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

2.0 g of succinic acid were dissolved in water and the solution made up to $250 \mathrm{~cm}^{3}$. This solution was placed in a burette and $18.4 \mathrm{~cm}^{3}$ was required to neutralise $25 \mathrm{~cm}^{3}$ of 0.1 M NaOH . Deduce the molecular formula of the acid and hence the value of $n$.

Answer:

|  | $\left(\mathrm{CH}_{2}\right)_{\mathrm{n}}(\mathrm{COOH})_{2(a q)}$ | + | $2 \mathrm{NaOH}_{(\mathrm{aq})}$ | $\rightarrow$ | $\begin{gathered} \left(\mathrm{CH}_{2}\right)_{n}(\mathrm{COONa})_{2}+ \\ 2 \mathrm{H}_{2} \mathrm{O} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Volume ( $\mathrm{cm}^{3}$ ) | 18.4 (0.0184 L) |  | 25 |  |  |
| Moles | $0.5 \times 2.5 \times 10^{-3}=1.25$ |  | 25/1000 x |  |  |
|  | $\times 10^{-3}$ |  | $0.1=2.5 \mathrm{x}$ |  |  |
|  |  |  | $10^{-3}$ |  |  |
| Concentration ( M | $1.25 \times 10^{-3} / 0.0184=$ |  | 0.1 |  |  |
|  | 0.68 |  |  |  |  |
| Reaction coefficie | 1 | : | 2 |  |  |

Number of moles of NaOH in $25 \mathrm{~cm}^{3}, 0.1 \mathrm{M} \mathrm{NaOH}=$ volume $\times$ concentration $=25 / 1000 \times$ $0.1=2.5 \times 10^{-3}$
At the end point, the number of moles of $\left(\mathrm{CH}_{2}\right)_{n}(\mathrm{COOH})_{2}$ in $18.4 \mathrm{~cm}^{3}=0.5 \times$ number of moles of NaOH

$$
=0.5 \times 2.5 \times 10^{-3}=1.25 \times 10^{-3}
$$

Number of moles of $\left(\mathrm{CH}_{2}\right)_{n}(\mathrm{COOH})_{2}$ in $250 \mathrm{~cm}^{3}=250 / 18.7 \times 1.25 \times 10^{-3}=0.017$ moles
Thus 0.017 moles of $\left(\mathrm{CH}_{2}\right)_{n}(\mathrm{COOH})_{2}$ has a mass of 2 g
$\mathrm{M}_{\mathrm{r}}\left[\left(\mathrm{CH}_{2}\right)_{\mathrm{n}}(\mathrm{COOH})_{2}\right]=$ mass $/$ number of moles $=2 / 0.017=118$
$\mathrm{Mr}_{\mathrm{r}}\left[\mathrm{CH}_{2}\right]=14$
$\mathrm{Mr}_{\mathrm{r}}\left[(\mathrm{COOH})_{2}\right]=90$
Thus $14 n+90=118$
Rearranging, $14 \mathrm{n}=118-90$ :
n = 28/14 = 2

## $?$ PRACTICE PROBLEMS

1. If it takes $24 \mathrm{~cm}^{3}$ of 0.1 M NaOH to neutralise $20 \mathrm{~cm}^{3}$ of an HCl solution, what is the concentration of the HCl ?
2. If it takes $1 \mathrm{~cm}^{3}$ of $0.05 \mathrm{M} \mathrm{HNO}_{3}$ to neutralise $25 \mathrm{~cm}^{3}$ of NaOH solution, what is the concentration of the NaOH solution?
3. If it takes $50 \mathrm{~cm}^{3}$ of 0.5 M KOH solution to completely neutralise $125 \mathrm{~cm}^{3}$ of sulfuric acid solution $\left(\mathrm{H}_{2} \mathrm{SO}_{4}\right)$, what is the concentration of the $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution?
4. An ammonia solution was reacted with sulfuric acid as shown in the equation below.

$$
2 \mathrm{NH}_{3(a q)}+\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})} \rightarrow\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4(\mathrm{aq})}
$$

Calculate the concentration of the ammonia solution given that it takes $30.8 \mathrm{~cm}^{3}$ of a 1.24 M solution of sulfuric acid to neutralise $25 \mathrm{~cm}^{3}$ of this ammonia solution for complete reaction.
5. A $50.0 \mathrm{~cm}^{3}$ sample of sulfuric acid was diluted to 1.00 L . A sample of the diluted sulfuric acid was analysed by titrating with aqueous sodium hydroxide. In the titration, $25.0 \mathrm{~cm}^{3}$ of 1.00 M aqueous sodium hydroxide required $20.0 \mathrm{~cm}^{3}$ of the diluted sulfuric acid for neutralisation. Calculate the concentration of the original concentrated sulfuric acid solution.

$$
\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq)}}+2 \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{Na}_{2} \mathrm{SO}_{4(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{aq})}
$$

Calculate the concentration of the original concentrated sulfuric acid solution.
6. How many grams of $\mathrm{Ca}(\mathrm{OH})_{2}$ are required to neutralise $52.68 \mathrm{~cm}^{3}$ of a 0.750 M $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution?
7. What volume of 1.0 M sulfuric acid will be needed to neutralise 25.00 cm of 0.8 M sodium hydroxide solution?
8. Calculate the volume of 0.10 M sodium hydroxide solution needed to neutralise $20.00 \mathrm{~cm}^{3}$ of 0.25 M hydrochloric acid.
9. $100 \mathrm{~cm}^{3}$ of a magnesium hydroxide solution required $4.5 \mathrm{~cm}^{3}$ of sulfuric acid (of concentration 0.100 M ) for complete neutralisation. Determine the concentration of the magnesium hydroxide in $\mathrm{gcm}^{-3}$.
10. A solution made from pure barium hydroxide contained 2.74 g in exactly $100 \mathrm{~cm}^{3}$ of water. Using phenolphthalein indicator, titration of $20.0 \mathrm{~cm}^{3}$ of this solution required $18.7 \mathrm{~cm}^{3}$ of a hydrochloric acid solution for complete neutralisation. Calculate the molarity of the HCl .

## Answers are given on the next page.

## ? Volumetric Analysis Answers:

1. If it takes $24 \mathrm{~cm}^{3}$ of 0.1 M NaOH to neutralise $20 \mathrm{~cm}^{3}$ of an HCl solution, what is the concentration of the HCl ?

Answer:

|  | $\mathrm{NaOH}_{(\text {aq) }}$ | + | $\mathrm{HCl}_{\text {(aq) }}$ | $\rightarrow$ | $\mathrm{NaCl}_{(\text {(aq) }}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Volume ( $\mathrm{cm}^{3}$ ) | 24 |  | 20 |  |  |
| No. of moles | $2.4 \times 10^{-3}$ |  | $2.4 \times 10^{-3}$ |  |  |
| Concentration (M) | 0.1 |  | 0.12 |  |  |
| Reaction Coefficients | 1 |  | 1 |  |  |

Number of moles of NaOH in $24 \mathrm{~cm}^{3} 0.1 \mathrm{M}=$ volume $\times$ concentration $=24 / 1000 \times 0.1=2.4 \times 10^{-3}$
At the end point the number of moles of NaOH in $24 \mathrm{~cm}^{3}=$ number of moles of HCl in $20 \mathrm{~cm}^{3}$
Therefore, number of moles of HCl in $20 \mathrm{~cm}^{3}(0.02 \mathrm{~L})=2.4 \times 10^{-3}$
Concentration = number of moles $/$ volume $=2.4 \times 10^{-3} / 0.02=\mathbf{0 . 1 2} \mathbf{~ M}$
2. If it takes $1 \mathrm{~cm}^{3}$ of $0.05 \mathrm{M} \mathrm{HNO}_{3}$ to neutralise $25 \mathrm{~cm}^{3}$ of NaOH solution, what is the concentration of the NaOH solution?

Answer:


Number of moles of $\mathrm{HNO}_{3}$ in $1 \mathrm{~cm}^{3}(0.001 \mathrm{~L}) 0.05 \mathrm{M}=$ volume $\times$ concentration $=0.001 \times 0.05=5 \times 10^{-5}$
At the end point the number of moles of $\mathrm{HNO}_{3}$ in $1 \mathrm{~cm}^{3}=$ number of moles of NaOH in $25 \mathrm{~cm}^{3}$
Therefore, number of moles of NaOH in $25 \mathrm{~cm}^{3}(0.025 \mathrm{~L})=5 \times 10^{-5}$
Concentration = number of moles $/$ volume

$$
=5 \times 10^{-5} / 0.025
$$

$$
=2 \times 10^{-3} \mathrm{M}
$$

3. If it takes $50 \mathrm{~cm}^{3}$ of 0.5 M KOH solution to completely neutralise $125 \mathrm{~cm}^{3}$ of sulfuric acid solution $\left(\mathrm{H}_{2} \mathrm{SO}_{4}\right)$, what is the concentration of the $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution?

| Answer: |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: |
|  | $2 \mathrm{KOH}_{(\mathrm{aq})}$ | $+\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq)}}$ | $\rightarrow$ | $\mathrm{K}_{2} \mathrm{SO}_{4(\mathrm{aq)}}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$ |
| Volume $\left(\mathrm{cm}^{3}\right)$ | 50 | 125 |  |  |
| No. of moles | 0.025 | 0.0125 |  |  |
| Concentration | 0.5 | $\mathbf{0 . 1}$ |  |  |
| (mol M) |  | 1 |  |  |
| Reaction coefficents | 2 |  |  |  |

Number of moles of KOH in $50 \mathrm{~cm}^{3} 0.5 \mathrm{M}=$ volume $\times$ concentration $50 / 1000 \times 0.5=0.025$
At the end point the number of moles of KOH in $50 \mathrm{~cm}^{3}=0.5 \times$ number of moles of $\mathrm{H}_{2} \mathrm{SO}_{4}$ in $125 \mathrm{~cm}^{3}$
Therefore, number of moles of KOH in $125 \mathrm{~cm}^{3}(0.125 \mathrm{~L})=1 / 2 \times 0.025=0.0125$

Concentration of $\mathrm{KOH}=$ number of moles $/$ volume $=0.0125 / 0.125=\mathbf{0 . 1} \mathbf{~ M}$
4. An ammonia solution was reacted with sulfuric acid as shown in the equation below.

$$
2 \mathrm{NH}_{3(a q)}+\mathrm{H}_{2} \mathrm{SO}_{4(a q)} \rightarrow \quad\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}(a q)
$$

Calculate the concentration of the ammonia solution given that it takes $30.8 \mathrm{~cm}^{3}$ of a 1.24 M solution of sulfuric acid to neutralise $25 \mathrm{~cm}^{3}$ of this ammonia solution for complete reaction.

Answer:

|  | $2 \mathrm{NH}_{3(a q)}$ | $+$ | $\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ | $\rightarrow$ | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Volume ( $\mathrm{cm}^{3}$ ) | 25 (0.025 L) |  | 30.8 |  |  |
| No. of moles | $\begin{gathered} 0.0382 \times 2 \\ =0.0764 \end{gathered}$ |  | 0.0382 |  |  |
| Concentration (M) | $\begin{gathered} 0.0764 \\ / 0.025=3.1 \end{gathered}$ |  | 1.24 |  |  |
| Reaction coefficients | 2 |  | 1 |  | 1 |

Number of moles in $30.8 \mathrm{~cm}^{3}$ of $1.24 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}=$ volume $\times$ concentration $=30.8 / 1000 \times 1.24=0.0382$
At the end point, the number of moles of $\mathrm{NH}_{3}=2 \times$ number of mole of $\mathrm{H}_{2} \mathrm{SO}_{4}=0.0382 \times 2=0.0764$
Thus number of moles of $\mathrm{NH}_{3}$ in $25 \mathrm{~cm}^{3}(0.025 \mathrm{~L})=0.076$
Concentration of $\mathrm{NH}_{3}=$ number of moles $/$ volume $=0.076 / 0.025=3.1 \mathbf{~ M}$
5. A $50.0 \mathrm{~cm}^{3}$ sample of sulfuric acid was diluted to 1.00 L . A sample of the diluted sulfuric acid was analysed by titrating with aqueous sodium hydroxide. In the titration, $25.0 \mathrm{~cm}^{3}$ of 1.00 M aqueous sodium hydroxide required $20.0 \mathrm{~cm}^{3}$ of the diluted sulfuric acid for neutralisation. Calculate the concentration of the original concentrated sulfuric acid solution.

$$
\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{Na}_{2} \mathrm{SO}_{4(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(l)}
$$

Calculate the concentration of the original concentrated sulfuric acid solution.

## Answer:

|  | $\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ | $+\quad 2 \mathrm{NaOH}_{(\mathrm{aq})}$ | $\rightarrow$ | $\mathrm{Na}_{2} \mathrm{SO}_{4}+\mathrm{H}_{2} \mathrm{O}$ |
| :--- | :---: | :---: | :---: | :---: |
| Volume $\left(\mathrm{cm}^{3}\right)$ | $20(0.02 \mathrm{~L})$ | 25 |  |  |
| No. of moles | $0.5 \times 0.025=$ | $25 / 1000 \times 1=$ |  |  |
|  | 0.0125 | 0.025 |  |  |
| Concentration $(\mathrm{M})$ | $0.0125 / 0.02$ | 1 |  |  |
| Reaction coefficients | 0.625 | 1 | 2 |  |

Number of moles in $25 \mathrm{~cm}^{3}$ of $1 \mathrm{M} \mathrm{NaOH}=$ volume $\times$ concentration $=25 / 1000 \times 1=0.025$
At the end point, the number of moles of $\mathrm{H}_{2} \mathrm{SO}_{4}=0.5 \times$ number of mole of $\mathrm{NaOH}=0.5 \times 0.025=0.0125$
Thus number of moles of $\mathrm{H}_{2} \mathrm{SO}_{4}$ in $20 \mathrm{~cm}^{3}(0.02 \mathrm{~L})=0.0125$
Concentration of $\mathrm{H}_{2} \mathrm{SO}_{4}=$ number of moles $/$ volume $=0.0125 / 0.02=0.625 \mathrm{M}$
Therefore, concentration of the original $\mathrm{H}_{2} \mathrm{SO}_{4}$ sample $=1000 / 50 \times 0.625=\mathbf{1 2 . 5} \mathbf{~ M}$
6. How many grams of $\mathrm{Ca}(\mathrm{OH})_{2}$ are required to neutralise $52.68 \mathrm{~cm}^{3}$ of a $0.750 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ solution?

## Answer:

|  | $\mathrm{Ca}(\mathrm{OH})_{2(a q)}$ | + | $\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ | $\rightarrow$ |
| :--- | :---: | :---: | :---: | :---: | $\mathrm{CaSO}_{4}+$

$\mathrm{M}_{\mathrm{r}}\left[\mathrm{Ca}(\mathrm{OH})_{2}\right]=74$
The number of moles in $52.68 \mathrm{~cm}^{3}$ of a $0.750 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}=$ volume $\times$ concentration $=52.88 / 1000 \times 0.75=$ 0.0395

According to the reaction coefficients, at the end point, the number of moles of $\mathrm{Ca}(\mathrm{OH})_{2}=$ the number of moles of $\mathrm{H}_{2} \mathrm{SO}_{4}$
Thus, the number of moles of $\mathrm{Ca}(\mathrm{OH})_{2}=0.0395$
Mass of 0.0395 moles $\mathrm{Ca}(\mathrm{OH})_{2}=$ number of moles $\times \mathrm{Mr}=0.0395 \times 74=\mathbf{2 . 9 2} \mathbf{g}$
7. What volume of 1.0 M sulfuric acid will be needed to neutralise 25.00 cm of 0.8 M sodium hydroxide solution?

Answer:

|  | $2 \mathrm{NaOH}_{(\text {(aq) }}$ | + | $\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ | $\rightarrow$ | $\mathrm{Na}_{2} \mathrm{SO}_{4}+\mathrm{H}_{2} \mathrm{O}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Volume ( $\mathrm{cm}^{3}$ ) | 25 |  | 10 (0.01 L) |  |  |
| Moles | 25/1000 x |  | 0.01/1 $=0.01$ |  |  |
|  | $0.8=0.02$ |  |  |  |  |
| Concentration (M) | 0.8 |  | 1 |  |  |
| Reaction coefficient | 2 | : | 1 |  |  |

Number of moles in $25 \mathrm{~cm}^{3}, 0.8 \mathrm{M} \mathrm{NaOH}=$ volume $\times$ concentration $=25 / 1000 \times 0.8=0.02$
At the end point, the number of moles of $\mathrm{H}_{2} \mathrm{SO}_{4}=0.5 \times$ number of moles of $\mathrm{NaOH}=0.5 \times 0.02=0.01$
Volume of $\mathrm{H}_{2} \mathrm{SO}_{4}=$ number of moles /concentration $=0.01 / 1=0.01 \mathrm{~L}=10 \mathrm{~cm}^{3}$
8. Calculate the volume of 0.10 M sodium hydroxide solution needed to neutralise 20.00 $\mathrm{cm}^{3}$ of 0.25 M hydrochloric acid.

## Answer:

|  | $\mathrm{NaOH}_{(a q)}$ <br> $5 \times 10^{-3} / 0.1$ <br> $=$ <br> Volume $\left(\mathrm{cm}^{3}\right)$ | $+\mathrm{HCl}_{\text {(aq) }}$ |
| :--- | :---: | :---: | :---: | :---: |$\quad \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$

The number of moles in $20 \mathrm{~cm}^{3}, 0.32 \mathrm{M} \mathrm{HCl}=$ volume $\times$ concentration $=20 / 1000 \times 0.25=5 \times 10^{-3}$

At the end point, the number of moles of $\mathrm{NaOH}=$ number of moles of $\mathrm{HCl}=5 \times 10^{-3}$ Volume of $\mathrm{NaOH}=$ number of moles/ concentration $=5 \times 10^{-3} / 0.1=0.05 \mathrm{~L}=50 \mathrm{~cm}^{3}$
9. $100 \mathrm{~cm}^{3}$ of a magnesium hydroxide solution required $4.5 \mathrm{~cm}^{3}$ of sulfuric acid (of concentration 0.100 M ) for complete neutralisation. Determine the concentration of the magnesium hydroxide in $\mathrm{g} \mathrm{cm}^{-3}$.

Answer:

|  | $\mathrm{Mg}(\mathrm{OH})_{2(\text { aq }}$ | + | $\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}$ | $\rightarrow$ | $\mathrm{MgSO}_{4}+$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\mathrm{H}_{2} \mathrm{O}$ |
| Volume ( $\mathrm{cm}^{3}$ ) | 100 |  | $\begin{gathered} 4.5(4.5 \times 10 \\ \left.{ }^{3} \mathrm{~L}\right) \end{gathered}$ |  |  |
| Moles | $4.5 \times 10^{-5}$ |  | $4.5 \times 10^{-3} \mathrm{x}$ |  |  |
|  |  |  | $\begin{gathered} 0.1=4.5 \\ \times 10^{-4} \end{gathered}$ |  |  |
| Concentration ( | $\begin{gathered} 4.5 \times 10^{-4} / 0.1= \\ 4.5 \times 10^{-3}= \end{gathered}$ |  | 0.1 |  |  |
| Reaction coeffic | 1 | : | 1 |  |  |

$\mathrm{Mr}\left[\mathrm{Mg}(\mathrm{OH})_{2}\right]=58$
Number of moles in $4.5 \mathrm{~cm}^{3} 0.1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}=$ volume $\times$ concentration $=4.5 / 1000 \times 0.1=4.5 \times 10^{-4}$
At the end point, the number of moles of $\mathrm{H}_{2} \mathrm{SO}_{4}=$ Number of moles of $\mathrm{Mg}(\mathrm{OH})_{2}$
Thus the number of moles of $\mathrm{Mg}(\mathrm{OH})_{2}$ in $100 \mathrm{~cm}^{3}(0.1 \mathrm{~L})=4.5 \times 10^{-4}$
Concentration of $\mathrm{Mg}(\mathrm{OH})_{2}=$ number of moles $/$ volume $=4.5 \times 10^{-5} / 0.1=\mathbf{4 . 5} \mathbf{\times 1 0 ^ { - 3 }} \mathbf{~ M}$
To convert from M to $\mathrm{g} / \mathrm{mol}$ multiply by $\mathrm{M}_{\mathrm{r}}$
Concentration of $\mathrm{Mg}(\mathrm{OH})_{2}=4.5 \times 10^{-3} \times 58=0.26 \mathrm{~g} / \mathrm{L}$
10. A solution made from pure barium hydroxide contained 2.74 g in exactly $100 \mathrm{~cm}^{3}$ of water. Using phenolphthalein indicator, titration of $20.0 \mathrm{~cm}^{3}$ of this solution required $18.7 \mathrm{~cm}^{3}$ of a hydrochloric acid solution for complete neutralisation. Calculate the molarity of the HCl.

## Answer:

|  | $\mathrm{Ba}(\mathrm{OH})_{2(\mathrm{aq})}$ | $+$ | $2 \mathrm{HCl}_{(\mathrm{aq})}$ | $\longrightarrow$ | $\mathrm{BaCl}_{2}+$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $2 \mathrm{H}_{2} \mathrm{O}$ |
| Volume ( $\mathrm{cm}^{3}$ ) | 20 (0.02L) |  | 18.7 |  |  |
| Moles | 20/1000 x |  | $6.4 \times 10^{-3}$ |  |  |
|  | $0.16=3.2 x$ |  |  |  |  |
|  | $10^{-3}$ |  |  |  |  |
| Concentration (M) | 0.16 |  | 1000/18.7 x |  |  |
|  |  |  | $6.4 \times 10^{-3}$ |  |  |
|  |  |  | $=0.34$ |  |  |
| Reaction coefficien | 1 | : | 2 |  |  |

$\mathrm{M}_{\mathrm{r}}\left[\mathrm{Ba}(\mathrm{OH})_{2}\right]=171$
Number of moles in $2.74 \mathrm{~g} \mathrm{Ba}(\mathrm{OH})_{2}=$ mass $/ \mathrm{M}_{\mathrm{r}}=2.74 / 171=0.016$
Concentration of $\mathrm{Ba}(\mathrm{OH})_{2}=$ number of moles $/$ volume $=0.016 / 0.1=0.16 \mathrm{M}$
At the end point of the titration, number of moles of $\mathrm{HCl}=2 \mathrm{x}$ the number of moles of $\mathrm{Ba}(\mathrm{OH})_{2}$
Thus number of moles of HCl in $18.7 \mathrm{~cm}^{3}(0.0187 \mathrm{~L})=2 \times$ number of moles $\mathrm{Ba}(\mathrm{OH}) 2$ in $20 \mathrm{~cm} 3(0.02 \mathrm{~L})$

$$
=2 \times 0.02 \times 0.16=6.4 \times 10^{-3}
$$

Concentration of $\mathrm{HCl}=$ number of moles/volume $=6.4 \times 10^{-3} / 0.0187=\mathbf{0 . 3 4} \mathbf{M}$

