Volumetric Analysis

Objectives

1. Concentrations of Solutions
   - define solution
   - define concentration
   - define molarity
   - express concentration of solutions in mol/L (molarity), g/L and also in % (w/v), % (v/v), % (w/w)
   - appreciate the everyday use of % v/v e.g. in alcoholic beverages
   - calculate molarity from concentration in grams per litre and vice versa
   - calculate number of moles from molarity and volume
   - perform simple calculations involving percentage concentrations
   - calculate the effect of dilution on concentration
   - apply knowledge of concentrations of solutions to everyday examples
   - describe how colour intensity can be used as an indicator of concentration
   - define a primary standard and a standard solution
   - prepare standard solution of sodium carbonate
   - identify appropriate apparatus used in volumetric analysis
   - use correct titrimetric procedure when carrying out titrations
   - solve volumetric problems from first principles
   - carry out a titration between hydrochloric acid and sodium hydroxide solutions and use this titration to make a sample of sodium chloride (OL only)
   - standardise a hydrochloric acid solution using a standard solution of sodium carbonate
   - calculate the relative molecular mass of a compound and of the amount of water of crystallisation in a compound from titration data
   - determine the concentration of ethanoic acid in vinegar
   - determine the amount of water of crystallisation in hydrated sodium carbonate

2. Volumetric Analysis
   (balanced equations will be given in all volumetric problems)

   - identify appropriate apparatus used in volumetric analysis
   - use correct titrimetric procedure when carrying out titrations
   - solve volumetric problems from first principles
   - carry out a titration between hydrochloric acid and sodium hydroxide solutions and use this titration to make a sample of sodium chloride (OL only)
   - standardise a hydrochloric acid solution using a standard solution of sodium carbonate
   - calculate the relative molecular mass of a compound and of the amount of water of crystallisation in a compound from titration data
   - determine the concentration of ethanoic acid in vinegar
   - determine the amount of water of crystallisation in hydrated sodium carbonate

Definition: A solution is a homogeneous mixture of a solute and a solvent.

Definition: The concentration of a solution is the amount of solute dissolved in a given volume of the solution.

1. \(\%(w/w)\)
   Means grams of solute per 100 g of solution, or g/100g.
   E.g. saline solution, 1\% (w/w) NaCl = 1 g NaCl in 100 cm\(^3\) solution.

2. \(\%(w/v)\)
   Means grams of solute per 100 cm\(^3\) of solution, or g/100 cm\(^3\).
   E.g. 37\% (w/v) HCl = 37 g HCl in 100 cm\(^3\) solution.

3. \(\%(v/v)\)
   Means volume of solute per 100 cm\(^3\) of solution, or cm\(^3\)/100 cm\(^3\).
   E.g. Alcoholic drinks – Vodka’s alcohol (ethanol) concentration is 37.5\% (v/v) = 37.5 cm\(^3\) ethanol in 100 cm\(^3\) vodka.

4. Parts per Million (ppm)
   Means the concentration in mg/L. This is calculated by multiplying the concentration in g/L by 1000.
   1000mg = 1 g.
5. **Molarity (M or mol/L)**

This is the main unit used in the chemistry course. This means the number of moles of solute in 1 litre of solution. E.g. A 0.125 M solution of KMnO₄ has 0.125 moles of KMnO₄ in 1 litre of solution.

**Calculations**

(a) **mol/L to g/L**

1. How many grams of FeSO₄ are present in a solution marked 0.35 M FeSO₄?

   \[ M_r \text{ of } [\text{FeSO}_4] = (56) + (32) + 4(16) = 152 \]
   
   We have 0.35 mol/L FeSO₄
   
   \[ \times 152 \quad [\text{mol to g } \rightarrow \times M_r] \]
   
   =53.2 g/L

2. Calculate the concentration in grams per litre of bench hydrochloric acid whose concentration is 12 mol/L.

   \[ M_r \text{ of HCl} = (1) + (35.5) = 36.5 \]
   
   We have 12 mol/L HCl
   
   \[ \times 36.5 \quad [\text{mol to g } \rightarrow \times M_r] \]
   
   =438 g/L HCl

(b) **g/L to mol/L**

1. What is the molarity of a solution that contains 7.36 g of NaOH per litre of solution?

   \[ M_r \text{ of NaOH} = (23) + (16) + (1) = 40 \]
   
   We have 7.36 g/L NaOH
   
   \[ \div 40 \quad [\text{g to mol } \rightarrow \div M_r] \]
   
   0.184 mol/L NaOH

2. Calculate the concentration of a solution containing 45 g of sulphuric acid in a litre of solution.

   \[ M_r \text{ of } \text{H}_2\text{SO}_4 = 2(1) + (32) + 4(16) = 98 \]
   
   We have 45 g/L H₂SO₄
   
   \[ \div 98 \quad [\text{g to mol } \rightarrow \div M_r] \]
   
   0.4592 mol/L H₂SO₄

(c) **How many moles in a certain volume, given the solution’s molarity**

1. Calculate how many moles of CH₃COOH are present in 25 cm³ of 0.55 M CH₃COOH.

   We have 0.55 mol/L CH₃COOH
   
   \[ \frac{0.55}{1000} \times 25 \]
   
   =0.01375 mol/25 cm³ CH₃COOH

   If question was phrased “Calculate how many grams of CH₃COOH are present in 25 cm³ of 0.55 M CH₃COOH”, we would then have to multiply 0.01375 by the Mᵣ of CH₃COOH.
2. How many moles of HCl are present in 60 cm\(^3\) of 0.4 M HCl?

We have 0.4 mol/L HCl

\[
\frac{0.4}{1000} \times 60 = 0.024 \text{ mol/60 cm}\(^3\) \text{ HCl}
\]

(d) Calculate moles per litre, given the mass of solute and volume of solution

1. Calculate the concentration in moles per litre of a solution containing 45 grams of sulphuric acid per 240 cm\(^3\) of solution.

\[
\text{Mr of H}_2\text{SO}_4 = 2(1) + (32) + 4(16) = 98
\]

We have 45 g/240 cm\(^3\) H\(_2\)SO\(_4\)

\[
\div 98 \quad \text{[g to mol} \rightarrow \div \text{Mr]} = 0.4592 \text{ mol/240 cm}\(^3\) \text{ H}_2\text{SO}_4
\]

\[
\frac{0.4592}{240} \times 1000 = 1.193 \text{ mol/L H}_2\text{SO}_4
\]

2. 7.6 g of anhydrous Na\(_2\)CO\(_3\) is dissolved in deionised water and made up to 300 cm\(^3\) of solution. Express the concentration of this solution in mol/L.

\[
\text{Mr of Na}_2\text{CO}_3 = 2(23) + (12) + 3(16) = 106
\]

We have 7.6 g/300 cm\(^3\) Na\(_2\)CO\(_3\)

\[
\div 106 \quad \text{[g to mol} \rightarrow \div \text{Mr]} = 0.0717 \text{ mol/300 cm}\(^3\) \text{ Na}_2\text{CO}_3
\]

\[
\frac{0.0717}{300} \times 1000 = 0.239 \text{ mol/L Na}_2\text{CO}_3
\]

(e) Compound calculations (combinations of (a) to (d))

1. What mass of sodium hydroxide is contained in 25 cm\(^3\) of a 1.5 M solution of sodium hydroxide?

\[
\text{Mr of NaOH} = (23) + (16) + (1) = 40
\]

We have 1.5 mol/L NaOH

\[
\times 40 \quad \text{[mol to g} \rightarrow \times \text{Mr]} = 60 \text{ g/L NaOH}
\]

\[
\frac{60}{1000} \times 25 = 1.5 \text{ g/25 cm}\(^3\) \text{ NaOH}
\]

2. What volume of 0.01 M KMnO\(_4\) solution will contain 5 g of KMnO\(_4\)?

\[
\text{Mr of KMnO}_4 = (39) + (55) + 4(16) = 158
\]

We have 0.01 mol/L KMnO\(_4\)

\[
\times 158 \quad \text{[mol to g} \rightarrow \times \text{Mr]} = 1.58 \text{ g/L KMnO}_4. \text{ This can be rewritten as } 1.58 \text{ g/1000 cm}\(^3\) \text{ KMnO}_4
\]

\[
\div 1.58 = 1 \text{ g/632.9 cm}\(^3\) \text{ KMnO}_4
\]

\[
\times 5 = 5 \text{ g/3164.6 cm}\(^3\) \text{ KMnO}_4
\]
**Dilution of solutions**

To find the volume of a concentrated solution needed to make a less concentrated solution, use the formula:

\[ V_c \times M_c = V_d \times M_d \]

- \( V_c \) = Volume of concentrated solution
- \( V_d \) = Volume of dilute solution
- \( M_c \) = Molarity of concentrated solution
- \( M_d \) = Molarity of dilute solution

**Examples:**

1. What volume of 12 M HCl is needed to make up 500 cm\(^3\) of 3 M HCl solution?

\[
V_c \times M_c = V_d \times M_d \\
V_c \times 12 = 500 \times 3 \\
\frac{500 \times 3}{12} = V_d \\
125 \text{ cm}^3 = V_d
\]

2. 15 cm\(^3\) of 2 M HNO\(_3\) solution is diluted to 250 cm\(^3\) in a volumetric flask. What is the new concentration of the nitric acid?

\[
V_c \times M_c = V_d \times M_d \\
15 \times 2 = 250 \times M_d \\
\frac{250}{15 \times 2} = M_d \\
0.12 \text{ M} = M_d
\]

**Standard Solutions**

*Def*°: A **standard solution** is one whose concentration is accurately known.

*Def*°: A **primary standard** is a substance that can be directly weighed and used to make a standard solution. It must:
- Be available in a pure and stable solid state
- Be soluble in water
- Have a high molecular mass
- Be anhydrous (no water of crystallisation)

Primary Standards: \( \text{Na}_2\text{CO}_3, \text{NaCl} \)

Not Primary Standards:
- \( \text{HCl} \) – it is a gas
- \( \text{I}_2 \) – it sublimes
- \( \text{H}_2\text{SO}_4 \) – it absorbs moisture from air
- \( \text{NaOH} \) – it absorbs \( \text{CO}_2 \) and moisture from air
- \( \text{KMnO}_4 \) – it is reduced by sunlight
Equipment used in Titrations

1. **Pipette:**
   Used to accurately measure a known volume of liquids/solutions.

   **Procedure for cleaning, filling and transferring solutions using a pipette:**
   - Rinse with dionised water.
   - Rinse with the solution it is to contain (name this solution if you know). *[This is done to remove the water, so the solution in the pipette doesn’t get diluted.]*
   - Using a pipette filler, fill pipette with solution until the bottom of the meniscus reaches the graduation mark, at eye level.
   - Let the pipette drain under gravity, touching the tip of the pipette against the flask to remove the last drop stuck to the tip.

2. **Burette:**
   Used to accurately measure the volume of liquid/solution added.

   **Procedure for cleaning and filling a burette:**
   - Rinse with deionised water.
   - Rinse with the solution it is to contain (name this solution if you know). *[This is done to remove the water, so the solution in the burette doesn’t get diluted.]*
   - Clamp vertically.
   - Using a funnel, fill the burette above the zero mark.
   - Remove the funnel.
   - Open the tap to bring the bottom of the meniscus to the zero mark, and to fill the jet below the tap.

3. **Conical Flask:**
   A specially shaped flask that allows swirling without spilling the contents.

   **Procedure for cleaning the conical flask:**
   - Clean with deionised water only. *[Any water droplets remaining won’t change the number of moles of reactant you add].*

**Acid/Base Titrations:**

1. **To standardise a solution of HCl using a standard solution of Na₂CO₃.**
   **Acid:** HCl – strong acid
   **Base:** Na₂CO₃ – weak base
   **Indicator:** Methyl Orange (SAWBMO)
   **Colour change:** Yellow to Red
   **Equation:** \( 2\text{HCl} + \text{Na}_2\text{CO}_3 \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \)
   **Ratio:** 2 HCl : 1 Na₂CO₃

G. Galvin
**Sample calculation: (2012 HL Q1)**

A student determined the concentration of a hydrochloric acid solution by titration with 25.0 cm$^3$ portions of a 0.05 M primary standard solution of anhydrous sodium carbonate. The portions of sodium carbonate solution were measured into a conical flask using a 25 cm$^3$ pipette. The hydrochloric acid solution was added from a burette. The mean titre was 20.8 cm$^3$.

The balanced equation for the titration reaction was:

\[
2\text{HCl} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2
\]

\(\text{(e) Calculate, correct to two decimal places, the concentration of the hydrochloric acid solution in}
\)

\(\text{\(i\)}\) moles per litre,

\(\text{\(ii\)}\) grams per litre. \(\text{(12)}\)

\(\text{(i) We have 0.05 mol/L Na}_2\text{CO}_3\)

\[
\frac{0.05 \times 25}{1000} = 0.00125 \text{ mol/25 cm}^3 \text{ Na}_2\text{CO}_3
\]

\[
\begin{array}{ccc}
\text{HCl} & : & \text{Na}_2\text{CO}_3 \\
2 & : & 1 \\
0.0025 & : & 0.00125
\end{array}
\]

\[
\frac{0.0025 \text{ mol/20.8 cm}^3 \text{ HCl}}{0.0025 \times 1000} = 0.12 \text{ mol/L HCl}
\]

\(\text{(ii) M}_r \text{ of HCl} = (1) + (35.5) = 36.5\)

\[
0.12 \times 36.5 = 4.38 \text{ g/L HCl} \quad [\text{mol to g } \rightarrow \text{xM}_r]
\]

2. **To determine the concentration of ethanoic acid in vinegar**

**Acid:** CH$_3$COOH – weak acid  \hspace{1cm} **Base:** NaOH – strong base

**Indicator:** Phenolphthalein (WASBPH)

**Colour change:** Pink to Colourless [NOT “clear”!]

**Equation:** CH$_3$COOH + NaOH \rightarrow CH$_3$COONa + H$_2$O

**Ratio:** 1 CH$_3$COOH : 1 NaOH

**Notes:** Vinegar must be diluted beforehand because it is too concentrated. Make sure to multiply the concentration of the *dilute* vinegar by the dilution factor to find the concentration of the *original* vinegar.

\[
\text{Dilution factor} = \frac{\text{Volume of Diluted Vinegar}}{\text{Volume of Original Vinegar}}
\]

Clear vinegar should be used to ensure the endpoint is clearly seen.
Sample calculation: (2016 HL Q1)

To determine the concentration of ethanoic acid in a sample of vinegar, 25.0 cm$^3$ of the vinegar were diluted to 250 cm$^3$ and then the diluted vinegar was titrated with a previously standardised solution which contained 1.20 g of sodium hydroxide in 500 cm$^3$ of solution. On average, 18.75 cm$^3$ of the diluted vinegar were required to neutralise 25.0 cm$^3$ of this sodium hydroxide solution.

The equation for the titration reaction is:

\[
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}
\]

(c) Calculate

(i) the number of moles of sodium hydroxide in each 25.0 cm$^3$ portion,

(ii) the number of moles of ethanoic acid per cm$^3$ of diluted vinegar. (12)

(d) Find the concentration of ethanoic acid in the original vinegar

(i) in terms of moles per litre,

(ii) as a percentage (w/v). (9)

(c)

(i) We have 1.20 g/500 cm$^3$ NaOH

\[
M_r \text{ of NaOH} = (23) + (16) + (1) = 40
\]

\[
1.20 \div 40 \quad \text{[g to mol } \div M_r\text{]}
\]

\[
= 0.03 \text{ mol/500 cm}^3 \text{NaOH}
\]

\[
0.03 \times 25
\]

\[
=0.0015 \text{ mol/25 cm}^3 \text{NaOH}
\]

(ii) \[
\begin{align*}
\text{CH}_3\text{COOH} & : \quad \text{NaOH} \\
1 & : \quad 1 \\
0.0015 & : \quad 0.0015
\end{align*}
\]

\[
0.0015 \text{ mol/18.75 cm}^3 \text{CH}_3\text{COOH (dilute)}
\]

\[
0.0015 \times 1
\]

\[
=0.00008 \text{ mol/1 cm}^3 \text{CH}_3\text{COOH (dilute)}
\]

(d)

(i) \[
0.00008 \text{ mol/1 cm}^3 \text{CH}_3\text{COOH (dilute)}
\]

\[
\text{Dilution Factor} = \frac{250}{25} = 10
\]

\[
\times 10
\]

\[
=0.0008 \text{ mol/1 cm}^3 \text{CH}_3\text{COOH (original)}
\]

\[
\times 1000
\]

\[
= 0.8 \text{ mol/L CH}_3\text{COOH (original)}
\]
(ii) \( \% (w/v) \) means g/100 cm\(^3\)

We have 0.8 mol/L CH\(_3\)COOH (original) \( \times 60 \) [mol to g \( \rightarrow \times M_1 \)]

\[ \text{= 48 g/L CH}_3\text{COOH (original)} \]

\[ \text{÷10} \]

\[ \text{= 4.8 g/100 cm}^3 \text{ CH}_3\text{COOH (original)} \]

\[ \text{= 4.8 % (w/v)} \]

3. To determine the amount of water of crystallisation in washing soda (hydrated sodium carbonate)

**Acid:** HCl – strong acid

**Base:** Na\(_2\)CO\(_3\) – weak base

**Indicator:** Methyl Orange (SAWBMO)

**Colour change:** Yellow to Red

**Equation:**

\[ 2\text{HCl} + \text{Na}_2\text{CO}_3 \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \]

**Ratio:** 2 HCl : 1 Na\(_2\)CO\(_3\)

**Notes:** Same as titration number 1, just with extra calculations.

The crystals are made up of Na\(_2\)CO\(_3\middot\)xH\(_2\)O. We need to find 2 things:

1. the percentage of water of crystallisation, and
2. the value of \( x \).

These calculations can also come up for other compounds – not just in in this experiment, e.g. finding the percentage water of crystallisation and value for \( x \) in hydrated copper (II) sulphate, CuSO\(_4\middot\)xH\(_2\)O.

**Sample Calculation:**

An experiment was carried out to determine the percentage water of crystallisation and the degree of water of crystallisation, \( x \), in a sample of hydrated sodium carbonate crystals (Na\(_2\)CO\(_3\middot\)xH\(_2\)O). An 8.20 g sample of the crystals was weighed accurately on a clock glass and then made up to 500 cm\(^3\) of solution in a volumetric flask. A pipette was used to transfer 25.0 cm\(^3\) portions of this solution to a conical flask. A previously standardised 0.11 M hydrochloric acid (HCl) solution was used to titrate each sample. A number of accurate titrations were carried out. The average volume of hydrochloric acid solution required in these titrations was 26.05 cm\(^3\).

The titration reaction is described by the equation:

\[ \text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \]

\( d \) From the titration figures, calculate the concentration of sodium carbonate (Na\(_2\)CO\(_3\)) in the solution in

(i) moles per litre,

(ii) grams per litre. \( \text{(9)} \)

\( e \) Calculate the percentage water of crystallisation present in the crystals and the value of \( x \), the degree of hydration of the crystals. \( \text{(12)} \)

G. Galvin
(d)

(i) We have 0.11 mol/L HCl

\[
\begin{array}{c}
0.11 \times 26.05 \\
\hline
1000 \\
\end{array}
\]

=0.0028655 mol/26.05 cm\(^3\) HCl

<table>
<thead>
<tr>
<th>HCl</th>
<th>Na(_2)CO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

0.0028655 : 0.00143275

(ii) \(M_r\) of Na\(_2\)CO\(_3\) = 2(23) + (12) + 3(16) = 106

\[\times 106 \quad [\text{mol to g } \rightarrow \times M_r]\]

=6.07486 g/L Na\(_2\)CO\(_3\)

(e)

(i) \[\text{Percentage water of crystallisation} = \frac{\text{Mass of water in your sample}}{\text{Mass of your sample}} \times 100\]

We had 6.07486 g/L Na\(_2\)CO\(_3\) but we only made 500 cm\(^3\) of the solution.

\[= 3.03743 \text{ g/500 cm}^3 \text{ Na}_2\text{CO}_3 \text{ in our solution.}\]

But we weighed out 8.20g of crystals.

The extra mass is the mass of water.

\[8.20 - 3.03743 = 5.16257\text{g of water in our crystals}\]

\[\% \text{ water of crystallisation} = \frac{5.16257}{8.20} \times 100\]

(ii) \[\frac{\text{Mass of Na}_2\text{CO}_3}{\text{Mr of Na}_2\text{CO}_3} = \frac{\text{Mass of } x\text{H}_2\text{O}}{\text{Mr of } x\text{H}_2\text{O}}\]

\(M_r\) of \(x\text{H}_2\text{O}\) = \(x[2(1) + (16)] = 18x\)

\[\frac{3.03743}{106} = \frac{5.16257}{18x}\]

\[x = \frac{5.16257 \times 106}{18 \times 3.03743}\]

\[x = 10 \quad [\text{round to a whole number if possible}]\]

This means our crystals are actually made up of Na\(_2\)CO\(_3\).10H\(_2\)O