

### Titration

- There are two quantitative methods of chemical analysis:
  - o Gravimetric analysis: This involves measuring the mass of a substance produced in a chemical reaction (to solve the problem)
    - This technique is often used when a precipitate is produced
  - o Volumetric analysis: This involves measuring the volume of solutions in a chemical reaction (to solve a problem)
    - This technique is often used in much of acid-base and reduction-oxidation reactions, since much of the reactions take place in solutions
    - The most common technique is when a solution of accurately known concentration is reacted with a fixed volume of a solution of a substance whose concentration we wish to find. By comparing the reacting volumes, we can determine the concentrations of the unknowns
    - The actual procedure of adding one solution (progressively) to another is called a titration. We will consider:
      - Acid-base titrations
      - Redox titrations

### Acid-Base Titrations

- A number of concepts must be well understood to understand acid-base titrations, including:
  - o Acid-base reactions
  - o The preparation of a solution of known concentration
  - o Equipment used in titrations and preparation of equipment
  - o The titration procedure
  - o Determining that the reaction is complete

## Acid-Base Reactions

## Acid Reactions

- React with reactive metals to produce hydrogen gas
  - o Acid + reactive metal → hydrogen + salt
    - $2\text{HCl}_{(aq)} + \text{Mg}_{(s)} \rightarrow \text{H}_{2(g)} + \text{MgCl}_{2(aq)}$
    - $2\text{H}^+_{(aq)} + \text{Mg}_{(s)} \rightarrow \text{H}_{2(g)} + \text{Mg}^{2+}_{(aq)}$
- React with carbonates and hydrogen carbonates to form carbon dioxide gas
  - o Acid + carbonate → carbon dioxide + water + salt
    - $\text{H}_2\text{SO}_{4(aq)} + \text{Na}_2\text{CO}_{3(s)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} + 2\text{Na}_2\text{SO}_{4(aq)}$
    - $2\text{H}^+_{(aq)} + \text{Na}_2\text{CO}_{3(s)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} + 2\text{Na}^+_{(aq)}$
  - o Acid + hydrogen carbonate → carbon dioxide + water + salt
    - $\text{HNO}_{3(aq)} + \text{KHCO}_{3(aq)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} + \text{KNO}_{3(aq)}$
    - $\text{H}^+_{(aq)} + \text{HCO}_3^-_{(aq)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$
- React with metal oxides and metal hydroxides to produce a salt and water
  - o Acid + metal oxide → salt + water
    - $2\text{HNO}_{3(aq)} + \text{CuO}_{(s)} \rightarrow \text{Cu}(\text{NO}_3)_2_{(aq)} + \text{H}_2\text{O}_{(l)}$
    - $2\text{H}^+_{(aq)} + \text{CuO}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + \text{H}_2\text{O}_{(l)}$
  - o Acid + metal hydroxide → salt + water
    - $2\text{HCl}_{(aq)} + \text{Ba}(\text{OH})_2_{(aq)} \rightarrow \text{BaCl}_2_{(aq)} + 2\text{H}_2\text{O}_{(l)}$
    - $\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}$
    - If the metal hydroxide is an insoluble hydroxide, or the acid is added to a solid rather than a solution, the equation is better written as:
      - $2\text{HCl}_{(aq)} + \text{Mg}(\text{OH})_2_{(s)} \rightarrow \text{MgCl}_2_{(aq)} + 2\text{H}_2\text{O}_{(l)}$
      - $2\text{H}^+_{(aq)} + \text{Mg}(\text{OH})_2_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2\text{H}_2\text{O}_{(l)}$
- React with sulphides to produce a salt solution and hydrogen sulphide
  - o Acid + sulfide → salt + hydrogen sulfide
- React with sulphites to produce a salt solution, sulphur dioxide gas and water
  - o Acid + sulfite → salt solution + sulfur dioxide + water
- If weak acids are involved in any of the reactions described in this section, they are represented in the ionic equation in their 'un-ionised' form
  - o E.g. The ionic equation for the reaction of acetic acid with a solution of potassium hydroxide would be:
    - $\text{CH}_3\text{COOH}_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{CH}_3\text{COO}^-_{(aq)} + \text{H}_2\text{O}_{(l)}$

**Base Reactions**

- React with acids to produce a salt and water (these include the metal carbonate, metal hydrogen carbonate, metal oxide and metal hydroxide reactions mentioned previously)
- React with compounds containing the ammonium ion (e.g.  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ , etc) to produce ammonia gas and water
  - o The  $\text{NH}_4^+$  acts as an acid and donates a hydrogen ion to the base, to form  $\text{NH}_3$   
$$\text{NH}_4^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{NH}_3_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$$
- Ammonia, a weak base, reacts with acids, but unlike most of the other acid-base reactions, water is not one of the products in these ammonia reactions
  - o Reaction of gaseous ammonia with gaseous hydrogen chloride to form ammonium chloride solid
    - $\text{NH}_3_{(\text{g})} + \text{HCl}_{(\text{g})} \rightarrow \text{NH}_4\text{Cl}_{(\text{s})}$
    - The  $\text{H}^+$  ions are transferred from the  $\text{HCl}$  molecules to the  $\text{NH}_3$  molecules to form  $\text{NH}_4^+$  and  $\text{Cl}^-$ . Because no water is present, the ammonium ions and the chloride ions form as the ionic solid, ammonium chloride
    - This ionic solid appears as a white smoke
  - o Reaction of gaseous ammonia or a solution of ammonia with an acid solution to form a solution containing an ammonium salt
    - E.g. When ammonia gas is bubbled through hydrochloric acid, a solution of ammonium chloride is formed
    - $\text{NH}_3_{(\text{g})} + \text{H}^+_{(\text{aq})} \rightarrow \text{NH}_4^+_{(\text{aq})}$  where  $\text{Cl}^-$  is the spectator ion
  - o Reaction of an ammonia solution with acetic acid:
    - $\text{NH}_3_{(\text{aq})} + \text{CH}_3\text{COOH}_{(\text{aq})} \rightarrow \text{NH}_4^+_{(\text{aq})} + \text{CH}_3\text{COO}^-_{(\text{aq})}$
- React with amphoteric oxides or hydroxides to form a complex ion
  - o Metals including copper, zinc, tin, lead, aluminium, and beryllium) form amphoteric oxides or hydroxides

## Preparation of a Solution of Known Concentration

- In a typical titration: **A variable volume of a solution of accurately known concentration is reacted with a fixed volume of the solution of a substance whose concentration we wish to find**
- Hence, the concentration of one of the two solutions involved in a titration must be accurately known
- A solution whose concentration is accurately known is called a standard solution
- There are two types of standard solutions:
  - o Primary standards: A primary standard is one that is prepared chemically, whereas the substance satisfies the following four criteria (whereas most common acid-base and redox chemicals lack)
    - It can be obtained with a high degree of purity and has a known formula
    - It is soluble in water
    - It should have a relatively high formula mass to minimise weighing errors
      - To produce solutions having the same concentration, a greater mass of the substance with the higher molar mass will need to be weighed out. Since the uncertainty in the balance is a fixed value, this fixed value, as a percentage of the larger mass, will be smaller
    - It must be stable (i.e. its composition does not change on exposure to the atmosphere or other chemical substances)
      - Sodium hydroxide is not a suitable primary standard because it is deliquescent (when exposed to air, it absorbs water, enough to form a solution)
        - o Also, it reacts with carbon dioxide in the atmosphere
      - Hydrochloric acid is not a suitable primary standard because it is because it is hygroscopic (when exposed to air, it absorbs water, but not enough to form a solution)
        - o Also, it has a relatively low formula mass
      - Hydrated sodium carbonate  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  is not a suitable primary standard because it is efflorescent (when exposed to air, they lose their moisture to the atmosphere)
  - o Secondary standards:
    - Once a solution of a primary standard has been prepared, it is possible to use this solution of accurately known concentration to titrate a second solution to determine its accurate concentration
    - This second solution, with its now known concentration, is referred to as a secondary standard solution
- Suitable primary standards for acid-base titrations include:
  - o Anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ )
  - o Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ )
- The two pieces of equipment used in the preparation of a standard solution, their function and preparation method are exemplified in the table below

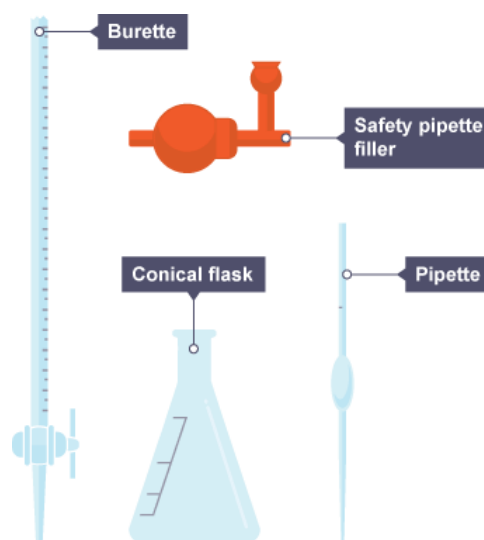
Equipment	Function	Preparation	Notes
<b>Volumetric flask</b>	Holds accurately known volume of solution	Rinsed with distilled or de-ionised water prior to use	Generally 250.0 mL or 500.0 mL
<b>Analytical balance</b>	Measure accurate masses of solids that are used to make up standard solutions		



### Equipment Used in Titrations and Preparation of Equipment

- In a typical titration: **A variable volume of a standard solution is reacted with a fixed volume of the solution of the substance whose concentration we wish to find**
- The three pieces of equipment used in a titration, their function and their preparation methods are exemplified in the table below

Equipment	Function	Preparation	Notes
<b>Pipette</b>	Delivers an accurate, fixed volume (aliquot) of solution	Rinsed with small amount of solution being delivered from it in the titration	Generally 20.00 mL or 25.00 mL
<b>Burette</b>	Delivers an accurate, variable volume (titre) of solution	Rinsed with small amount of solution delivered for the titre	
<b>Conical flask</b>	Used to hold an aliquot of solution under the burette (i.e. reaction mixture during titration)	Rinsed with distilled or de-ionised water prior to use	Should be transparent and clean to easily detect a colour change



Titration Procedure

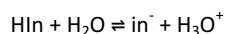
- In a typical titration: **A titre (variable volume) of a standard solution is reacted with an aliquot (fixed volume) of a solution whose concentration we wish to find**
  - o A pipette is used to deliver a fixed, accurate volume (aliquot) of one of the reactants
  - o A burette is used to deliver a variable volume (titre) of the second reactant
    - The solution in the burette is added carefully to the solution in the conical flask until the reaction is complete
    - The volume of the titre is calculated by subtracting the final volume from the initial volume
  - o The first titration is usually performed relatively fast to give a rough estimate of the titre volume that needs to be delivered to achieve complete reaction
  - o After this, the experiment is repeated several times. In each of these titrations, a volume close to that estimated from the first rough experiment is added quickly. Then the volume of solution being delivered from the burette is carefully controlled with drop-by-drop addition and swirling of the conical flask to ensure thorough mixing of the two reactants
    - The purpose of repeating a titration is to establish two or three results that are within  $\pm 0.2$  mL of each other. The average of the titres value is then used

#### Determining that the Reaction is Complete

- When two colourless solutions undergo a reaction that does not produce a gas or precipitate, it is very difficult (or even impossible) to determine when stoichiometric (equivalent) amounts of the two reactants have combined. Some method needs to exist to determine when we have reached this **equivalence point**
  - For acid-base titrations, acid-base indicators are used
    - o An acid-base indicator is a substance whose colour depends on the pH of the solution in which they are dissolved
    - o The point at which the indicator changes colour is called the **end point**
    - o Since the products of an acid-base reaction may be acidic, basic or neutral, it is important to choose an indicator such that the end point matches the equivalence point, thus reducing experimental error
      - An appropriately chosen indicator will show a colour change (end point) when the reaction is complete (equivalence point)
      - Acid-base reactions are generally called neutralisation reactions. However only those reactions that involve a strong acid and a strong base produce a salt that has a pH of 7 (neutral)
        - E.g.  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ , where NaCl is neutral
      - The salts or alternate products produced from other combinations involving weak acids or weak bases do not produce solutions with a pH of 7 at the equivalence point
        - E.g.  $\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$ , where  $\text{NH}_4\text{NO}_3$  is acidic
        - E.g.  $2\text{CH}_3\text{COOH} + \text{K}_2\text{O} \rightarrow 2\text{KCH}_3\text{COO} + \text{H}_2\text{O}$ , where  $\text{KCH}_3\text{COO}$  is basic
        - E.g.  $2\text{HCl} + \text{MgCO}_3 \rightarrow 2\text{MgCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ , where  $\text{MgCl}_2$  is neutral but  $\text{CO}_2$  is acidic
- All non-metal oxides are acidic
- $$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$
- $$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$$
- $$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$$

### Indicators

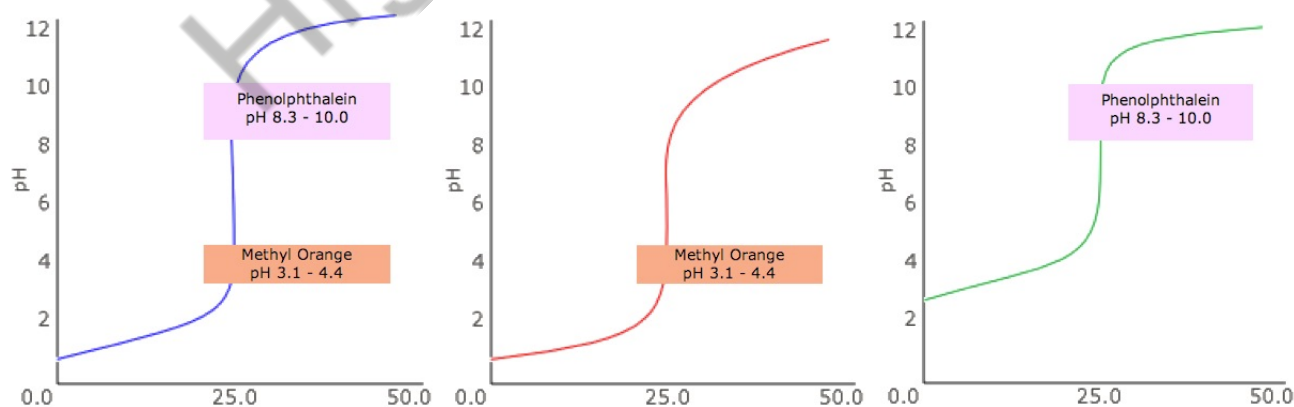
- Indicators are molecular substances that are used because they change colour depending on the pH of the solution
- An indicator is a weak acid or base and its conjugate pair. The acid and its conjugate base have different colours
- Consider an indicator that is a weak acid, with the formula HIn (colour A). At equilibrium, the following equilibrium equation is established with its conjugate base In<sup>-</sup> (colour B):



- o At a low pH, the weak acid indicator is almost entirely in the HIn form (colour A), the colour of which predominates
- o As the pH increases, the intensity of the colour of HIn decreases and the equilibrium is pushed to the right. Therefore the intensity of the colour of In<sup>-</sup> (colour B) increases
- o An indicator is thus most effective if the colour change is distinct and over a low pH range
- The table below exemplifies commonly used acid-base indicators, the pH range where the colour change occurs (i.e. end point range), the colour change from acidic to basic conditions and the titrations they are suitable for

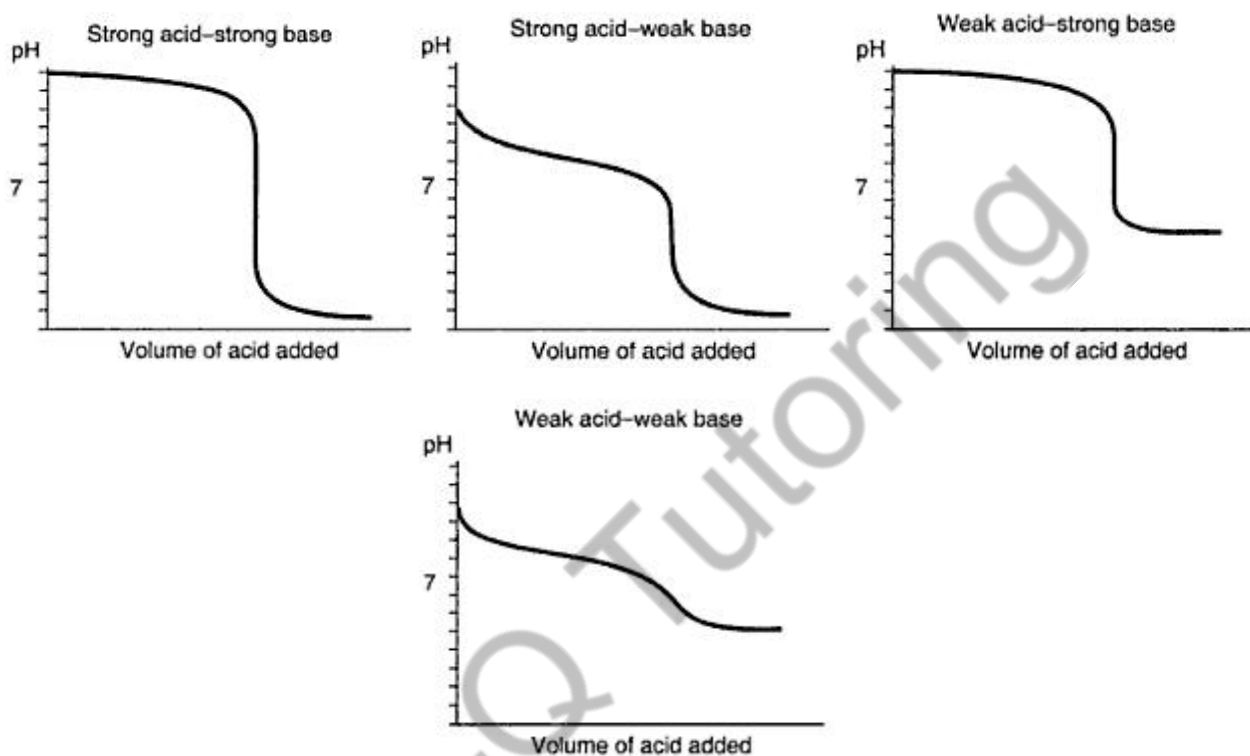
Indicator	pH range	Colour change acid → base	Suitable for
Methyl orange	3.1 – 4.4	Red → yellow	Strong acid + Weak base
Methyl red	4.4 – 6.2	Red → yellow	Strong acid + Strong base
Phenolphthalein	8.3 – 10.0	Colourless → pink	Weak acid + Strong base

- Let us consider three reaction types and their respective pH curves:
  - o Strong acid (e.g. HCl) and strong base (e.g. NaOH)
    - The solution mixture at equivalent point is neutral, thus a suitable indicator could be methyl orange, methyl red or phenolphthalein
  - o Strong acid (e.g. HNO<sub>3</sub>) and weak base (e.g. NH<sub>3</sub>)
    - The solution mixture at equivalence point is acidic, thus a suitable indicator would be methyl orange
  - o Weak acid (e.g. CH<sub>3</sub>COOH) and weak base (e.g. K<sub>2</sub>O)
    - The solution mixture at equivalence point is basic, thus a suitable indicator would be phenolphthalein



### Back Titrations

- The first three pH curves during a titration shown below exemplify a distinct decrease in pH at the equivalence point, hence a suitable indicator can be selected such that its end point matches the equivalence point
- However, the pH curve of the titration between a weak acid and weak base shows no significant change in pH at the equivalence point, hence making it difficult to identify. Thus there is no indicator that can detect an accurate end point
  - o For this reason, titrations of weak acids and weak bases are generally not performed directly, but instead a back titration is used



- A back titration, or indirect titration, is generally a two-stage analytical technique:
  1. Reactant A of unknown concentration is reacted with excess reactant B of known concentration
  2. A titration is then performed to determine the amount of reactant B in excess
- Back titrations are used when:
  - o An acid or a base is an insoluble salt, however will still react
  - o A particular reaction is too slow and hence difficult to identify a clearly defined end point
  - o Direct titration would involve a weak acid and weak base titration, in which the end point of this type of direct titration is very difficult to identify
    - A back titration is useful in this case as the endpoint of this indirect titration is easier to identify than the end point of the direct titration