ACID-BASE TITRATIONS

The reaction of acid and base involves transfer of a proton from acid to base and is often called a neutralisation reaction. It is important to note that only a few reactions produce a neutral solution due to hydrolysis in the resultant solution.

Common titrants

A major requirement of an acidic or basic titrant is that the species is a strong acid or base. If a weak acid or base were used to titrate a weak base or weak acid then the equivalence point could not be detected. A strong acid or base enhances the equivalence point making it easier to detect.

Common acid titrants include:
- Hydrochloric acid
- Nitric acid
- Sulfuric acid

Common base titrants include:
- Sodium hydroxide
- Potassium hydroxide

Primary standards for standardisation of an acid

Sodium carbonate (anhydrous), \( \text{Na}_2\text{CO}_3 \). Formula weight = 106
- Commercially available in very pure state
- Slightly hygroscopic so should be dried for an hour and allowed to cool in a desiccator before use
- Weak base which can react with two lots of \( \text{H}^+ \) and so has 2 end-points.
- At pH 8.3 \( \text{CO}_3^{2-} \rightarrow \text{HCO}_3^- \)
- At pH 3.8 \( \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3 \)
- Titration is always carried out to the second endpoint where there is a noticeable change in pH from pH 11.7 (of \( \text{Na}_2\text{CO}_3 \)) to pH 3.8
- Indicator should change colour in the acidic region eg methyl orange or methyl red
- Low relative formula weight which can lead to increased weighing errors. This may be overcome by preparing a large volume and taking aliquots for the titration

Borax, \( \text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O} \). Formula weight = 381.44
- Sodium tetraborate is a weak base
- Reacts with two \( \text{H}^+ \) for complete reaction
- Has waters of crystallisation which introduce errors
- Weighing errors are reduced as the borax has a large formula weight
Primary standards for standardisation of a base

Potassium hydrogen phthalate (KHP) \( \text{KC}_8\text{H}_4\text{O}_4 \) Formula weight 204.22
- Organic compound (see Fig 3.1)
- Monoprotic
- Has high formula weight
- Non-hygroscopic
- Water-soluble
- Available commercially in very pure form
- Equivalence point is in the basic region therefore an indicator such as phenolphthalein should be used.

Fig 3.1 Structure of potassium hydrogen phthalate

Endpoint Detection
Acid-base titrations result in a marked change in solution pH at the equivalence point. It is this change that is detected using the appropriate indicator. Away from the equivalence point the pH changes only gradually, but close to the equivalence point it changes rapidly. Note the changes in pH shown in Fig 3.2 for the titration of 25.0 mL of 0.1M HCl with 0.1M NaOH.

Fig 3.2 pH changes during an acid-base titration
There is a large pH change in the vicinity of the equivalence point for the addition of a very small volume of titrant. The indicator chosen for the reaction must change colours within the pH range, for Fig 3.2 a suitable indicator would change colours between pH 4 and 10.

**Indicators**

An acid-base indicator is an organic compound which has weak acidic or basic functional groups such as –NH$_2$, -COOH, -OH or –SO$_3$H. As the solution pH changes from acid to base, the acid form is changed into its conjugate base. These two forms must have distinctly different colours if the compound is to be an indicator.

Fig 3.3 shows the forms of phenolphthalein which is colourless in the acid form and pink in the basic form

![Acid form](image1) ![Base form](image2)

**Acid form**

**Base form**

Fig 3.3 Forms of phenolphthalein

It is important to note that the **colour change of an indicator is not dependent on the solution being titrated**. The indicator changes colour at a particular pH. The indicator chosen for a titration must change colours at the pH of the equivalence point.

**Table 3.1** Some common acid-base indicators

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH range of Colour Change</th>
<th>Colour Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>3.2-4.4</td>
<td></td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.8-6.0</td>
<td></td>
</tr>
<tr>
<td>Bromothymol Blue</td>
<td>6.0-7.6</td>
<td></td>
</tr>
<tr>
<td>Phenol Red</td>
<td>6.8-8.4</td>
<td></td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>8.2-10.0</td>
<td></td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>9.3-10.5</td>
<td></td>
</tr>
</tbody>
</table>
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Choosing the correct indicator

The pH at equivalence point varies depending on the reaction. It may be neutral, alkaline or acidic even though the products are a salt and water.

**Strong Acid vs Strong Base**
The equivalence point for this reaction is pH 7 as a neutral salt is formed

\[
\text{Strong acid} + \text{Strong Base} \rightarrow \text{Neutral salt} + \text{water}
\]

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}
\]

Fig 3.4 shows the dramatic change in pH at the equivalence point. For the strong acid and strong base this is at pH 7. A suitable indicator would be one that has its colour change range in this region. The salt formed in this reaction is neutral, it does not undergo hydrolysis.

![Titration diagram](image)

Fig 3.4 Titration of strong acid by strong base

Draw a diagram for the titration of a strong base by a strong acid and select a suitable indicator for the titration from Table 3.1
The salt formed in the titration is not always neutral. Where a weak acid or base is involved, the salt becomes the conjugate partner i.e. at equivalence point the solution will contain a weak acid or base and therefore have a pH greater or less than 7 as the salt undergoes hydrolysis with water.

**Strong Acid vs Weak Base**
The equivalence point for this reaction is less than 7 and the indicator chosen must therefore change colour in the acid region.

\[
\text{Strong Acid} + \text{Weak Base} \rightarrow \text{Acidic Salt} + \text{water}
\]

\[
\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}
\]

![Graph showing pH vs mL weak base added](image)

Fig 3.5  Strong acid titrated with a weak base
Note that the equivalence point is below 7 in Fig 3.5

Draw a diagram for the titration of a weak base with a strong acid and choose a suitable indicator from Table 3.1
**Strong Base vs Weak Acid**

The equivalence point for this reaction is greater than 7 and the indicator must change colour in the alkaline region.

\[
\text{Weak acid} + \text{Strong Base} \rightarrow \text{Basic salt} + \text{water}
\]

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

Fig 3.6  Titration of a weak acid by a strong base

Note that the equivalence point is above 7 in Fig 3.6

Draw a diagram representing the change in pH for the titration of a strong base by a weak acid and choose a suitable indicator from those provided in Table 3.1
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A weak acid titrated with a weak base (or vice versa) does not exhibit the same dramatic pH change in the vicinity of the equivalence point. There is only an inflection point, which does not allow using an indicator to show the approximate equivalence point.

The most appropriate indicator for an acid-base titration is one which has its colour change in the vicinity of the equivalence point. Where there is a large pH jump more than one indicator would be satisfactory. When selecting the indicator factors such as the nature of the colour change may also need to be considered.

Phenolphthalein has a dramatic colour change, from colourless to bright purple/pink. This makes it easy to recognise.

Methyl orange has a colour change of red to yellow…….this fades to orange as the titration proceeds …..this makes the actual colour change difficult to detect. A sharper and more pronounced colour change can be obtained by mixing the indicator solution with a neutral dye. The new solution is known as a screened indicator. The pH at the colour change is not altered, only the colours. For screened methyl orange the colour change is from green (at high pH) through to grey and then to red (at low pH).

Universal indicators are mixtures of a number of standard indicators, designed so there is a series of colour changes at intervals across a wide pH range. The commonly encountered formulation contains, phenolphthalein, methyl orange, methyl red and bromothymol blue. The gradual change of colour with pH makes them generally unsuitable for endpoint detection.

QUESTIONS

Concepts
1. Give three reasons why KHP is an ideal primary standard for alkaline solutions
2. Why is phenolphthalein ideal for the detection of neutral or alkaline endpoint titrations?
3. Explain the difference between normal, screened and universal indicators.
4. What indicator would be suitable for the following titrations (a) NaHCO₃ with HCl (b) white wine with NaOH?
5. Why would the MgCO₃ content of a rock sample be analysed by back titration?
6. Explain why an acid-base titration would not be suitable for the analysis of citric acid only in a fruit juice sample.
7. Calculate the molarity of the unknown solution
   a. 25.3 mL of 0.103M NaOH solution neutralises 20.0 mL of H₃PO₄
   b. 0.4926 g of potassium hydrogen phthalate is neutralised by 18.3 mL of NaOH
   c. 0.2173g of sodium carbonate is neutralised by 23.5 mL H₂SO₄
   d. 21.8 mL of 0.0946 M KOH neutralises 10.0 mL HCH₃COO
8. Baking soda is essentially pure sodium hydrogen carbonate, NaHCO₃. Routine analysis requires titration with standardised HCl. A new batch of approximately 0.1M HCl is standardised with anhydrous Na₂CO₃. After standardisation, samples of the baking soda are titrated to endpoint with the HCl. Calculate the purity of the baking soda, given the following results:  
   **HCl standardisations**
   Mass of Na₂CO₃ (g): 0.1502  0.1496  0.1482  
   Volume of HCl (mL) 27.4  27.3  27.0  
   **Baking soda analysis**
   Mass of baking soda (g) 0.1943  0.2031  0.1985  
   Volume of HCl (mL) 21.8  22.7  22.3
9. A 25.0 mL sample of white wine was titrated to the endpoint with 25.6 mL of 0.0809M NaOH. Determine the acid content of the wine as grams tartaric acid (FW = 150) per 100mL, given that two moles of OH\(^-\) are required to neutralise one mole of tartaric acid.

10. Vitamin C tablets contain a weak acid, ascorbic acid (FW = 176). A 6-tablet sample is dissolved in 250.0 mL of purified water. 50.0 mL aliquots are titrated with 0.163 M NaOH, the reaction having a 1:1 ratio and require an average of 12.55 mL to reach endpoint. What is the average mass of ascorbic acid in each tablet?

11. A solution of KOH is standardised by titrating potassium hydrogen phthalate. 0.3720g of the primary standard requires 16.7 mL of KOH solution to reach endpoint. The KOH is then used to analyse the total acidity of a lemon juice sample. 20.0 mL of juice was diluted to 100.0 mL and a 25.0 mL aliquot of this required 19.4 mL of KOH to reach endpoint. What is the acid content of the lemon juice (in grams of citric acid/100 mL), given that citric acid has a formula weight of 192 g and is triprotic.

12. A sample of impure calcium carbonate weighing 0.3448g is treated with 50.0 mL of 0.136 M HCl. The excess acid requires 7.4 mL of 0.0925M NaOH for back titration. Calculate the % CaCO\(_3\) in the sample.

13. A toothpaste sample weighing 1.008 g is to be analysed by back titration for its CaCO\(_3\) content. It is known that the % CaCO\(_3\) is approximately 40%. What volume of 0.2M HCl should be pipetted into the flask containing the toothpaste to give a back titration of about 20 mL of 0.1M NaOH?

14. A 0.9943g sample containing sodium carbonate and sodium hydrogen carbonate is dissolved in purified water and titrated with 0.114M HCl. The burette reading at the phenolphthalein endpoint is 17.5 mL; at the methyl orange endpoint it is 40.1 mL. Calculate the percentage composition of each component.

15. A 0.5219 g sample of a hydroxide of a metal from Group 2A in the Periodic Table is dissolved in 50.0 mL of 0.226M HCl. If 26.3 mL of 0.104 M NaOH is used in the back titration, which metal ion is in the sample?