

VOLUMETRIC ANALYSIS

Neutralisation reactions are widely used in what is called volumetric analysis.

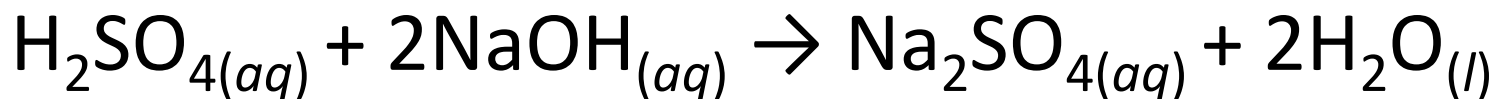
Volumetric analysis is a form of chemical analysis in which the concentration (or amount) of a substance A is determined by **measuring the volume of a solution of known concentration** of another substance B which is **just sufficient** to react with all of the sample of A.

- The process of determining the 'just sufficient' volume is called **titration**
- For a titration to work we need to be able to detect what is called the **equivalence point** of the reaction.

Equivalence point

- The equivalence point of a chemical reaction is the point at which the amounts of the two reactants are just sufficient to cause complete consumption of both reactants.
- The equivalence point is sometimes called the end point.
- We detect the equivalence point of a titration by using an indicator.

- If we have, say, 0.10 mole of sodium hydroxide, then the equivalence point is when 0.050 mole of sulfuric acid has been added, because the equation for the reaction is:



- Volumetric analysis requires that one solution must have an **accurately known concentration**.
- This solution is called the *standard solution*.
The standard solution may be either a **primary standard** or a secondary standard.

A Primary standard

The properties of a primary standard are:

- high level of purity
- accurately known composition
- free of moisture
- stable and unaffected by air during weighing
- readily soluble in pure (distilled) water
- high molar weight solid to reduce the percentage error in weighing
- reacts instantaneously and completely

Many pure substances do not have all these properties.

For example:

- concentrated hydrochloric acid is not suitable as a primary standard as it fumes and loses HCl gas
- concentrated sulfuric acid is not a suitable primary standard as it absorbs water from the atmosphere
- sodium hydroxide is unsuitable as a primary standard as it absorbs moisture from the air during weighing; this property is called *deliquescence*; it also reacts with carbon dioxide in the air and forms sodium hydrogen carbonate
- hydrated sodium carbonate is also unsuitable as a primary standard as it effloresces (loses water) as it is being weighed. Its composition is therefore uncertain.

Primary Standard

- Anhydrous sodium carbonate, however, is a suitable primary standard.
- The white solid is dried in a drying oven and then allowed to cool in a desiccator. The final product is free of water.

Acid standards	Base standards
potassium hydrogen phthalate	sodium carbonate
benzoic acid	sodium hydrogen carbonate
oxalic acid	borax

Secondary standards

Secondary standards are solutions whose concentrations have been determined using primary standards.

Thus a **hydrochloric acid** solution can become a secondary standard by reacting it first with a known primary standard such as sodium carbonate solution.

Sodium hydroxide can be used as a secondary standard after standardising against a standard acid such as potassium hydrogen phthalate solution.

- *describe the correct technique for conducting titrations and preparation of standard solutions*

Preparing a primary standard

- The following steps describe the procedure to prepare 250 mL of 0.0500 mol/L sodium carbonate solution. The mass of sodium carbonate required can be calculated as follows:

$$M(\text{Na}_2\text{CO}_3) = 105.99 \text{ g/mol}$$

$$n = cV$$

$$= (0.0500)(0.250)$$

$$= 0.0125 \text{ mol Na}_2\text{CO}_3$$

$$m(\text{Na}_2\text{CO}_3) = nM$$

$$= (0.0125)(105.99)$$

$$= 1.325 \text{ g}$$

Preparing a primary standard



1. Weigh the solid



2. Stir to dissolve solid



3. Transfer to solution

4. Add water upto the mark. Add stopper and mix.

(the volumetric flask must be rinsed with *distilled water* only)

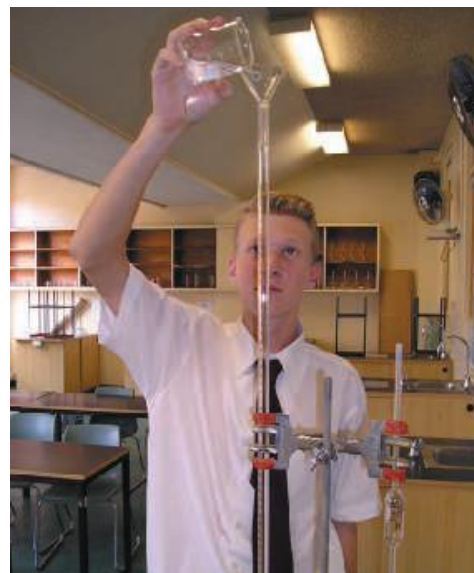
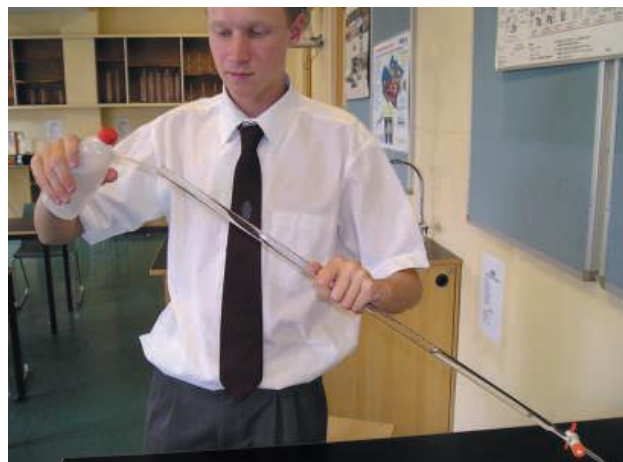
Titration techniques and calculations

- Example:

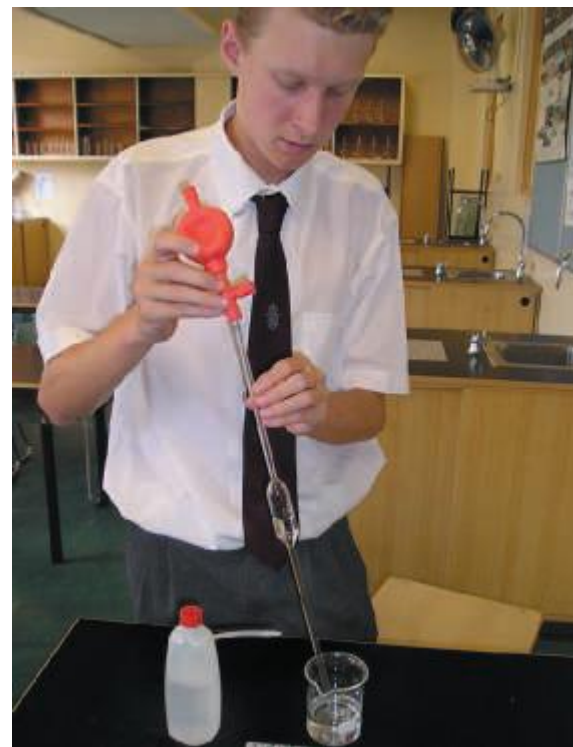
Standardising 0.1 mol/L Nitric acid using 0.0500 mol/L sodium carbonate

Rinse the burette first with distilled water and finally with the *solution to be measured*.

- Fill a *burette* with a solution of known concentration (0.1 mol/L Nitric acid) and adjust the solution level in the burette to the zero mark; the solution in the burette is called the **titrant**.
- *titrant: the solution that is added from the burette*



- Place a solution of the sample to be analysed (0.0500 mol/L sodium carbonate) in a flask under the burette. This is the aliquot.
- Measure this solution using a pipette, first rinsed with distilled water and then with the *solution to be measured*.
- Rinse the conical flask with *distilled water* only.
- *aliquot: a known volume of a liquid (taken in the conical flask)*



- Add one or two drops of a suitable indicator to the flask.

CHOICE OF INDICATOR

Titration	Suitable indicator	Colour change	pH range
strong acid–weak base	methyl orange	red–yellow	3.1–4.4
	bromophenol blue	yellow–blue	3.0–4.6
	bromocresol green	yellow–blue	3.8–5.4
	methyl red	pink–yellow	4.4–6.0
strong acid–strong base	litmus	red–blue	6–8
	bromothymol blue	yellow–blue	6.2–7.6
	phenol red	yellow–red	6.8–8.4
weak acid–strong base	thymol blue	yellow–blue	8.0–9.6
	phenolphthalein	colourless–red	8.3–10.0

- Place a white tile or card under the flask to make it easier to detect the colour change in the indicator without overshooting the equivalence point.
- Slowly run solution from the burette into the flask with continuous swirling until the indicator just changes colour; near the equivalence point add the titrant slowly, one drop at the time.



- Read the volume delivered by the burette as accurately as possible.
- Repeat the titration several times until a consistent volume of titrant is obtained (volumes differing by no more than about ± 0.1 or ± 0.2 mL); often the first titration will overshoot the equivalence point, because we do not know at what approximate volume it will occur.

Calculating the concentration of the unknown acid

The following data were collected for the sodium carbonate – nitric acid titration.

Volume of sodium carbonate solution = 25.00 mL

Concentration of sodium carbonate solution = 0.0500 mol/L

Run	Volume of nitric acid (mL)
Rough	22.65
1	22.40
2	22.35
3	22.35
4	22.40
Mean	22.38

Calculations

The neutralisation equation shows a 2 : 1 (acid : base) reaction



- ***Sample calculation:***

Number of moles of base used:

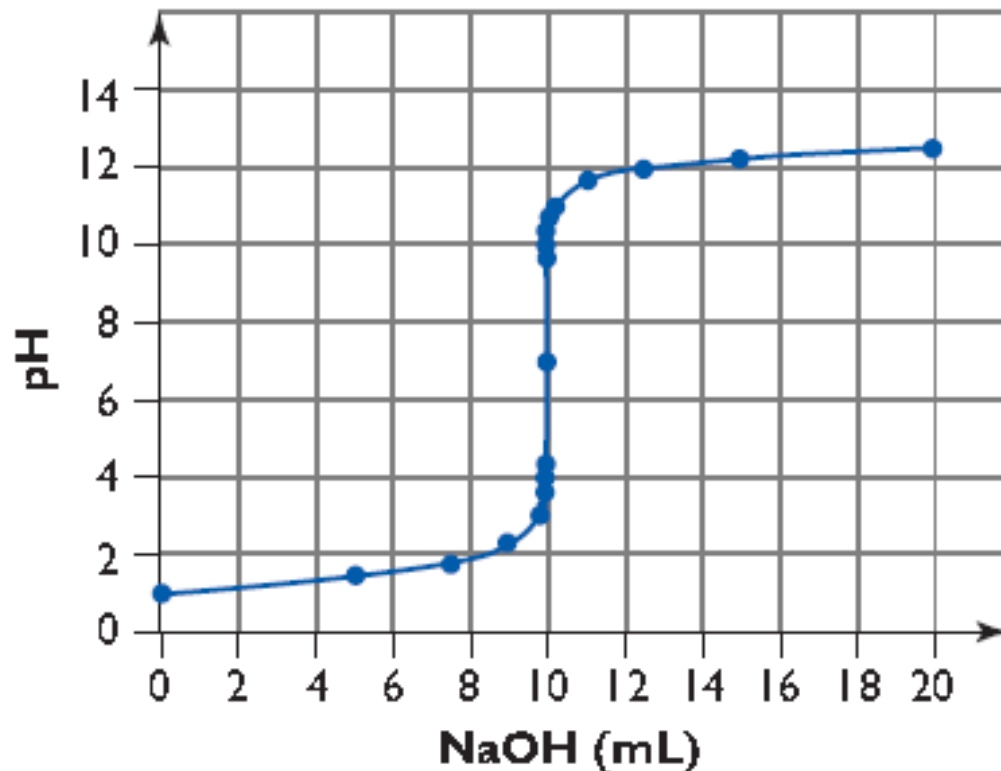
$$\begin{aligned} n(\text{Na}_2\text{CO}_3) &= cV \\ &= (0.0500)(25.00 \times 10^{-3}) \\ &= 1.250 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} n(\text{HNO}_3) &= 2n(\text{Na}_2\text{CO}_3) \\ &= 2(1.250 \times 10^{-3}) \\ &= 2.500 \times 10^{-3} \text{ mol} \end{aligned}$$

Concentration, c , of nitric acid:

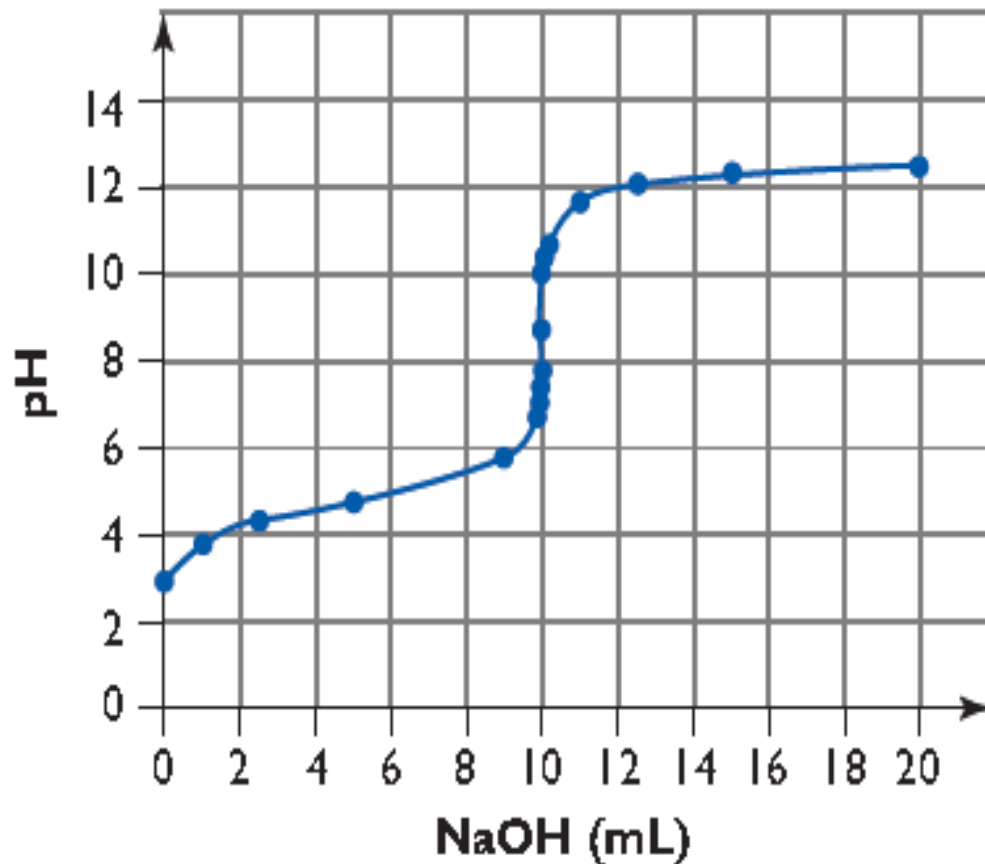
$$\begin{aligned} c &= n/V \\ &= (2.500 \times 10^{-3}) / (22.38 \times 10^{-3}) \\ &= 0.112 \text{ mol/L} \end{aligned}$$

Strong-acid – strong-base titration



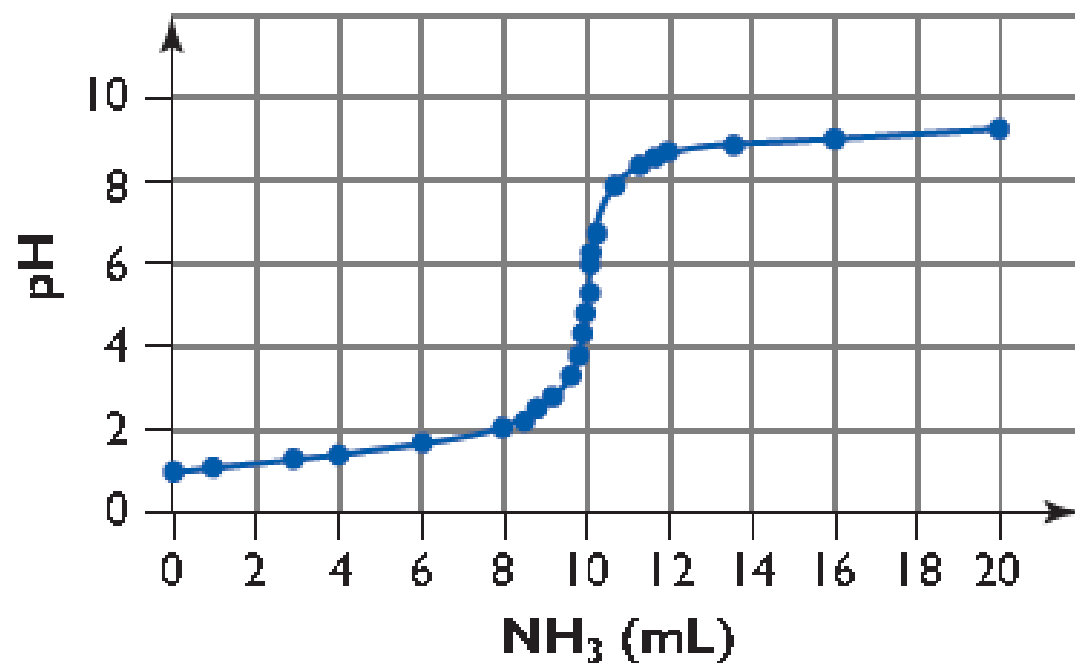
During the titration of HCl with NaOH the pH does not rise appreciably until near the equivalence point. The pH rises rapidly from 3 to 10 on the addition of about 1 drop of base. The equivalence point for this titration occurs at a pH of 7.

Weak acid – Strong base titration



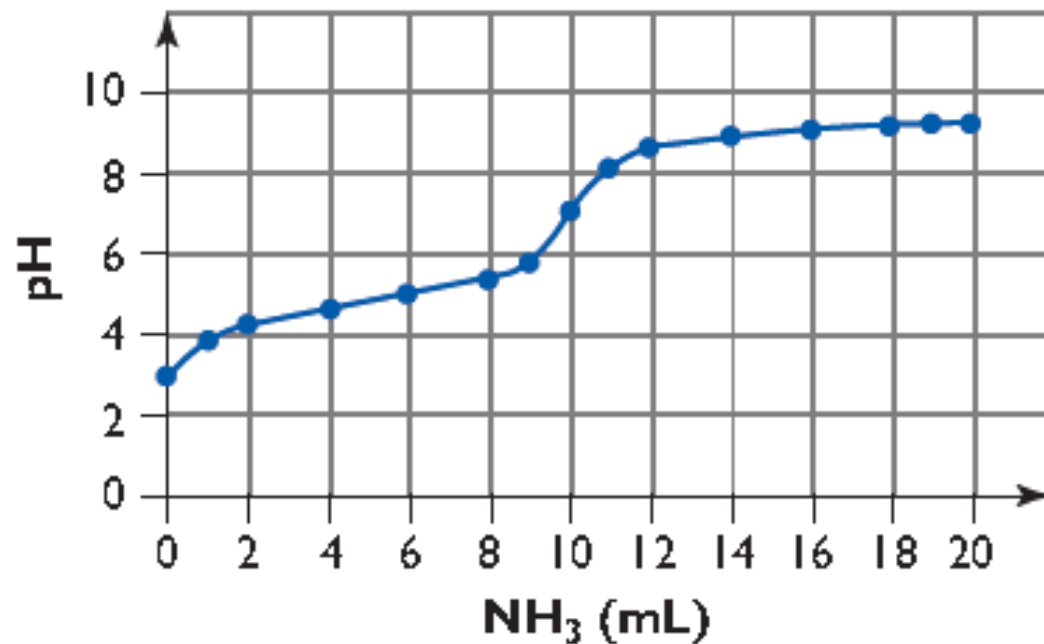
During the titration of acetic acid with sodium hydroxide solution, the pH rise at the equivalence point is not as marked as in the strong-acid – strong-base titration. The equivalence point occurs at about pH 8.7.

Strong acid - Weak base titration



During the titration of HCl with NH₃ solution, the pH change at the equivalence point is not as marked as in the strong-acid – strong base titration. The equivalence point occurs at about pH 5.3.

Weak acid – Weak base titration



In the titration of 0.10 mol/L acetic acid with 0.10 mol/L ammonia solution there is only a gradual rise in pH. No single indicator can detect the equivalence point as there is no sharp end point. The equivalence point occurs at about pH 7.0.

Questions

Figure 9.27 shows some titration curves involving different acids and bases.

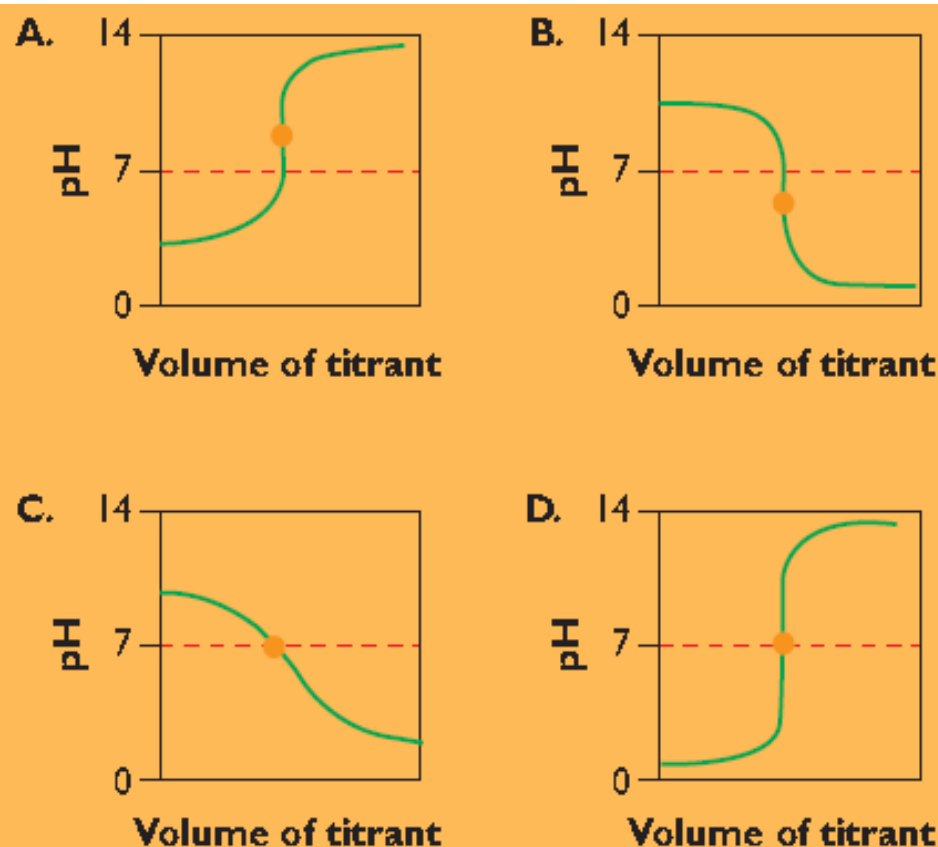


Figure 9.27 Use these pH graphs to answer the following question.

Identify the:

- (a) titration (A, B, C and/or D) in which phenolphthalein would have been a suitable indicator
- (b) titration(s) in which a weak acid was initially present in the conical flask
- (c) titration in which a weak base was neutralised by a strong acid
- (d) titration(s) in which an acid is added from the burette.

2

The following steps are used in the preparation of a standard solution of sodium carbonate. The steps are listed in random order. Select the response in which the steps are placed in the correct order.

- (i) Stopper the volumetric flask and invert it to mix the contents thoroughly.
 - (ii) Transfer the sodium carbonate solution from the beaker into the volumetric flask.
 - (iii) The dry solid is weighed into a clean, dry 50 mL beaker on an electronic balance.
 - (iv) Use a plastic wash bottle to add a little distilled water to the beaker; and use a fine, short, glass rod to stir the mixture to dissolve the sodium carbonate.
 - (v) The solid is dried at 150–180°C in a drying oven for 30 minutes and then allowed to cool in a desiccator containing drying crystals.
- A (v), (iii), (iv), (ii), (i)
 - B (iii), (v), (ii), (iv), (i)
 - C (i), (ii), (iv), (iii), (v)
 - D (iv), (v), (iii), (i), (ii)

3

A 50 mL burette is to be used in a titration. Identify the procedure that is used to prepare the burette for use.

- A Rinse the burette with tap water several times and leave it wet.
- B Rinse the burette with distilled water several times and then with the solution to be used several times.
- C Rinse the burette, using only the solution to be used in it.
- D Dry the burette in a low temperature drying oven prior to use.

4

Select the correct procedures to be used in preparing a pipette and conical flask for use in a titration.

- A Rinse both the pipette and flask with water several times prior to use.
- B Rinse the pipette with water, but dry the flask in the drying oven.
- C Rinse both the conical flask and pipette with water and then rinse the pipette several times with the solution to be placed in it.
- D Wash the flask and pipette, using only the solution to be placed in them.

$$\text{Number of moles} = \frac{\text{mass}}{\text{molar mass}} \quad \dots (5.14)$$

$$\text{Molarity} = \frac{\text{number of moles}}{\text{volume of solution in litres}} \quad \dots (5.15)$$

Example 1

15.922 g sodium carbonate was dissolved in water and made up to 500 mL in a volumetric flask. Calculate the molarity of this solution.

We calculate the molarity of the sodium carbonate solution using Equations 5.14 and 5.15.

$$\begin{aligned} \text{Molar mass of Na}_2\text{CO}_3 &= 2 \times 23.0 + 12.0 + 3 \times 16.0 \\ &= 106.0 \text{ g/mol} \end{aligned}$$

From Equation 5.14:

$$\begin{aligned} \text{number of moles of Na}_2\text{CO}_3 \text{ taken} &= \frac{15.922}{106.0} \\ &= 0.1502 \text{ mol} \end{aligned}$$

From Equation 5.15:

$$\begin{aligned} \text{molarity} &= \frac{0.1502}{0.500} \\ &= 0.3004 \text{ mol/L} \end{aligned}$$

Example 2

To standardise a roughly 0.4 mol/L hydrochloric acid solution, 25.0 mL of the sodium carbonate solution from Example 1 was titrated with this hydrochloric acid. It required 38.2 mL of the acid to reach the equivalence point. Calculate the accurate molarity of the hydrochloric acid solution.

From the titration, using Equation 5.15 rearranged,

$$\begin{aligned}\text{number of moles of Na}_2\text{CO}_3 \text{ used} &= \frac{0.3004 \times 25}{1000} \\ &= 7.51 \times 10^{-3} \text{ mol}\end{aligned}$$

The equation for the titration is:



$$\therefore \frac{\text{number of moles of HCl present}}{\text{number of moles of Na}_2\text{CO}_3 \text{ used}} = \frac{2}{1}$$

$$\begin{aligned}\text{So number of moles of HCl present} &= 2 \times (\text{number of moles of Na}_2\text{CO}_3 \text{ used}) \\ &= 2 \times 7.51 \times 10^{-3} \\ &= 0.0150 \text{ mol}\end{aligned}$$

This amount of HCl was present in 38.2 mL (= 0.0382 L)

\therefore by Equation 5.15

$$\begin{aligned}\text{molarity of HCl solution} &= \frac{0.0150}{0.0382} \\ &= 0.393 \text{ mol/L}\end{aligned}$$

The accurate concentration of the 'roughly 0.4 mol/L' hydrochloric acid is **0.393 mol/L**.

Example 3

In order to determine the concentration of acetic acid in a particular brand of vinegar, a chemist first diluted 10 mL of the vinegar to exactly 100 mL, then took 25 mL of the dilute solution and titrated it with 0.105 mol/L sodium hydroxide. 15.9 mL of the sodium hydroxide solution was needed. Calculate the molarity and the percentage (w/v) of acetic acid in the original vinegar.

$$\begin{aligned}\text{Number of moles of NaOH used in the titration} &= 0.0159 \times 0.105 \\ &= 1.67 \times 10^{-3} \text{ mol}\end{aligned}$$

The chemical equation for the titration reaction is:



From this equation:

$$\begin{aligned}\text{number of moles of acetic acid} \\ \text{present in the titrated sample} &= \text{number of moles of NaOH used} \\ &= 1.67 \times 10^{-3}\end{aligned}$$

This amount of acetic acid was in 25 mL (= 0.025 L) of the dilute solution

$$\begin{aligned}\text{so} \quad \text{molarity of dilute solution} &= \frac{1.67 \times 10^{-3}}{0.025} \\ &= 0.0668 \text{ mol/L}\end{aligned}$$

This is the molarity of acetic acid in the *diluted* vinegar. To calculate the molarity of the concentrated solution (Z_1 , say),

$$\begin{array}{l} \text{number of moles of acetic acid} \\ \text{in 10 mL concentrated solution} \end{array} = \begin{array}{l} \text{number of moles of acetic} \\ \text{acid in 100 mL dilute solution} \end{array}$$

Therefore

$$\frac{Z_1 \times 10}{1000} = \frac{0.0668 \times 100}{1000}$$

giving

$$\begin{array}{l} \text{molarity of acetic acid} \\ \text{in the original vinegar, } Z_1 = \mathbf{0.668 \text{ mol/L}} \end{array}$$

The percentage (w/v) is the mass of acetic acid per 100 mL of solution. From the molarity we have 0.0668 mol per 100 mL.

$$\begin{aligned} \text{Molar mass of acetic acid, CH}_3\text{COOH} &= 2 \times 12.0 + 4 \times 1.01 + 2 \times 16.0 \\ &= 60.0 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{so } 0.0668 \text{ mol/100 mL} &= 0.0668 \times 60.0 \\ &= 4.01 \text{ g/100 mL} \end{aligned}$$

Therefore the percentage of acetic acid in the original vinegar is **4.01%(w/v)**.

A cleaning product called 'cloudy ammonia' can be purchased at the supermarket. It is used to clean floors and greasy surfaces.

A sample of the cloudy ammonia was analysed by titration to determine the ammonia concentration. The cloudy ammonia was first diluted by a factor of 1 in 100. A sample of 25.00 mL of the diluted ammonia was pipetted into a conical flask and titrated against a standardised hydrochloric acid solution (0.0210 mol/L). Using a phenolphthalein indicator, the average titre was 32.85 mL.

Calculate the concentration of ammonia in the cloudy ammonia in (a) mol/L (b) g/L.

Step 1. Write a balanced equation for the neutralisation reaction.



There is a 1 : 1 reaction stoichiometry.

Step 2. Calculate the number of moles of HCl required to achieve the end point.

$$\begin{aligned} n &= cV = (0.0210) (32.85 \times 10^{-3}) \\ &= 6.899 \times 10^{-4} \text{ mol} \end{aligned}$$

Step 3. Calculate the number of moles of NH_3 in the 25 mL of ammonia solution.

$$\begin{aligned} n(\text{NH}_3) &= n(\text{HCl}) \\ \text{so } n(\text{NH}_3) &= 6.899 \times 10^{-4} \text{ mol} \end{aligned}$$

Step 4. Calculate the concentration of the diluted ammonia solution

$$\begin{aligned}c(\text{NH}_3) &= n/V = 6.899 \times 10^{-4}/0.02500 \\ &= 0.0276 \text{ mol/L}\end{aligned}$$

Step 5. Calculate the concentration of ammonia in the cloudy ammonia.

$$\begin{aligned}c(\text{NH}_3) &= 100 \times 0.0276 \\ &= 2.76 \text{ mol/L}\end{aligned}$$

Step 6. Calculate the concentration in g/L

$$\begin{aligned}M(\text{NH}_3) &= 17.034 \text{ g/mol} \\ c(\text{NH}_3) &= 2.76 \times 17.034 \\ &= 47.0 \text{ g/L}\end{aligned}$$