# Volumetric analysis

There are two main types of chemical analysis—qualitative and quantitative. In qualitative analysis, chemists identify the substances that are present. For example, they might determine what type of acid, what metal or whether a salt is a chloride or a bromide. Quantitative analysis determines how much of a substance is present. Quantitative analysis can use physical methods or chemical methods for determining quantities of chemicals. Volumetric analysis is an example of chemical quantitative analysis. It involves using a chemical reaction, and the equation for that reaction, to calculate the unknown amount of one chemical, in this case, an acid or a base, from the known quantity of the acid or base that it is reacting with.

There are many situations in which a chemist may want to find the amount of a substance in solution, such as the amount of a chemical present in industrial or mining wastes, the composition of antacid tablets or the acidity of polluted rainwater.

This chapter begins by introducing a few examples of where knowing the amount or concentration of an acid or a base is important. It then describes a method used for the analysis of acids and bases in water. This is volumetric analysis, often called titration, and involves chemical reactions between accurately measured quantities of substances in aqueous solution. During this chapter, you will be using chemistry calculation skills that you have learnt earlier in the course, as well as knowledge of acids and bases, and indicators as encountered in Chapters 4 and 6.

Volumetric analysis requires the measuring of accurate volumes using specialised pieces of glassware. This chapter also includes the equipment and techniques of volumetric analysis, as well as the specific calculation skills involved. It concludes by considering the issues of accuracy of measurements and sources of error in volumetric analysis.

## Science understanding

- acid–base indicators are weak acids, or weak bases, in which the acidic form is a different colour from the basic form
- volumetric analysis methods involving acid–base reactions rely on the identification of an equivalence point by measuring the associated change in pH, using appropriate acid–base indicators or pH meters, to reveal an observable end point
- data obtained from acid–base titrations can be used to calculate the masses of substances and concentrations and volumes of solutions involved

# 7.1 Acids and bases in water

Pure water has a pH of 7 at 25°C, which is described as neutral. A substance that dissolves in water to give a pH of less than 7 is described as acidic while a substance that gives a pH greater than 7 is described as basic. pH is a measure of the acidity of an acidic or basic solution and the pH of a solution is linked to the concentration of the hydrogen ions in the solution.

Volumetric analysis is a technique that can be used in a range of situations to calculate accurate quantities of acid or base in a sample of a substance. This data can then be used to compare different substances (for example, the acid contents of different wines or car batteries) or measure changes in the acidity of solutions over time (for example, monitoring the acidity of rain water or run-off from polluted industrial or mine sites)

Common acids include hydrochloric acid, produced naturally in the stomach to help with digestion and citric acid, naturally found in citrus fruits. Another common acid is sulfuric acid, an important industrial acid. It is used in many different industries, for example to treat steel, to make fertiliser and in car batteries.

The following situations are examples of where it may be important to determine the concentration and/or the amount of acid or base present.

## NATURAL ACIDITY OF RAIN AND RIVER WATER

You might expect rainwater, oceans and mountain streams to have a neutral pH. However, unpolluted rainwater has a pH between 5.5 and 6, and rainwater falling near large cities and industrial areas can be even more acidic.

Water in even the most pristine, unpolluted rivers and lakes has a pH in the range 6.5–8.5. Domestic, agricultural and industrial wastes discharged into rivers can further affect the pH.

### pH of rainwater

The natural acidity of rainwater is due to the presence of carbon dioxide in the atmosphere. Carbon dioxide dissolves in rain, forming a very dilute solution of carbonic acid ($H_2CO_3$):

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
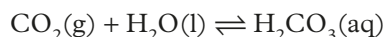
Carbonic acid is a weak acid and only donates a proton to a limited extent to form hydrogencarbonate ions ($HCO_3^-$) and hydronium ions ($H_3O^+$) in solution. You will recall that the properties of acid solutions are due to the presence of hydronium ions. This process is represented by the following equation:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$
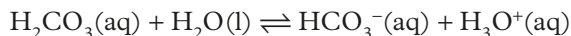
Small amounts of oxides of nitrogen, NO and $NO_2$, are formed during lightning strikes. Sulfur dioxide ($SO_2$) is emitted by volcanic eruptions. The acidic oxides, $NO_2$ and $SO_2$, in the atmosphere only make a minor contribution to the natural acidity of rainwater.

### ACID RAIN

Since the Industrial Revolution, human activity has produced more acidic gases than the amount produced by natural processes. This has resulted in an increase in the acidity (decrease in pH) of rain falling near or downwind from industrial areas, as shown in Figure 7.1.1. This is known as **acid rain**.

The pH of unpolluted rainwater is between 5.5 and 6, but the pH of rainwater in industrial areas may be close to 4 and has even been measured to be as low as 2.4.

Sulfur dioxide gas is the main cause of acid rain. It is produced by the burning of sulfur-containing fossil fuels:
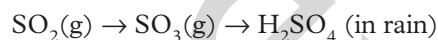
$$S(s) + O_2(g) \rightarrow SO_2(g)$$
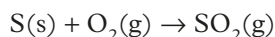
Sulfur dioxide is also produced in power stations and from the smelting of ores such as copper sulfide.
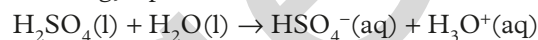
**FIGURE 7.1.1** Acid rain is formed downwind of industries that produce acidic gases such as sulfur dioxide. The acid rain leaches nutrients and toxic metals out of the soil, damaging vegetation.

The sulfur dioxide is converted to sulfuric acid in a series of reactions that occur in the atmosphere:

$$SO_2(g) \rightarrow SO_3(g) \rightarrow H_2SO_4 \text{ (in rain)}$$

Sulfuric acid is a strong, diprotic acid:

$$H_2SO_4(l) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$

The internal combustion engine is responsible for the emission of large amounts of nitrogen(II) oxide (NO) and nitrogen(IV) oxide ($NO_2$). Nitrogen(IV) oxide dissolves in water, forming acid rain. This acid rain is a mixture of nitrous acid ($HNO_2$) and nitric acid ($HNO_3$):

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

The acid rain created by power stations and smelters is particularly severe in parts of the United States, eastern Canada, Europe and Asia. Some industries, such as the smelting of ores containing metal sulfides, have produced localised acid rain in Australia. Stricter government regulations and international treaties aimed at reducing the emissions of sulfur dioxide and nitrogen oxides have been adopted. Regulations have decreased the concentration of these gases over recent years.

The acidity of rainwater can be measured by using an indicator such as universal indicator or by using a pH probe, which is more accurate. However, quantitative analysis techniques, such as volumetric analysis can be used to calculate more accurate data relating to the concentration of hydrogen (or hydronium) ions, and therefore the acidity of the water.

## ACIDS IN WINE

Grapes and several plants contain the naturally occurring acid tartaric acid (Figure 7.1.2). There are several acids present in wine, many of which form during the fermentation process. Two of the main acids present in wine occur naturally in the grape (fixed acids). Tartaric acid is the primary and strongest acid, giving wine its crisp, tart flavour. Malic acid is the other main acid. Both of these acids are weak dicarboxylic acids. Their structures are shown in Figure 7.1.3. Citric acid is also present in significant amounts and gives wine its fruity taste.

FIGURE 7.1.2 Malic acid is a common acid found in fruit but tartaric acid is mainly found in grapes

It is important that the wine has the correct level of acid, as too much will cause it to taste tart and sour, while too little will leave the wine tasting flat. The acidity of wine is referred to as total acidity (TA) and is expressed in grams per litre or as a percentage. TA will vary depending on the wine. Sweet wines for example tend to have a higher TA or $7.0–8.5\,\text{g}\,\text{L}^{-1}$, while dry wines have a TA of $6.0–7.5\,\text{g}\,\text{L}^{-1}$. To determine the total acidity of wine an acid-base titration can be performed.

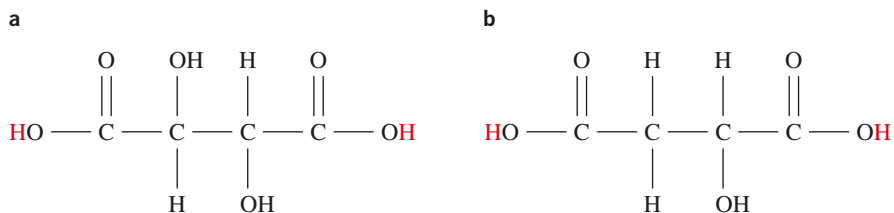Total acidity is also referred to as titratable acidity, as the acidity of wine is determined by titration.

FIGURE 7.1.3 The structural formula of the dicarboxylic acids (a) tartaric acid and (b) malic acid. They have two carboxyl groups and therefore two protons that can ionise (shown in red)

## The wine making process

The winemaking process will vary depending on whether the wine is red, white or sparkling, and then there are also fortified wines such as port and sherry to consider. Below is a general outline of the winemaking process.

1 The ripe grapes are picked and crushed in a press.

2 The crushed grapes and juice are drained from the stems and seeds. At this stage the juice is referred to as the must. The skin is left with the must for red wine. For white wines the skin is separated and only the pulp is used. Red wines are fermented with their skins to give colour and tannins to the wine.

3 The must is added to a vat, barrel or tank along with yeast to ferment for two to four weeks. To ensure the process is proceeding correctly, the fermenting must is checked regularly for acceptable pH levels. This can be done using volumetric analysis.

4 The wine is stored in oak barrels or stainless steel tanks for aging, which can take from a few months to several years.

5 The wine is racked (by siphoning or pouring) to remove it from the lees (impurities, including the yeast, insoluble salts and remnants of grapes). Some winemakers leave the wine in contact with the lees to allow more flavour to develop.

6 The wine is bottled. Further ageing may occur in the bottle (Figure 7.1.4).

7 Sample testing of the wine, including using volumetric analysis, continues during this storage period.



**FIGURE 7.1.4** The bottling of wine is an automated process in many wineries. After bottling, further ageing may occur, particularly for red wine

# 7.1 Review

### SUMMARY

- Natural and artificial processes affect the acidity of rainwater and waterways.
- Rainwater is naturally acidic due to the presence of dissolved carbon dioxide.
- Waste gases such as sulfur dioxide and nitrogen oxides that are produced by industry can cause acid rain.
- Unpolluted water in rivers and lakes has a natural pH between 6.5 and 8.5.
- Dissolved carbon dioxide tends to make river water acidic.
- There are many acids present in wine including the two naturally occurring, dicarboxylic acids, tartaric acid and malic acid.
- Total acidity is a measure of all the acid content of wine and is determined by titration.

### KEY QUESTIONS

1 What type of compounds tend to react with rainwater to lower its pH?

2 What is the source of nitrogen oxides and what effect do they have on the pH of rainwater?

3 Write a balanced equation for the reaction between sulfuric acid in acid rain and the limestone found in many statues and buildings.

4 Draw the structural formula of ethanoic (acetic) acid and tartaric acid. Circle the carboxylic acid functional groups in each and highlight the ionisable protons. Explain why ethanoic acid is a monoprotic acid and tartaric acid is called a diprotic acid.

# 7.2 Calculations involving acids and bases

In this section, you will revise how to calculate how much product is produced and how much reactant is required in these reactions.

For example, it is very useful to be able to determine how much:

- lime should be added to soil to increase its pH
- calcium carbonate should be used to neutralise hazardous acidic wastes from an industrial plant or a mine site
- phosphoric acid is in a cola drink
- stomach acid can be neutralised by an antacid tablet.

You will use your knowledge of the reactions of acids, your ability to write balanced chemical equations, and your understanding of the mole concept and mole relationships to carry out calculations involving acids and bases.

## REACTING QUANTITIES OF ACIDS AND BASES

Calculations based on the reactions of acids usually involve determining the number of moles of a substance.

You will recall from earlier chapters that the:

- coefficients in a balanced chemical equation give the ratio in which substances react
- amount of solid, in moles, can be calculated from the expression $n = \dfrac{m}{M}$
- where $m$ is the mass in grams and $M$ is the molar mass in $g\,mol^{-1}$
- amount of solute, in moles, in a solution is given by $n = cV$
- where $c$ is the concentration in $mol\,L^{-1}$ and $V$ is the volume in litres.

The following worked examples show the four main steps in solving calculation problems involving solutions of acids and bases.

1  Write a balanced equation for the reaction.
2  Identify the substance that is the 'known'. This is the substance for which there is enough information (normally the volume and concentration) to calculate the number of moles and calculate the amount, in mol, of this known substance.
3  Use the mole ratio from the equation to calculate the amount, in mol, of the 'unknown' substance.
4  Calculate the volume or concentration from the number of moles.

The steps in a stoichiometric calculation can be summarised as shown in the flow chart in Figure 7.2.1.
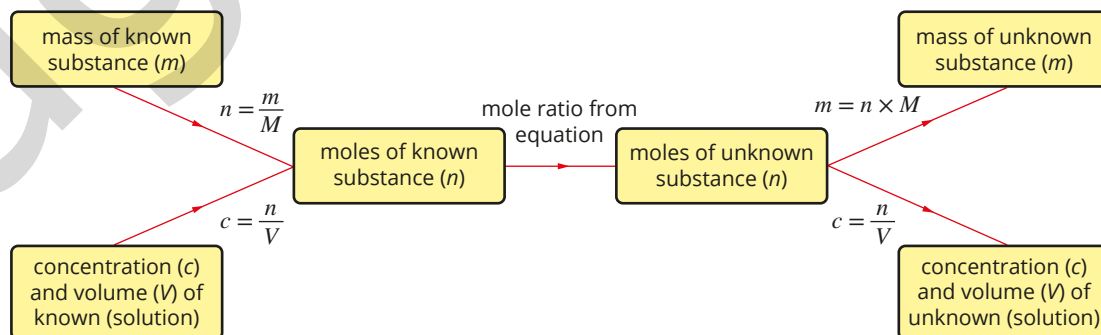


**FIGURE 7.2.1** Flow chart for mass and solution calculations

## Worked example 7.2.1

**A SOLUTION VOLUME–VOLUME CALCULATION**

What volume of $0.100 \, mol \, L^{-1}$ sulfuric acid reacts completely with $17.8 \, mL$ of $0.150 \, mol \, L^{-1}$ potassium hydroxide?

| Thinking | Working |
|---|---|
| Write a balanced full equation for the reaction. | $2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$ |
| Identify the 'known', and calculate the amount, in mol, of the substances with known volume and concentration. | Known is potassium hydroxide (the volume and concentration of potassium hydroxide solution are given). <br><br> Use $n = cV$ (remember that volume must be expressed in litres). <br><br> $n(KOH) = cV$ <br> $\qquad = 0.150 \times 0.0178$ <br> $\qquad = 0.00267 \, mol$ |
| Use the mole ratio from the equation to calculate the amount, in mol, of the required substance. | The balanced equation shows that 1 mol of sulfuric acid reacts with 2 mol of potassium hydroxide. <br><br> $\dfrac{n(H_2SO_4)}{n(KOH)} = \dfrac{1}{2}$ <br><br> $n(H_2SO_4) = \dfrac{1}{2} \times n(KOH)$ <br> $\qquad\quad = \dfrac{1}{2} \times 0.00267$ <br> $\qquad\quad = 0.00134 \, mol$ |
| Calculate the volume required. | The volume of $H_2SO_4$ is found by using $n = cV$. <br><br> $V(H_2SO_4) = \dfrac{n}{c}$ <br> $\qquad\quad\;\; = \dfrac{0.00134}{0.100}$ <br> $\qquad\quad\;\; = 0.134 \, L = 13.4 \, mL$ <br><br> So $13.4 \, mL$ of $0.100 \, mol \, L^{-1}$ $H_2SO_4$ will react completely with $17.8 \, mL$ of $0.150 \, mol \, L^{-1}$ KOH solution. |

## Worked example: Try yourself 7.2.1

**A SOLUTION VOLUME–VOLUME CALCULATION**

What volume of $0.500 \, mol \, L^{-1}$ hydrochloric acid (HCl) reacts completely with $25.0 \, mL$ of $0.100 \, mol \, L^{-1}$ calcium hydroxide ($Ca(OH)_2$) solution? The salt formed in this acid–base reaction is calcium chloride.

## Worked example 7.2.2

**A SOLUTION VOLUME–CONCENTRATION CALCULATION**

15.5 mL of dilute hydrochloric acid reacts completely with 20.8 mL of $0.0100$ mol L$^{-1}$ calcium hydroxide. Calculate the concentration of the hydrochloric acid.

| Thinking | Working |
|---|---|
| Write a balanced full equation for the reaction. | $Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$ |
| Identify the 'known', and calculate the amount, in mol, of the substance with known volume and concentration. | Known is calcium hydroxide (the volume and concentration of calcium hydroxide solution are given).<br><br>Use $n = cV$ (remember that volume must be expressed in litres).<br><br>$n(Ca(OH)_2) = cV$<br>$\qquad\qquad = 0.0100 \times 0.0208$<br>$\qquad\qquad = 0.000208$ mol |
| Use the mole ratio from the equation to calculate the amount, in mol, of the required substance. | The balanced equation shows that 2 mol of hydrochloric acid reacts with 1 mol of calcium hydroxide.<br><br>$\dfrac{n(HCl)}{n(Ca(OH)_2)} = \dfrac{2}{1}$<br><br>$n(HCl) = \dfrac{2}{1} \times n(Ca(OH)_2)$<br><br>$\qquad\quad = \dfrac{2}{1} \times 0.000208$<br><br>$\qquad\quad = 0.000416$ mol |
| Calculate the concentration required. | The concentration of HCl is found by using $c = \dfrac{n}{V}$.<br><br>$c(HCl) = \dfrac{n}{V}$<br><br>$\qquad\quad = \dfrac{0.000416}{0.0155}$<br><br>$\qquad\quad = 0.0268$ mol L$^{-1}$ |

## Worked example: Try yourself 7.2.2

**A SOLUTION VOLUME–CONCENTRATION CALCULATION**

20.5 mL of $0.200$ mol L$^{-1}$ hydrochloric acid reacts completely with 18.8 mL of sodium hydroxide solution. Calculate the concentration of the sodium hydroxide.

# 7.2 Review

## SUMMARY

- Given the quantity of one of the reactants or products in a chemical reaction, the quantity of all other reactants and products can be predicted by working through the following steps.
  1. Write a balanced equation for the reaction.
  2. Calculate the amount, in mol, of the known substance.
  3. Use the mole ratio of reactants and products in the balanced chemical equation to calculate the amount, in mol, of the unknown substance.
  4. Convert the amount, in mol, of the required substance to the quantity required in the question.
- The most common unit of concentration is moles per litre ($mol\,L^{-1}$). Volumes should be converted to litres before being used in these calculations.

## KEY QUESTIONS

1. A $0.100\,mol\,L^{-1}$ $H_2SO_4$ solution is neutralised with $10.0\,mL$ of a solution of $0.300\,M$ KOH.
   a. Write a balanced equation for this reaction.
   b. What volume of sulfuric acid was neutralised?
2. $15.0\,mL$ of a nitric acid solution is required to react completely with $10.0\,mL$ of a $0.100\,mol\,L^{-1}$ $Ca(OH)_2$ solution.
   a. Write a balanced equation for this reaction.
   b. What is the concentration of the nitric acid solution?
3. $18.26\,mL$ of dilute nitric acid reacts completely with $20.00\,mL$ of $0.09927\,mol\,L^{-1}$ potassium hydroxide solution.
   a. Write a balanced chemical equation for the reaction between nitric acid and potassium hydroxide.
   b. Calculate the amount, in mol, of potassium hydroxide consumed in this reaction.
   c. What amount, in mol, of nitric acid reacted with the potassium hydroxide in this reaction?
   d. Calculate the concentration of the nitric acid.

# 7.3 Standard solutions

**Volumetric analysis** can be used to accurately determine the concentration of solutions of acids and bases. This involves reacting the solution of unknown concentration with a solution of accurately known concentration (a **standard solution**). This section focuses on the preparation of standard solutions. Some of the equipment used to prepare a standard solution is shown in Figure 7.3.1.

## PRIMARY STANDARDS

Pure substances are widely used in the laboratory to prepare solutions of accurately known concentrations.

Substances that are so pure that the amount of substance, in moles, can be calculated accurately from their mass are called **primary standards**.

A primary standard should:
- be readily obtainable in a pure form
- have a known chemical formula
- be easy to store without deteriorating or reacting with the atmosphere
- have a high molar mass to minimise the effect of errors in weighing

Examples of primary standards are the base anhydrous sodium carbonate ($Na_2CO_3$) and the acid hydrated oxalic acid ($H_2C_2O_4.2H_2O$). (The term **anhydrous** indicates there is no water present in the compound.)

## PREPARING STANDARD SOLUTIONS

Standard solutions are prepared by dissolving an accurately measured mass of a primary standard in an accurately measured volume of water.

Digital balances are used in analytical laboratories to accurately weigh primary standards. A top-loading balance can weigh to an accuracy of between 0.1 g and 0.001 g depending on the model. Analytical balances can weigh to an accuracy of between 0.0001 g and 0.00001 g. The two types of balances commonly used can be seen in Figure 7.3.2.
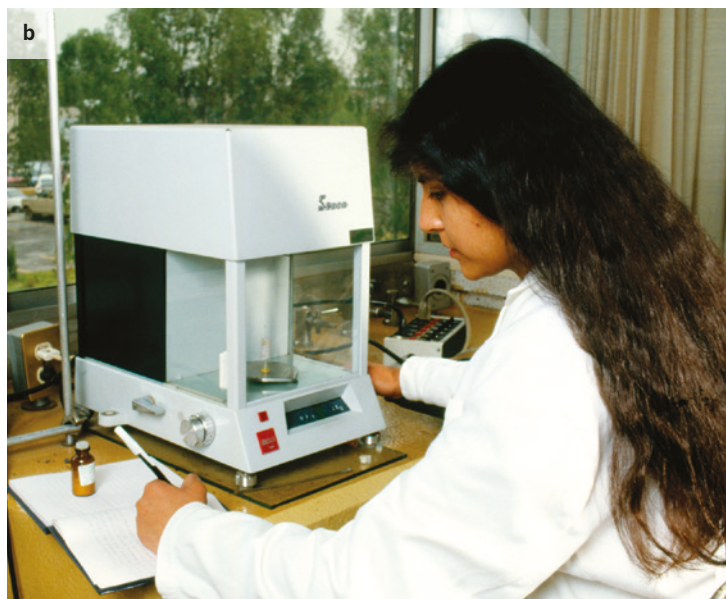


**FIGURE 7.3.1** Apparatus and materials needed to prepare a standard solution. The measured mass of solid will be dissolved in water in a volumetric flask to make an accurate volume of solution.



**FIGURE 7.3.2** (a) A top-loading balance and (b) an analytical balance can be used to accurately weigh substances used in chemical analysis.

A **volumetric flask** or standard flask (Figure 7.3.3) is used to prepare a solution that has an accurately known volume. Volumetric flasks of 50.00 mL, 100.00 mL and 250.0 mL are frequently used in the laboratory.

A volumetric flask is filled so that the bottom of the meniscus is level with the graduation line on the neck of the flask (Figure 7.3.4). Your eye should be level with the line to avoid **parallax errors**.



**FIGURE 7.3.4** This close-up view of the neck of a volumetric flask shows the bottom of the meniscus level with the graduation line.



**FIGURE 7.3.3** Volumetric flasks of various sizes are used to prepare standard solutions.

To prepare a standard solution from a primary standard, you need to dissolve an accurately known amount of the substance in distilled water to produce a solution of known volume. The steps in this process are shown in Figure 7.3.5.
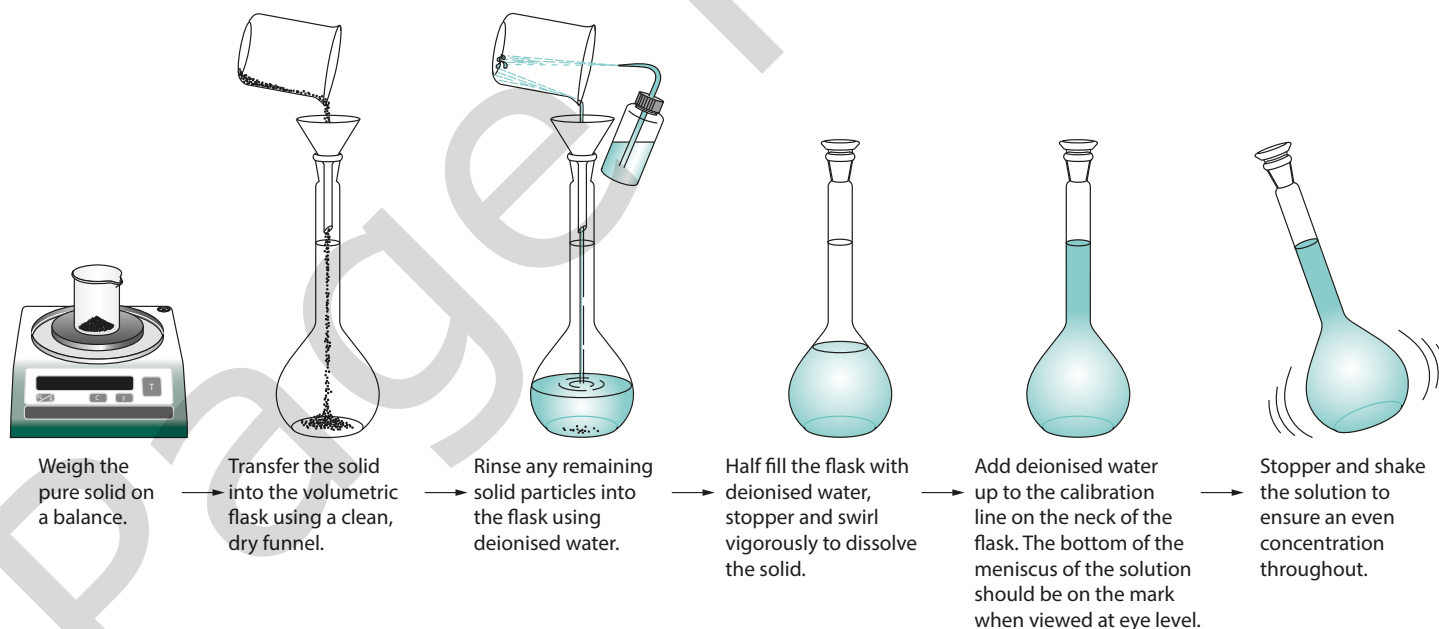


Weigh the pure solid on a balance.

Transfer the solid into the volumetric flask using a clean, dry funnel.

Rinse any remaining solid particles into the flask using deionised water.

Half fill the flask with deionised water, stopper and swirl vigorously to dissolve the solid.

Add deionised water up to the calibration line on the neck of the flask. The bottom of the meniscus of the solution should be on the mark when viewed at eye level.

Stopper and shake the solution to ensure an even concentration throughout.

**FIGURE 7.3.5** Preparing a standard solution from a primary standard

The molar concentration of the standard solution is then found by using these formulas:

$$\text{amount in mol, } n = \frac{\text{mass of solute (in g)}}{\text{molar mass (in g mol}^{-1})} = \frac{m}{M}$$

$$\text{concentration, } c = \frac{\text{amount of solute (in mol)}}{\text{volume of solution (in L)}} = \frac{n}{V} = \frac{m}{M \times V}$$

In practice, making a standard solution directly from a primary standard is only possible for a few of the chemicals found in the laboratory. Many chemicals are impure because they decompose or react with chemicals in the atmosphere. For example:

- strong bases, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), absorb water and react with carbon dioxide in the air
- many hydrated salts, such as hydrated sodium carbonate ($Na_2CO_3.10H_2O$), lose water to the atmosphere over time.

In addition, the concentrations of commercial supplies of strong acids (HCl, $H_2SO_4$ and $HNO_3$) cannot be accurately specified.

Solutions such as HCl(aq), $H_2SO_4$(aq), NaOH(aq) and KOH(aq) must be standardised to determine their concentration. An accurately measured volume of the solution is reacted with a known amount of a standard solution such as $Na_2CO_3$(aq). This is done by titration, which is discussed in the next section.

## Concentration of standard solutions

Figure 7.3.6 summarises the steps involved in calculating the concentration of a standard solution from the accurately measured mass of a primary standard.
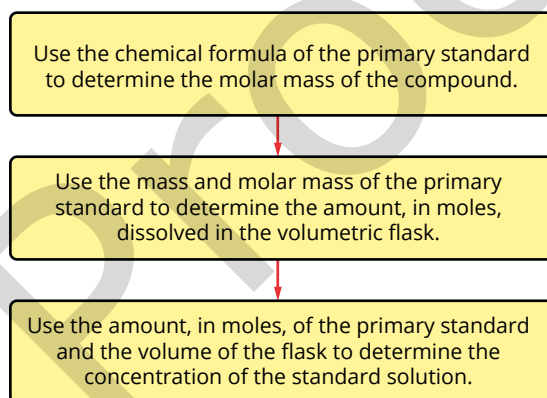


Use the chemical formula of the primary standard to determine the molar mass of the compound.

↓

Use the mass and molar mass of the primary standard to determine the amount, in moles, dissolved in the volumetric flask.

↓

Use the amount, in moles, of the primary standard and the volume of the flask to determine the concentration of the standard solution.

**FIGURE 7.3.6** A summary of the steps used in the calculation of the concentration of a standard solution prepared from a primary standard.

## Worked example 7.3.1

**CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD**

The primary standard sodium carbonate is used to standardise solutions of acids. Calculate the concentration of a standard solution prepared from 5.05 g of sodium carbonate ($Na_2CO_3$) dissolved in a 500 mL volumetric flask.

| Thinking | Working |
|---|---|
| Use the chemical formula to determine the molar mass ($M$) of the compound. | The molar mass ($M$) of $Na_2CO_3$ is $(22.99 \times 2) + 12.01 + (16.00 \times 3) =$ $105.99\,g\,mol^{-1}$ |
| Use the mass ($m$) and molar mass ($M$) of the compound and the formula $n = \dfrac{m}{M}$ to determine the amount, in mol. | $n = \dfrac{5.05}{105.99}$ $= 0.04765\,mol$ |
| Use the amount, in mol, to determine the concentration of the solution using the formula $c = \dfrac{n}{V}$. | $c = \dfrac{0.04765}{0.500}$ $= 0.0953\,mol\,L^{-1}$ |

## Worked example: Try yourself 7.3.1

**CALCULATING THE CONCENTRATION OF A STANDARD SOLUTION PREPARED FROM A PRIMARY STANDARD**

Calculate the concentration of a standard solution prepared from 17.0 g of oxalic acid dihydrate ($H_2C_2O_4.2H_2O$) dissolved in a 250.0 mL volumetric flask.

# 7.3 Review

## SUMMARY

- A substance is suitable for use as a primary standard if it:
  - is readily obtainable in a pure form
  - has a known chemical formula
  - is easy to store without deteriorating or reacting with the atmosphere
  - has a high molar mass to minimise the effect of errors in weighing.

- A standard solution is a solution of an accurately known concentration.
- The concentration, in $mol\,L^{-1}$, of a prepared standard solution can be determined by measuring the mass of solid dissolved and the volume of solution prepared.

## KEY QUESTIONS

1. Describe the steps required for the correct preparation of a standard solution.

2. Potassium hydrogen phthalate ($KH(C_8H_4O_4)$) is used as a primary standard for the analysis of bases. Calculate the concentration of a standard solution prepared in a 50.00 mL volumetric flask by dissolving 2.042 g of potassium hydrogen phthalate in deionised water. The molar mass of $KH(C_8H_4O_4)$ is $204.2\,g\,mol^{-1}$.

3. Calculate the mass of anhydrous sodium carbonate ($Na_2CO_3$) required to prepare 250.0 mL of a 0.500 $mol\,L^{-1}$ standard solution.

# 7.4 Volumetric analysis

The pain caused by indigestion occurs when your stomach produces excessive quantities of acidic gastric juices. The protein-digesting enzyme pepsin in gastric secretions works best at pH 3. This pH is due to hydrochloric acid contained in the gastric juice. Commercial antacids (Figure 7.4.1) contain bases such as magnesium hydroxide, sodium hydrogencarbonate and aluminium hydroxide to neutralise the acid secretions and relieve the discomfort.



**FIGURE 7.4.1** The suitability of antacids can be assessed by acid–base reactions.

To compare the effectiveness of antacids, you could design experiments to find out what volume of hydrochloric acid reacts with each brand. This would allow you to determine which antacid is best at neutralising the acidic secretions.

There are many situations when you may want to find the amount of a substance in solution. For example, you might want to determine the composition of antacid tablets, the chemicals present in industrial waste, or the acidity of polluted rainwater.

This section describes a method used for the analysis of acids or bases in a solution. The method is called volumetric analysis and involves chemical reactions between substances in aqueous solution.

You will also learn how specialised glassware is used during volumetric analysis.
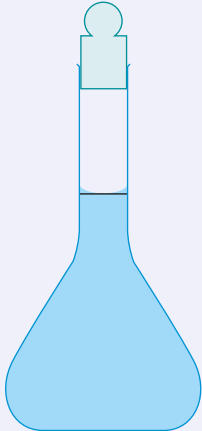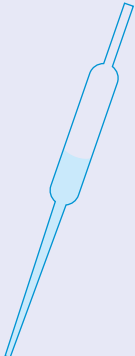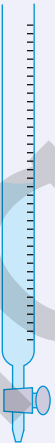
## ACID–BASE TITRATIONS

### Volumetric equipment

Often the concentrations of acids and bases used in industry are unknown. The laboratory equipment shown in Table 7.4.1 is used to make precise measurements of mass and volume. These instruments, combined with calculations similar to those in section 7.2 of this chapter, can help scientists determine unknown concentrations of acids and bases.

If you want to find the concentration of a solution of hydrochloric acid, you can react the hydrochloric acid with a standard solution of sodium carbonate. Precisely calibrated glassware is used to carry out the analysis.

The solution of sodium carbonate is slowly added (titrated) to the acid solution in the conical flask until the reactants are present in equivalent amounts. These amounts are indicated by the coefficients in the equation for the reaction. This is called the **equivalence point**.

**TABLE 7.4.1** Laboratory equipment used to determine the concentration of a solution of hydrochloric acid by volumetric analysis

| Equipment | Visual reference | Use |
|---|---|---|
| Volumetric flask |  | A volumetric flask is used to prepare a standard solution of sodium carbonate. An accurately weighed sample of sodium carbonate is placed in the flask and dissolved in deionised water to form a specific volume of solution. |
| Pipette |  | A **pipette** is used to accurately measure a specific volume of the solution of hydrochloric acid. This known volume, or **aliquot**, is then poured into a conical flask ready for analysis. |
| Burette |  | The standard solution of sodium carbonate is placed in a **burette**, which delivers accurately known, but variable, volumes of solution. The volume of liquid delivered by a burette is called a **titre**. |

For the reaction between hydrochloric acid and sodium carbonate solution:

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$
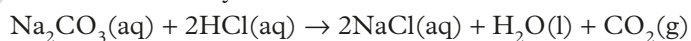
the equivalence point occurs when exactly 2 mol of HCl has been added for each 1 mol of $Na_2CO_3$. This whole process is called a **titration**.

The reaction is complete when the equivalence point is reached. The concentration of the standard sodium carbonate solution is known, and volume of sodium carbonate is now known (measured from the burette), as is the volume of the aliquot of hydrochloric acid used. The concentration of the acid can then be calculated.

As both acid and base solutions are often colourless, an **indicator** is added to determine when the reaction is complete. The indicator chosen should change colour when the solutions are neutralised. The **end point** is the point during the titration at which the indicator changes colour. For an accurate analysis, the end point should be very close to the equivalence point.

Figure 7.4.2 shows how the equipment listed would be used to complete the titration for the reaction of $Na_2CO_3$ and HCl.
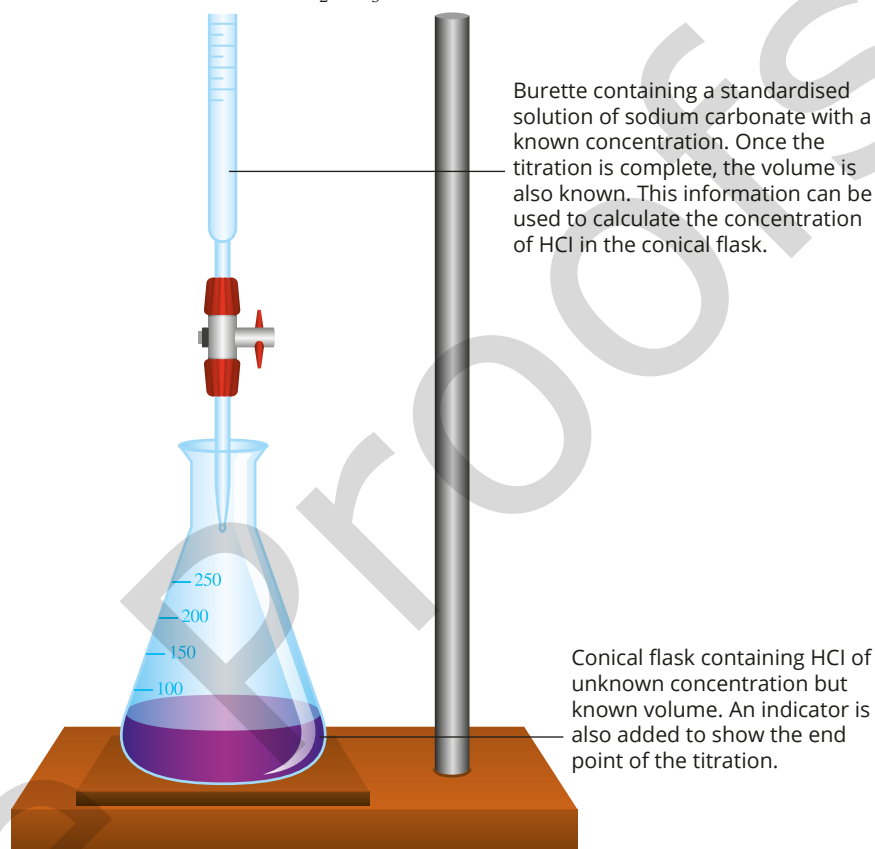


Burette containing a standardised solution of sodium carbonate with a known concentration. Once the titration is complete, the volume is also known. This information can be used to calculate the concentration of HCl in the conical flask.

Conical flask containing HCl of unknown concentration but known volume. An indicator is also added to show the end point of the titration.

**FIGURE 7.4.2** The equipment used in the titration of $Na_2CO_3$ (in the burette) to determine the concentration of HCl (in the conical flask)

## Using a burette

Burettes are usually calibrated in intervals of 0.10 mL. The volume of liquid in a burette is measured at the bottom of the meniscus of the liquid. The reading is estimated to the nearest 0.02 mL, as shown in Figure 7.4.3.

To minimise errors, the titration is repeated several times and the **average titre** is found. Usually three **concordant titres** are used to find this average. Concordant titres are within 0.20 mL from highest to lowest of each other.

The volume of one single drop from a burette is about 0.05 mL, so taking the average of three results assumes that the results will be no more than a couple of drops over or under the accurate titre.

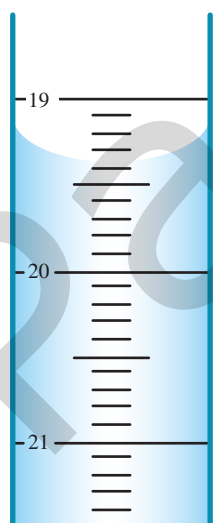Consider the titration data represented in Table 7.4.2.



**FIGURE 7.4.3** The burette is read from the bottom of the meniscus and the volume is estimated to the second decimal place. The volume measurement in this case is 19.38 mL.

**TABLE 7.4.2** Titration data collected over five trials

| Titration number | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Final burette reading | 20.20 | 40.82 | 20.64 | 41.78 | 21.86 |
| Initial burette reading | 0.00 | 21.00 | 1.00 | 22.00 | 2.00 |
| Titre (mL) | 20.20 | 19.82 | 19.64 | 19.78 | 19.86 |

The first reading is a rough reading that gives an idea of the approximate end point. Titres 2, 4 and 5 are the concordant titres: they are within 0.20 mL from highest to lowest of each other. The difference between the highest and lowest readings is 19.86 − 19.78 = 0.08 mL, which is within the acceptable range for concordant results. The mean (average) titre is:

$$\frac{19.82+19.78+19.86}{3}=19.82\,\text{mL}$$

## INDICATORS

You will recall from Chapter 6 that one of the characteristic properties of acids and bases is their ability to change the colour of certain chemicals called indicators.

The colours of indicators are usually intense and highly visible, even at low concentrations. As Figure 7.4.4 and Table 7.4.3 show, different indicators change colour over different pH ranges.
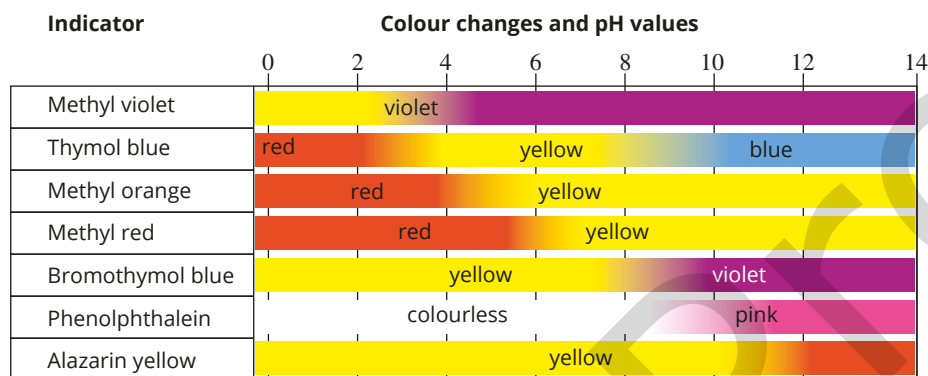


**FIGURE 7.4.4** The colours of common indicators at different pH values

**TABLE 7.4.3** The pH ranges of a number of common acid–base indicators

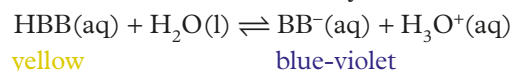| Indicator | Colour of acid form | Colour of base form | pH range |
|---|---|---|---|
| Methyl orange | Red | Yellow | 3.2–4.4 |
| Bromothymol blue | Yellow | Blue-violet | 6.0–7.6 |
| Phenolphthalein | Colourless | Pink | 8.2–10.0 |

## Characteristics of indicators

- Indicators are large organic molecules whose colour changes in response to changes in the pH of the solution they are dissolved in.
- They are either weak acids or weak bases.
- In solution, the acid form of the indicator is in equilibrium with its conjugate base as shown in the following equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

- The position of equilibrium depends on the pH.
- The colour of the acid form of an indicator, HIn, and the colour of its conjugate base, In⁻, are different.
- The acid or base colour of an indicator is visible at low indicator concentrations.

To better understand the characteristics of indicators in titrations, review the section on the common laboratory indicators in Chapter 6 (page xxx).

As an example of an indicator, bromothymol blue is a widely used indicator. The indicator is yellow in acidic solutions and blue-violet in basic solutions. The simplified equation for the ionisation of bromothymol blue in water is:

$$HBB(aq) + H_2O(l) \rightleftharpoons BB^-(aq) + H_3O^+(aq)$$
yellow                          blue-violet

FIGURE 7.4.5 Titration curve for a strong acid being added to a strong base

The indicator colour we see depends on the relative concentrations of HBB and BB⁻.

## pH change during a titration

The change in pH when a strong acid such as HCl is titrated against a strong base such as NaOH can be represented on a graph called a **titration curve** or **pH curve**. The equivalence point occurs when the gradient of the pH curve is steepest. An example of a pH curve is shown in Figure 7.4.5.

Near the equivalence point, the addition of a very small volume of HCl produces a large change in pH. In this titration, the pH changes from 10 to 4 with just one drop of acid. By using an indicator that changes colour within this pH range, such as bromothymol blue (pH 6.0–7.6), one drop will cause a colour change. This is referred to as a sharp end point. Therefore, knowing the pH range of an indicator is an important tool to ensuring a sharp end point.

The volume of acid added at this point indicates the amount needed to react according to the balanced equation. This volume is the titre that is recorded for the titration.

For a reaction between a strong acid and a strong base, the pH at the equivalence point is 7. The equation for the reaction can be written as:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
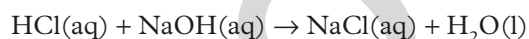
Only $H_2O(l)$ and $NaCl(aq)$ are present at the equivalence point, making the solution neutral.

Other indicators, including phenolphthalein (pH 8.3–10.0), could be used for this titration because they would also produce a sharp end point for this reaction.

Figure 7.4.6 compares the titration curves obtained when a strong acid is added to a strong base and when a strong acid is added to a weak base. Note that there is a sharp drop in pH in both graphs at the equivalence point. However, because this drop occurs over different ranges, the choice of indicator is important in detecting the equivalence point. Phenolphthalein can be used successfully for the first titration but not for the second.
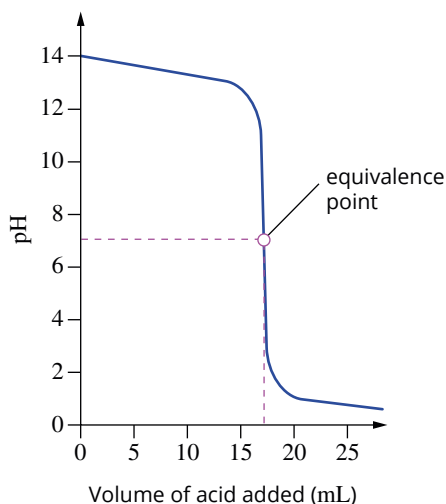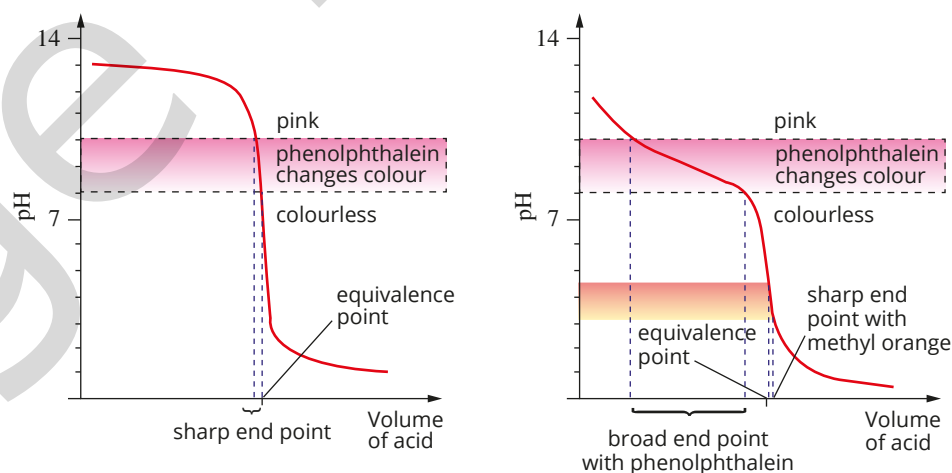


FIGURE 7.4.6 Titration curves showing the pH during a titration of (a) a strong base with a strong acid, and (b) a weak base with a strong acid. Phenolphthalein, which changes colour between pH 8.3 and 10.0, gives a sharp end point in (a) but a broad end point in (b). Methyl orange, which changes colour between pH 3.2 and 4.4, would be a more suitable indicator for the second titration.

# 7.4 Review

## SUMMARY

- Volumetric analysis is an analytical technique for determining the concentration of a solution by titrating it against a solution of known concentration (a standard solution) and volume.
- Volumetric flasks, pipettes and burettes are accurately calibrated pieces of glassware used in volumetric analysis.
- The point during a titration at which the reactants are present in equivalent amounts, as indicated by the coefficients in the equation for the reaction, is called the equivalence point.

- The end point is the point at which the indicator changes colour.
- Indicators used in acid–base titrations must have a sharp end point.
- The end point in an acid–base titration must be at or close to the equivalence point.

## KEY QUESTIONS

**1** The titration curve in Figure 7.4.7 shows the change in pH as a solution of $0.10\,mol\,L^{-1}$ sodium hydroxide is added to a 20.00 mL solution of $0.10\,mol\,L^{-1}$ hydrochloric acid.
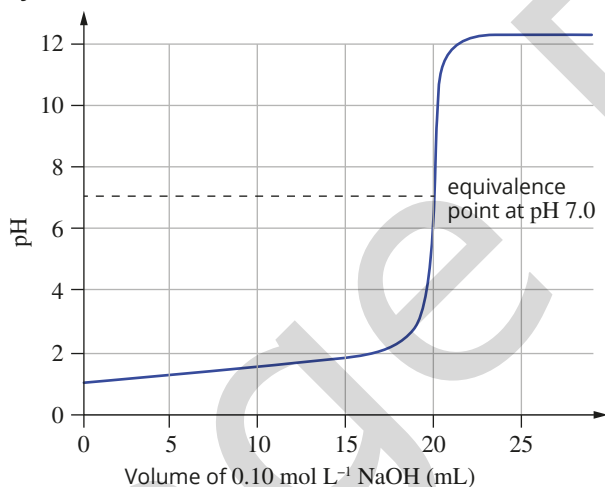


FIGURE 7.4.7 Titration curve

The titration is repeated using $0.20\,mol\,L^{-1}$ sodium hydroxide solution. Which one of the following statements about the second titration is correct?

**A** The equivalence point occurs when 10 mL of NaOH is added and the pH is then 7.

**B** The equivalence point occurs when 10 mL of NaOH is added and the pH is then greater than 7.

**C** The equivalence point occurs when 40 mL of NaOH is added and the pH is then 7.

**D** The equivalence point occurs when 40 mL of NaOH is added and the pH is then greater than 7.

**2** Five test-tubes each contain the same solution, which has a pH of 5. A different indicator is added to the solution in each test-tube, as shown in the table below. Use the indicator colour chart in Figure 7.4.4 on page 165 to find the colour of each solution after the indicator was added.

| Indicator | Colour after adding indicator |
|---|---|
| Alizarin yellow | |
| Bromothymol blue | |
| Methyl red | |
| Methyl orange | |
| Phenolphthalein | |

**3** The following titres were obtained when a solution of sulfuric acid was titrated against a standard solution of potassium hydroxide.

| Trial | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Titre (mL) | 26.28 | 25.46 | 25.38 | 25.62 | 25.42 |

Calculate the average volume of sulfuric acid that would be used in volumetric calculations.

# 7.5 Calculations in volumetric analysis

Using volumetric analysis, chemists are able to determine the amount, in mol, of an unknown substance in solution by reacting it with a known standard solution.

This section shows you how to use data from a titration to calculate the concentration of the acid or base being analysed. You will also be introduced to ideas of accuracy and precision in experimental work.

## TITRATIONS

Consider the data gained in an acid–base titration in which the concentration of a dilute solution of hydrochloric acid was determined by titration with a standard solution of sodium hydroxide.

The data gained from the titration is summarised in Table 7.5.1.

**TABLE 7.5.1** Sample data obtained from a volumetric analysis

| | |
|---|---|
| Volume of aliquot of HCl (mL) | 25.00 |
| Concentration of standard NaOH solution $mol\,L^{-1}$ | 1.00 |
| Titre volumes of NaOH (mL) | 25.05, 22.10, 22.00, 22.05 |

The concentration of hydrochloric acid is calculated by following a number of steps. These steps are summarised in the flow chart shown in Figure 7.5.1.
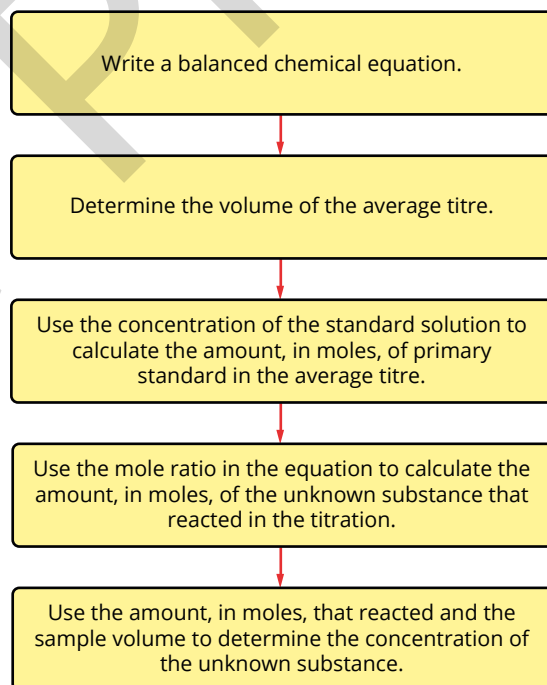


**FIGURE 7.5.1** This flow chart summarises the steps in the calculation of the concentration of an unknown substance using the data from a titration in which the standard solution was in the burette.

## Worked example 7.5.1

**SIMPLE TITRATIONS**

The concentration of hydrochloric acid was determined by titration with a standard solution of sodium hydroxide.

A 25.00 mL aliquot of HCl was titrated with a $1.00 \, mol \, L^{-1}$ solution of sodium hydroxide. Titres of 25.05 mL, 22.10 mL, 22.05 mL and 22.00 mL were required to reach the end point.

What is the concentration of the hydrochloric acid solution?

| Thinking | Working |
|---|---|
| Write a balanced chemical equation for the reaction. | An acid is reacting with a metal hydroxide, or base, so the products will be a salt and water. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ |
| Determine the volume of the average titre. | The titre of 25.05 mL is discarded because it is not concordant (i.e. it is not within a range of 0.20 mL from highest to lowest of the other titre volumes). Average titre $= \dfrac{22.10 + 22.05 + 22.00}{3}$ $= 22.05 \, mL$ |
| Calculate the amount, in mol, of the standard ('known') solution that was required to reach the end point. Remember the volume must be expressed in litres. | $n(NaOH) = cV$ $= 1.00 \times 0.02205$ $= 0.02205 \, mol$ |
| Use the mole ratio in the equation to calculate the amount, in mol, of the unknown substance that would have reacted with the given amount, in mol, of the standard solution. | mole ratio $= \dfrac{n(HCl)}{n(NaOH)} = \dfrac{1}{1}$ $n(HCl) = n(NaOH)$ $= 0.02205 \, mol$ |
| Determine the concentration of the unknown substance. | $c(HCl) = \dfrac{n}{V}$ $= \dfrac{0.02205}{0.02500}$ $= 0.882 \, mol \, L^{-1}$ |
| Express your answer to the appropriate number of significant figures. | The final result is rounded off to three significant figures corresponding to the smallest number of significant figures in the original data. Four significant figures are used in the earlier steps of the calculation to avoid rounding off errors. Concentration of HCl $= 0.882 \, mol \, L^{-1}$ |

## Worked example: Try yourself 7.5.1

**SIMPLE TITRATION**

The concentration of a solution of barium hydroxide ($Ba(OH)_2$) was determined by titration with a standard solution of hydrochloric acid.

A 10.00 mL aliquot of $Ba(OH)_2$ solution was titrated with a $0.125 \, mol \, L^{-1}$ solution of HCl. Titres of 17.23 mL, 17.28 mL and 17.21 mL of HCl were required to reach the end point.

What is the concentration of the barium hydroxide solution?

## Titrations that involve dilution

It is often necessary to dilute a solution before carrying out a titration in order to obtain concentrations that are more convenient to use. This will result in titres that are within the volume range of the burette.

Suppose you want to perform an acid–base titration to find the concentration of hydrochloric acid in concrete cleaner. The concrete cleaner is so concentrated that it has to be accurately diluted before the titration. The following additional data is recorded:

- the volume of the aliquot of undiluted concrete cleaner
- the volume of diluted solution that is prepared.

The data obtained from such a titration is summarised in Table 7.5.2.

**TABLE 7.5.2** Data from a titration involving diluted concrete cleaner

| | |
|---|---|
| Volume of undiluted concrete cleaner | 25.00 mL |
| Volume of diluted concrete cleaner | 250.0 mL |
| Volume of titre of diluted concrete cleaner | 19.84 mL |
| Concentration of standard $Na_2CO_3$ solution | 0.4480 mol L$^{-1}$ |
| Volume of aliquot of $Na_2CO_3$ solution | 20.00 mL |

In this titration, 25.00 mL of concrete cleaner was diluted to 250.0 mL in a volumetric flask prior to taking a sample for titration. This means the **dilution factor** is $\frac{250.0}{25.00} = 10.00$. The undiluted concrete cleaner will be 10.00 times more concentrated than the concentration of the aliquot. This will be taken into account later in the calculations.

The steps required to calculate the concentration of undiluted concrete cleaner are summarised in the flow chart shown in Figure 7.5.2.
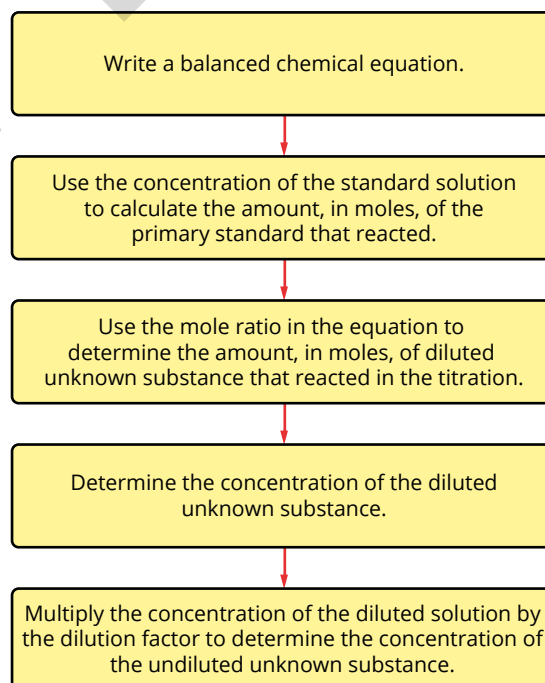


FIGURE 7.5.2 This flow chart shows the steps used in the calculation of the concentration of an unknown substance that has been diluted for use in a titration.

## Worked example 7.5.2

**TITRATION THAT INVOLVES DILUTION**

A commercial concrete cleaner contains hydrochloric acid. A 25.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask.

A 20.00 mL aliquot of 0.4480 mol L$^{-1}$ sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to red when 19.84 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.

| Thinking | Working |
|---|---|
| Write a balanced chemical equation. | A dilute acid is reacting with a metal carbonate so the products will be a salt, water and carbon dioxide gas.<br>$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$ |
| Using the concentration of the standard solution, calculate the amount, in mol, of the known substance that reacted in the titration. Remember that volume must be expressed in litres. | $n(Na_2CO_3) = cV$<br>$\qquad = 0.4480 \times 0.02000$<br>$\qquad = 0.008960 \, mol$ |
| Use the mole ratio in the equation to calculate the amount, in mol, of the diluted unknown solution that reacted in the titration. | $\dfrac{n(HCl)}{n(Na_2CO_3)} = \dfrac{2}{1}$<br>$n(HCl) = \dfrac{2}{1} \times n(Na_2CO_3)$<br>$\qquad = \dfrac{2}{1} \times 0.008960$<br>$\qquad = 0.01792 \, mol$ |
| Calculate the concentration of diluted unknown solution reacting in the titration. | $V(\text{diluted HCl}) = 0.01984 \, L$<br>$c(HCl) = \dfrac{n}{V}$<br>$\qquad = \dfrac{0.01792}{0.01984}$<br>$\qquad = 0.9032 \, mol \, L^{-1}$ |
| Multiply by the dilution factor to determine the concentration of undiluted concrete cleaner. | Dilution factor $= \dfrac{250.0}{25.00} = 10.00$<br>So undiluted $c(HCl) = $ diluted $c(HCl) \times 10.00$<br>$\qquad = 0.9032 \times 10.00$<br>$\qquad = 9.032 \, mol \, L^{-1}$ |

## Worked example: Try yourself 7.5.2

**TITRATION THAT INVOLVES DILUTION**

A commercial concrete cleaner contains hydrochloric acid. A 10.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask.

A 20.00 mL aliquot of 0.2406 mol L$^{-1}$ sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 18.68 mL of the cleaner was added.

Calculate the concentration of hydrochloric acid in the concrete cleaner.

## Back titrations

Some acids or bases do not lend themselves to a 'normal' titration. This is often because they have limited solubility in water, so it is not possible to dissolve them to make a completely homogeneous solution. Examples of this are measuring the amount of an insoluble hydroxide in an indigestion tablet, the amount of carbonate in sea shells or the amount of ammonia in the cleaner 'cloudy ammonia', which is a colloid containing ammonia and soap.

A method called **back titration** can be used to determine the amount of acid or base in this situation. The concentration of the acid or base is determined by reacting it with a known amount of excess reagent, usually a standard solution of a strong acid or base.

Some of the added acid or base reacts with the sample being analysed. The remaining excess reagent is titrated with a standard solution of a strong acid or base. Once the amount of excess reactant is determined by the titration, this can be compared to the initial total amount of the acid or base added in excess to calculate, by subtraction, the amount of the acid or base that actually reacted with the sample being analysed.

This process can be illustrated using the following example.

Back titration is used to determine the concentration of ammonium ions ($NH_4^+$) in lawn feed. The analysis involves two different chemical reactions.

- A measured mass of a lawn feed sample is mixed and heated with a known excess amount of sodium hydroxide (NaOH). All of the ammonium ions in the lawn feed react, leaving some of the strong base unreacted:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$$
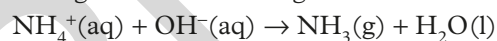
- The unreacted NaOH is then titrated with a standard solution of a strong acid, hydrochloric acid (HCl):

$$NaOH(aq) + HCl(aq) \rightarrow NaOH(aq) + H_2O(l)$$
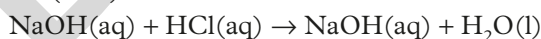
The flow chart in Figure 7.5.3 shows the steps followed to calculate the amount, and therefore the concentration of $NH_4^+$ that was present in the sample of lawn feed.
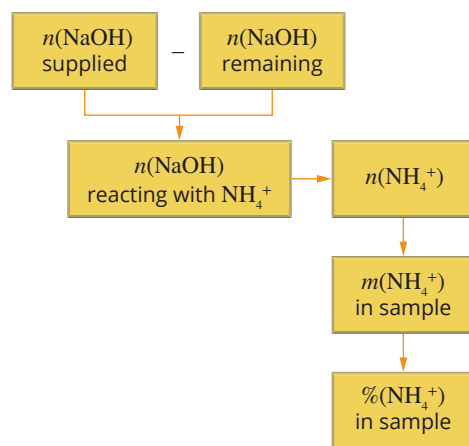


**FIGURE 7.5.3** Steps in the calculation of the ammonium content in lawn fertiliser using a back titration

A similar procedure can be used to determine the concentration of a weak base by adding an excess of a strong acid.

## Worked example 7.5.3

**BACK TITRATION**

A student was asked to determine the concentration of ammonia in cloudy ammonia solution used for cleaning. First she pipetted 20.00 mL of the cloudy ammonia solution into a 250.0 mL conical flask.

She then added 50.00 mL of 0.100 mol L$^{-1}$ HCl(aq) to the conical flask to react with the ammonia in solution. The resultant mixture of excess, unreacted, HCl was then titrated with 0.050 mol L$^{-1}$ $Na_2CO_3$(aq). A volume of 20.50 mL of $Na_2CO_3$(aq) was required.

Calculate the concentration of the ammonia in the cloudy ammonia solution.

**Step 1: From the titration results determine the amount of HCl in excess. This is the HCl that is left over after all the ammonia is used up in the first step.**

| Thinking | Working |
|---|---|
| Write the equation for the titration: | $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$ |
| Calculate the moles, $n$, of $Na_2CO_3$(aq) that reacted in the titration:<br>moles = concentration (mol L$^{-1}$) × volume (L) | $n(Na_2CO_3) = c \times V$<br>$c(Na_2CO_3) = 0.050$ mol L$^{-1}$<br>$V(Na_2CO_3) = 20.50$ mL = 0.02050 L<br>$n(Na_2CO_3) = 0.050 \times 0.02050 = 0.001025$ mol |
| Use the balanced chemical reaction for the titration to determine the moles of excess HCl that reacted in the titration. | From the balanced chemical equation, 1 mole $Na_2CO_3$ reacts with 2 moles of HCl<br>So, 0.001025 mol $Na_2CO_3$ reacted with 2 × 0.001025 mol HCl<br>$n(HCl)_{excess} = 0.001025$ mol = 0.002050 mol |

**Step 2: Determine the amount of ammonia in the cloudy ammonia solution**

| Thinking | Working |
|---|---|
| Calculate the total moles of HCl originally added to the diluted cloudy ammonia solution:<br>moles = concentration (mol L$^{-1}$) × volume (L) | $n(HCl) = c \times V$<br>$c(HCl) = 0.100$ mol L$^{-1}$<br>$V(HCl) = 50.00$ mL = 0.05000 L<br>$n(HCl)_{total\ added} = 0.100 \times 0.05000 = 0.05000$ mol |
| Calculate the moles of HCl that reacted with the ammonia in the diluted cloudy ammonia solution by taking away the amount in excess from the total amount. | $n(HCl)_{titrated} + n(HCl)_{reacted\ with\ ammonia} = n(HCl)_{total\ added}$<br>$n(HCl)_{total\ added} = 0.0500$ mol<br>$n(HCl)_{titrated} = 0.002050$ mol (calculated in Step 1)<br>$n(HCl)_{reacted\ with\ ammonia} = n(HCl)_{total\ added} - n(HCl)_{titrated}$<br>$n(HCl)_{reacted\ with\ ammonia} = 0.0500 - 0.002050 = 0.00295$ mol |
| Write the balanced chemical equation for the reaction between ammonia in the cloudy ammonia solution and the HCl(aq). | $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$ |
| From the balanced chemical equation, calculate the moles of $NH_3$ that reacted with HCl. | From the equation, 1 mol HCl reacts with 1 mol $NH_3$<br>$n(NH_3) = (1/1) \times n(HCl)$<br>$\qquad\quad = 0.00295$ mol |
| Calculate the ammonia concentration in the cloudy ammonia solution.<br>concentration (mol L$^{-1}$) = $\dfrac{n}{V}$<br>$\qquad\qquad\qquad$ = moles / volume (L) | $c(NH_3) = \dfrac{n}{V}$<br>$n(NH_3) = 0.00295$ mol (moles of $NH_3$ that reacted with HCl)<br>$V(NH_3) = 20.00$ mL = 0.02000 L (volume of ammonia solution that reacted with HCl)<br>$c(NH_3) = \dfrac{0.00295}{0.02000} = 0.1475$ mol L$^{-1}$ |
| State the concentration of ammonia in the cloudy ammonia solution to the correct number of significant figures. | $c(NH_3)$ in the cloudy ammonia = 0.147 mol L$^{-1}$ |

## Worked example: Try yourself 7.5.3

**BACK TITRATION**

A student was given a 0.122 g sample of chalk and asked to determine the mass, in grams, of calcium carbonate in the chalk.

The student made the following notes:

- The chalk sample was placed in a 250 mL conical flask.
- Using a 50.00 mL pipette, 50.00 mL of standardised 0.198 mol L$^{-1}$ HCl solution was added to the flask.
- The excess HCl left in the 250 mL conical flask was then titrated using 0.250 mol L$^{-1}$ NaOH solution.
- The experiment was repeated three times and volumes of NaOH added: Trial 1: 32.15 mL, Trial 2: 32.05 mL, Trial 3: 32.10 mL
- The average volume of NaOH titrated was 32.10 mL

Using the student's results calculate the mass of calcium carbonate, in grams, present in the chalk sample.

## UNCERTAINTIES

In this course you are required to estimate the degree of **uncertainty** in experiments such as titration experiments. The accuracy with which the volumes of the aliquot and titre are measured in volumetric analysis depends on the calibration of the pieces of equipment used. There are always errors associated with measurements of quantities such as mass and volume made during experimental work.

These are some typical uncertainties associated with volumetric analysis:

- 20 mL pipette: ±0.03 mL
- 50 mL burette: ±0.02 mL for each reading
- 250 mL volumetric flask: ±0.3 mL
- 100 g capacity top loading balance: ±0.001 g
- 60 g capacity analytical balance: ±0.0001 g.

Other graduated laboratory glassware provides less precise measures:

- 50 mL measuring cylinder: ±0.3 mL
- 50 mL graduated beaker: ±5 mL.

## PRECISION AND ACCURACY

Every measurement in a **quantitative analysis** is subject to some form of error. Therefore, a calculation that makes use of these measurements will produce a result in which the errors have accumulated.

If repeated measurements of the same quantity yield values that are in close agreement, then the measurement is said to be **precise**. For example, a titration is generally repeated until at least three titres are obtained that are within narrowly specified limits. These are called concordant titres. Repeated measurement of the titres increases the precision of the result and minimises errors that may have affected one titre more than others.

If the average of a set of measurements of a quantity is very close to the true or accepted value of the quantity, then the measurement is said to be **accurate**. Figure 7.5.4 compares accuracy and precision.

You can see that it is possible for a result to be precise but inaccurate.

Methods used for accurate quantitative analysis should be designed to minimise errors. Where errors cannot be avoided, any discussion of results should refer to the level of inaccuracy that may have accumulated. This requires an understanding of the different types of errors.
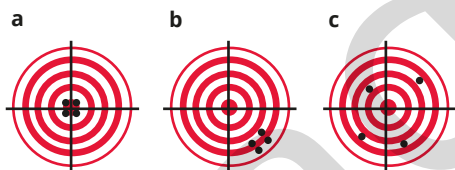


**FIGURE 7.5.4** The holes in the targets illustrate the difference between accuracy and precision. Target (a) shows good accuracy and good precision. Target (b) illustrates poor accuracy but good precision, and target (c) shows both poor accuracy and poor precision. Analytical chemists aim to produce results that are both precise and accurate.

# TYPES OF ERRORS

## Systematic errors

A **systematic error** produces a constant bias in a measurement that cannot be eliminated by repeating the measurement. Systematic errors that affect an acid–base titration could include:

- a faulty balance
- a 20.0 mL pipette that delivers 20.2 mL
- some of a substance or solution being left in the original container, such as a beaker, when being transferred to a new container
- an unsuitable indicator being used
- the mass of the primary standard being inflated because it hasn't been dried properly and contains some water
- a person reading the scale on a burette with a constant parallax error.

Whatever the cause, the resulting error is in the same direction for every measurement and the average will be either always higher than or always lower than the true value.

Systematic errors are eliminated or minimised through calibration of apparatus and the careful design of a procedure. If you cannot eliminate the error, then you should try to determine its size so that the error can be taken into account in calculations.

## Random errors

**Random errors** follow no regular pattern. The measurement is sometimes too large and sometimes too small. Random errors in volumetric analysis could include:

- inherent uncertainty in the last value after the decimal place in the measurement of the mass of a primary standard on an analytical balance
- difficulty in judging where the meniscus sits on the line when using a pipette to measure a volume
- difficulty in judging the fraction between two 0.1 mL scale markings on a burette.

The effects of random errors can be reduced by taking multiple measurements of the same quantity, then calculating an average. In volumetric analysis, the average of three concordant titres is used to reduce random error.

## Mistakes

**Mistakes** made during acid–base titrations could include:

- misreading the numbers on a scale
- mistakenly using a pipette of incorrect volume
- spilling a portion of a sample.

The effects of incorrectly rinsing volumetric glassware are detailed in Table 7.5.3.

**TABLE 7.5.3** Rinsing glassware for volumetric analysis

|  | Correct | Incorrect |
| --- | --- | --- |
| Burette Pipette | The final rinse should be with the acid or base they are to be filled with. | Rinsing with water only would dilute the acid or base solution. |
| Volumetric flask Titration flask (conical flask) | Should only be rinsed with deionised water. | Rinsing with acidic or basic solutions will introduce unmeasured amounts of acids or bases into the flask that can react and affect the results. |

A measurement that involves a mistake must be rejected and not included in any calculations or averaged with other measurements of the same quantity. Mistakes are not generally referred to as errors.

# 7.5 Review

## SUMMARY

- The concentration of acidic or basic solutions can be determined by volumetric analysis.
- Dilution of the unknown solution is sometimes required to obtain manageable titre volumes.
- The mole ratio in a balanced chemical equation allows the amount, in mol, of a species in the equation to be calculated from the amount, in mol, of any other species.
- All quantitative measurements involve an error and have an uncertainty associated with them.

- Accuracy refers to how closely a measurement agrees with the true value.
- Precision refers to how closely a set of measurements are to each other.
- A systematic error produces a constant bias in a measurement, which cannot be eliminated by repeating the measurement.
- A random error has a chance of being greater or lower than the true value.

## KEY QUESTIONS

1   A 20.00 mL aliquot of sulfuric acid solution is neutralised by the addition of 22.98 mL of 1.34 mol L$^{-1}$ potassium hydroxide solution. The equation for the reaction is:

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

Calculate the concentration of the sulfuric acid solution.

2   The concentration of ethanoic acid ($CH_3COOH$) in vinegar was determined by titration with a standardised solution of sodium hydroxide. A 25.00 mL aliquot of vinegar required 21.56 mL of 0.995 mol L$^{-1}$ NaOH to reach the end point.
   a   Write an equation for the reaction between ethanoic acid and sodium hydroxide.
   b   Calculate the amount, in mol, of NaOH used in the titration.
   c   Calculate the amount, in mol, of ethanoic acid that reacted.
   d   Calculate the concentration of ethanoic acid in the vinegar.

3   A commercial concrete cleaner contains hydrochloric acid. A 25.00 mL volume of cleaner was diluted to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of 0.5000 mol L$^{-1}$ sodium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner.

The indicator changed permanently from yellow to red when 23.92 mL of the diluted cleaner had been added.
The equation for the reaction is:

$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

Calculate the concentration of hydrochloric acid in the concrete cleaner.

4   Determine the concentration of ammonia in a cloudy ammonia cleaning solution given the following laboratory notes recorded by a student.
Pipetted 25.00 mL of the cloudy ammonia solution into a 250.0 mL conical flask.
Reacted the ammonia in the conical flask with 50.00 mL of 0.102 mol L$^{-1}$ HCl(aq).
Titrated the excess HCl(aq) in the conical flask with 0.050 mol L$^{-1}$ $Na_2CO_3$(aq).
After three trials, I calculated an average volume of 21.50 mL of $Na_2CO_3$(aq) was required.

# Chapter review

## KEY TERMS

accurate
acid rain
aliquot
anhydrous
average titre
back titration
burette
concordant titres

dilution factor
end point
equivalence point
indicator
mistake
parallax error
pH curve
pipette

precise
primary standard
quantitative analysis
random errors
standard solution
systematic error
titration
titration curve

titre
uncertainty
volumetric analysis
volumetric flask

## Acids and bases in water

1   What are the main gases that contribute to acid rain, and what are the sources of these gases?

2   The following reactions can occur in unpolluted river water.

$$CO_2(g) + 2H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$
$$CaCO_3(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq) + OH^-(aq)$$

A sample of river water has pH 8.0. Which one of the following statements is true?

   A   The first reaction is the only reaction occurring.
   B   The second reaction is the only reaction occurring.
   C   The first reaction occurs to a greater extent than the second.
   D   The second reaction occurs to a greater extent than the first.

3   Name two weak acids present in wine.

4   Explain why the control and monitoring of the acidity in wine is an important part of the manufacturing process.

## Calculations involving acids and bases

5   What volume of $0.200\,mol\,L^{-1}$ KOH is required to react with 30.0 mL of $0.100\,mol\,L^{-1}$ $HNO_3$?

6   What volume of $0.100\,mol\,L^{-1}$ of NaOH is required to react with 20.00 mL of $0.200\,mol\,L^{-1}$ HCl?

## Standard solutions

7   Sodium borate ($Na_2B_4O_7.10H_2O$) is used as a primary standard in volumetric analysis. Some properties of $Na_2B_4O_7.10H_2O$ are listed below. Which one of these properties is not important in its use as a primary standard?

   A   It is highly soluble in water.
   B   Its purity is greater than 99.5%.
   C   It is a soft, white crystalline solid.
   D   It has a molar mass of $381\,g\,mol^{-1}$.

8   Calculate the concentration of a standard solution of hydrated oxalic acid ($H_2C_2O_4.2H_2O$) prepared by dissolving 25.21 g of hydrated oxalic acid in 250.0 mL of deionised water.

9   Calculate the mass of $Na_2CO_3$ required to make a 500 mL standard solution of $0.400\,mol\,L^{-1}$ $Na_2CO_3$.

## Volumetric analysis

10   Explain the use of each of the following pieces of equipment during a titration.
   a   Burette
   b   Pipette
   c   Volumetric flask

11   Explain the difference between the end point and the equivalence point of a titration.

12   Why is it important to select an indicator with an end point close to the equivalence point for the reaction?

## Calculations in volumetric analysis

13   A standard solution of potassium carbonate is made by adding 1.227 g of $K_2CO_3$ to a 250.0 mL volumetric flask and filling to the mark with water. 20.00 mL aliquots are taken and titrated against a sulfuric acid solution, using methyl orange indicator. The average titre was 22.56 mL of sulfuric acid.
   a   Write the equation for the reaction.
   b   Calculate the concentration of the $K_2CO_3$ solution.
   c   Calculate the concentration of the sulfuric acid solution.

14   A chemistry student is required to determine accurately the concentration of a solution of hydrochloric acid. First she makes up 250.0 mL of a standard solution of sodium carbonate. This solution contains 1.358 g of $Na_2CO_3$. She then takes a 20.00 mL aliquot of this standard solution and titrates it against the acid. An average titre of 20.24 mL of acid was required to reach the end point.
   a   Write a balanced equation for the reaction involving the titration.
   b   Calculate the concentration of the sodium carbonate solution.
   c   Find the concentration of the acid as indicated by the student's results.
   d   If sulfuric acid of the same concentration as the hydrochloric acid was used instead of the hydrochloric acid, what effect would this have had on the volume of acid required for the titration?

**15** 1.104 g of sodium carbonate ($Na_2CO_3$) is dissolved in water in a 250.0 mL volumetric flask. 20.00 mL aliquots of this solution were titrated with nitric acid. An average titre of 23.47 mL was found.

   **a** What is the concentration of the $Na_2CO_3$ solution?

   **b** What is the concentration of the nitric acid?

**16** A student added 50.00 mL of 0.100 mol L$^{-1}$ HCl(aq) to 25.00 mL of a commercial ammonia-based cleaner. The excess hydrochloric acid was titrated against a standardised sodium hydroxide solution. It was neutralised by 21.50 mL of the 0.100 mol L$^{-1}$ NaOH(aq). Calculate the concentration of ammonia in the cleaner.

**17** A 3.86 g sample of limestone was analysed using a back titration in order to determine the percentage of calcium carbonate in the rock. The sample was dissolved in 50.00 mL of 2.00 mol L$^{-1}$ HCl(aq). The reaction mixture of excess HCl was made up to 250.00 mL in a volumetric flask. 25.0 mL aliquots of this solution of excess HCl(aq) were titrated using standardised solution of 0.100 mol L$^{-1}$ NaOH(aq) using phenolphthalein indicator. The average NaOH(aq) titre was 38.15 mL. Calculate the:

   **a** number of moles of excess HCl(aq) as determined by the titration

   **b** number of moles of HCl(aq) used to dissolve the calcium carbonate in the sample

   **c** mass, in grams, of $CaCO_3$

   **d** percentage mass of $CaCO_3$ in the limestone sample.

## Connecting the main ideas

**18** A manufacturer wants to know the exact concentration of hydrochloric acid in the concrete cleaner it produces.

   **a** What substance would you use to make a standard solution for use in this titration and why have you chosen this substance?

   **b** How would you prepare this standard solution for volumetric analysis?

   **c** How should each piece of glassware used in a titration be rinsed to ensure you obtain accurate and precise results?

   **d** A 25.00 mL sample of the concrete cleaner was diluted to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of 0.5000 mol L$^{-1}$ potassium carbonate solution was placed in a conical flask. Methyl orange indicator was added and the solution was titrated with the diluted cleaner. The indicator changed permanently from yellow to pink when 18.44 mL of the diluted cleaner had been added. Calculate the concentration of hydrochloric acid in the concrete cleaner.

   **e** Would the concentration calculated be different if you used a standard solution of another base other than potassium carbonate? Explain.

**19** A particular brand of indigestion tablet has magnesium oxide as its active ingredient. Determine the mass, in grams, and percentage mass of magnesium oxide in the tablet. A back titration method was used to analyse one of the tablets. The procedure and results are recorded below.

Mass of tablet = 1.75 g

The tablet was dissolved in 45.00 mL of 2.00 mol L$^{-1}$ HCl solution

The reaction mixture was then made up to 250 mL in a volumetric flask

20.00 mL aliquots were titrated against a 0.100 mol L$^{-1}$ standardised solution of sodium hydroxide using phenolphthalein indicator

The average NaOH titre used was 18.60 mL.

   **a** Write an equation for the reaction of the MgO(s) in the tablet with the HCl solution.

   **b** Write an equation for the titration reaction of the excess HCl solution with the standardised NaOH solution.

   **c** Explain why phenolphthalein indicator was used and describe the colour change observed.

   **d** Calculate the average number moles of NaOH used in the titration.

   **e** Calculate the moles of excess HCl found by titration.

   **f** Calculate the moles of HCl that reacted with the MgO.

   **g** Calculate the mass of MgO in the tablet.

   **h** Determine the percentage of MgO in the tablet.