

3

CHAPTER

Stimulus questions

- 1 What percentage of an aspirin tablet is actually aspirin?
- 2 Which type of antacid medication provides the fastest relief from indigestion?
- 3 How do you select the appropriate indicator for an acid–base titration?

acid–base volumetric analysis

By the end of this chapter you should be able to:

- recall the Lowry–Brønsted theory of acids and bases
- explain the meaning of the terms ‘amphiprotic’, ‘polyprotic’, ‘conjugate pair’, ‘concentrated’, ‘dilute’, and ‘strong’ and ‘weak’ when applied to acids
- write balanced equations for reactions involving acids and bases
- describe how to prepare a standard solution
- list the properties of a substance that is a primary standard
- describe how to perform a volumetric analysis involving acids and bases
- explain the difference between a direct titration and a back titration
- carry out stoichiometric calculations for volumetric analyses involving acids and bases.



We saw in the previous chapter that many everyday substances can be analysed by measuring the mass of the substances and their reaction products. Many of the substances we use daily are solutions. While some of these may be analysed gravimetrically, they are more suited to volumetric analysis, a form of analysis involving measuring the concentrations and volumes of solutions. Volumetric analysis is particularly suited to consumer products in which the active ingredient is an acid, base, oxidant or reductant. In this chapter and the next we will explore volumetric analysis—a rapid, convenient method appropriate for school laboratory work.

3.1 ACIDS AND BASES REVISITED

Many household substances contain either an acid or a base as their active ingredient, and many are solutions. These solutions are ideal for analysis using volumetric techniques. Before considering examples of this, we need to review aspects of acid–base reactions. Acid–base reactions were considered in detail in *Chemistry Dimensions 1*, chapter 13. The summary below outlines definitions and ideas concerning this important reaction type.

- Typical reactions of acids include:
 - Reacting with most metals (not Cu, Ag or Hg) to produce a salt and hydrogen gas. For example:
$$2\text{HCl}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})$$
 - Reacting with metal hydroxides to produce a salt and water. For example:
$$2\text{HCl}(\text{aq}) + \text{Mg(OH)}_2(\text{s}) \rightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$
 - Reacting with metal oxides to produce a salt and water. For example:
$$2\text{HCl}(\text{aq}) + \text{MgO}(\text{s}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
 - Reacting with metal carbonates to produce a salt, water and carbon dioxide gas. For example:
$$2\text{HCl}(\text{aq}) + \text{MgCO}_3(\text{s}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$
 - Reacting with metal hydrogen carbonates to produce a salt, water and carbon dioxide gas. For example:
$$\text{HCl}(\text{aq}) + \text{NaHCO}_3(\text{s}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$



Figure 3.1.1 While modern laboratories use advanced instrumental analysis techniques, some volumetric analyses are made using the standard glassware found in most school laboratories.



Figure 3.1.2 Many household substances contain acids or bases.

CHEM SNIPPET

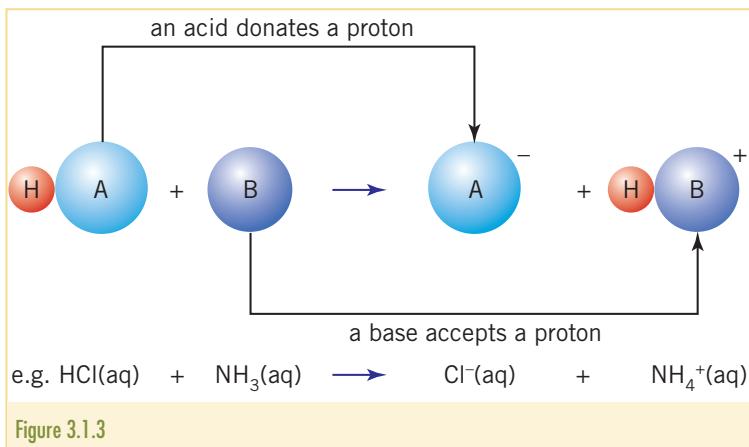


More than one definition

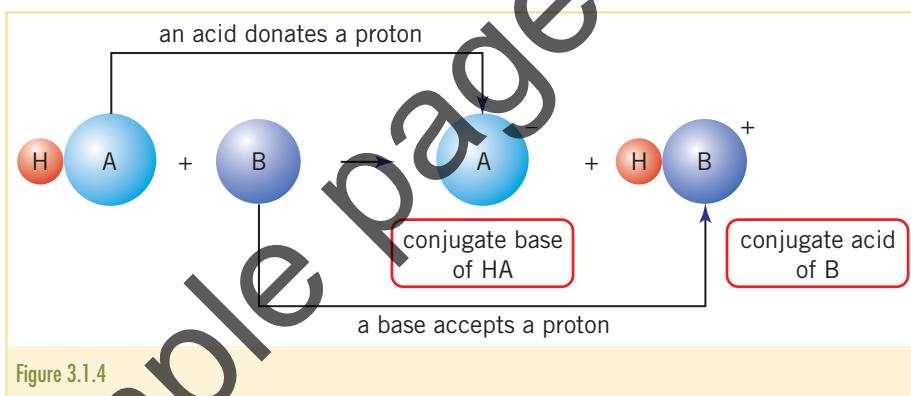
Because of their importance, there have been many attempts to define acids and bases and explain their properties. Antoine Lavoisier made an early attempt in the 1700s, when he put forward the hypothesis that all acids contain oxygen. The oxides of many non-metallic elements, such as sulfur dioxide and carbon dioxide, do form acids when dissolved in water. However, oxides of some non-metallic elements and the oxides of metals are basic. Lavoisier's idea was shown to be incorrect when, in 1810, Humphry Davy showed that hydrochloric acid did not contain oxygen. He proposed that all acids contained hydrogen rather than oxygen. The German chemist Justus von Liebig refined the definition in 1838 by stating that acids were compounds containing hydrogen that can react with a metal to produce hydrogen gas.

The first to develop a theory that explained the properties of acids was the Swedish chemist Svante Arrhenius (1859–1927), who defined acids as substances that release hydrogen ions (H^+) when dissolved in water, and bases as substances that dissociate or ionise in water to produce hydroxide ions (OH^-). In 1923, Thomas Lowry in England and Johannes Brønsted in Denmark developed the proton donation and acceptance model. However, this was not the final word on acid–base theories. For a Lowry–Brønsted base to accept a proton, it must have at least one unshared pair of electrons. In 1932, an American chemist, Gilbert Lewis, developed a more general theory of acids and bases based on the idea of species donating and accepting electron pairs.

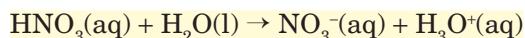
- A Lowry–Brønsted acid is a species that donates a hydrogen ion (proton) to another species—a base.



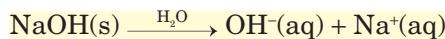
- Lowry–Brønsted reactions involve the transfer of a proton from an acid to a base to form a conjugate base and a conjugate acid.



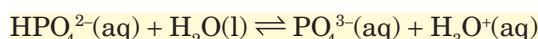
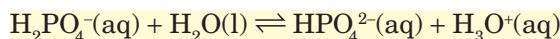
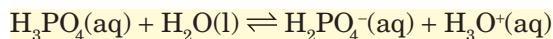
- Conjugate acid–base pairs** are two species that differ by one proton. Examples include: HCl/Cl^- , H_2O/OH^- , H_2SO_4/HSO_4^-
 - Amphiprotic** species—water, for example—can act as both acids and bases, donating and accepting a proton.
- (H_2O as base) $HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$
- (H_2O as acid) $NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$
- Acids **ionise** when placed in water; that is, the acid molecules react with water molecules to produce ions.



This ionisation may be contrasted with the process of **dissociation**, where an ionic solid, placed in water, separates to release ions into the solution.

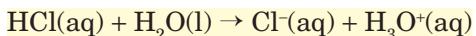


- Acids may be **monoprotic** (donating one proton per acid molecule), **diprotic** (donating two protons) or **triprotic** (donating three protons). For example, phosphoric acid is triprotic. Equations for the successive ionisations, which occur to progressively smaller extents, are:



- Acids and bases vary in strength. Strength is a measure of how readily protons are donated or accepted. Strong acids will ionise completely when placed in water. Weak acids only partially ionise when placed in water. (A quantitative treatment of acid strength will be considered in chapter 11.)

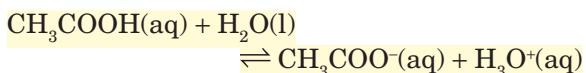
Strong acid:



For an 0.1 M HCl solution:

$$[\text{H}_3\text{O}^+] = 0.1 \text{ M}$$

Weak acid:



For an 0.1 M CH₃COOH solution:

$$[\text{H}_3\text{O}^+] < 0.1 \text{ M}$$

- The pH scale is used to describe the acidity or basicity of a solution.
- pH is a measure of the hydrogen ion concentration of a solution. The following relationships are used when calculating the pH of a solution of a strong acid or a strong base. (Calculation of pH for weak acids will be considered in chapter 11.)

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 10^{-14} \text{ at } 25^\circ\text{C}$$

For acidic solutions at 25°C:

$$[\text{H}_3\text{O}^+] > [\text{OH}^-], \text{ pH} < 7$$

For neutral solutions at 25°C:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-], \text{ pH} = 7$$

For basic solutions at 25°C:

$$[\text{H}_3\text{O}^+] < [\text{OH}^-], \text{ pH} > 7$$

CHEM SNIPPET



Why doesn't gastric juice dissolve the stomach?

We know that strong acids are corrosive. The gastric juice in your stomach has a pH of close to 1.0 when first released. When mixed with food this becomes diluted, but its pH remains low at around 2. Why doesn't this strong acid destroy the stomach lining? A viscous layer of mucus protects the cells lining the stomach. This mucus serves as a physical barrier. It also contains bicarbonate ions (HCO_3^-) that neutralise the acid in the gastric juice. Damage to the mucus—caused by aspirin, alcohol, bacteria or other agents—leaves the cells exposed, resulting in a painful ulcer.

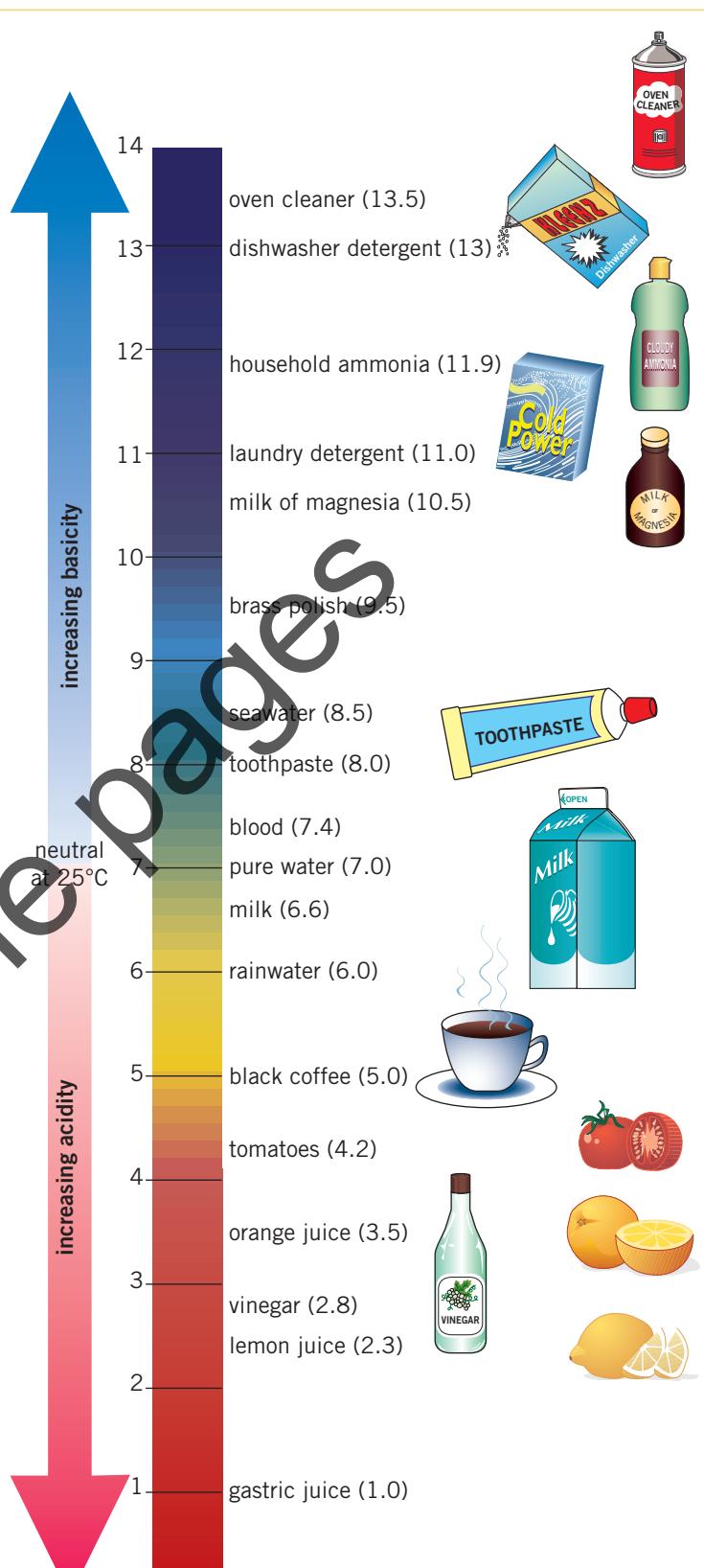


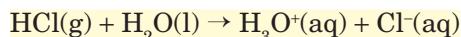
Figure 3.1.5 The pH values for some commonly used substances.

Worked example 1

Calculate the hydronium and hydroxide ion concentrations and the pH of a 0.10 M HCl solution.

Solution

HCl is a strong, monoprotic acid. It completely ionises in water.



Every hydrogen chloride molecule ionises to produce a hydronium ion, hence the concentration of hydronium ion is 0.10 M.

$$[\text{H}_3\text{O}^+] = 0.10 = 10^{-1.0} \text{ M}$$

$$\therefore \text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}10^{-1.0} = 1.0$$

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 10^{-14}$$

$$\therefore 10^{-1.0} \times [\text{OH}^-] = 10^{-14}$$

$$\therefore [\text{OH}^-] = 10^{-13} \text{ M}$$

Worked example 2

Calculate the hydronium and hydroxide ion concentrations and the pH of a 0.10 M NaOH solution.

Solution

NaOH completely dissociates in water, hence the concentration of hydroxide ion is 0.10 M.

$$[\text{OH}^-] = 0.10 = 10^{-1.0}$$

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = 10^{-14}$$

$$\therefore 10^{-1.0} \times [\text{H}_3\text{O}^+] = 10^{-14}$$

$$\therefore [\text{H}_3\text{O}^+] = 10^{-13} \text{ M}$$

$$\therefore \text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}10^{-13} = 13$$

Questions

- 1 Write balanced equations to illustrate the following reactions.
 - a Ionisation of nitric acid in aqueous solution.
 - b Dissociation of barium hydroxide in aqueous solution.
 - c Neutralisation of hydrochloric acid solution with potassium hydroxide solution.
 - d Successive ionisations of sulfuric acid.
- 2 Calculate the volume of 0.100 M HCl needed to neutralise:
 - a 25.00 mL of 0.159 M Ba(OH)₂ solution
 - b 20.00 mL of 0.0519 M NH₃ solution
 - c 0.269 g of anhydrous Na₂CO₃.
- 3 For each of the following reactions, identify the Lowry–Brønsted conjugate acid–base pairs.
 - a HCO₃⁻(aq) + H₂O(l) → H₂CO₃(aq) + OH⁻(aq)
 - b H₂C₂O₄(aq) + H₂O(l) → HC₂O₄⁻(aq) + H₃O⁺(aq)
 - c HCrO₄⁻(aq) + NH₃(aq) → CrO₄²⁻(aq) + NH₄⁺(aq)

- 4** **a** **i** Write a balanced equation for the reaction of zinc oxide with dilute hydrochloric acid.
ii Show that this reaction is an acid–base reaction.
- b** **i** Write a balanced equation for the reaction of zinc with dilute hydrochloric acid.
ii Show that this reaction is not an acid–base reaction.
iii What type of reaction is it? Explain your answer.

- 5** Rank the following solutions (all 0.1 M) in order of decreasing pH:
KOH, H₂SO₄, CH₃COOH, NH₃, HCl, NaCl

- 6** Match each solution to its correct pH value.

Solution	pH
Oven cleaner	1.0
0.02 M HCl	11.0
0.02 M NaOH	3.5
Orange juice	1.7
0.05 M Ba(OH) ₂	12.3
Cloudy ammonia	12.0
Gastric juice	13.0

- 7** **a** Calculate the hydronium ion and hydroxide ion concentrations and the pH of each of the following solutions.
- i** 0.020 M HCl
ii 0.20 M NaOH
iii 0.020 M Ba(OH)₂
- b** Calculate the hydronium ion and hydroxide ion concentrations of each of the following solutions.
- i** Lemon juice with a pH of 2.3.
ii A laundry detergent with a pH of 11.
iii Blood with a pH of 7.4

3.2 VOLUMETRIC ANALYSIS

Volumetric analysis is a form of quantitative analysis that involves measuring the volumes of solutions taking part in a chemical reaction. During volumetric analysis, a solution of accurately measured, known concentration is added so as to completely react with the substance being analysed. From the concentration and volume of the known solution, along with the balanced chemical equation for the reaction, the amount of the unknown substance can be determined. The technique is widely used to analyse solutions of acids and bases.

Worked example

A 0.412 g sample of a drain cleaner, containing sodium hydroxide, was dissolved in 20.00 mL of distilled water. This solution required 21.02 mL of a 0.205 M hydrochloric acid solution for neutralisation. Calculate the concentration of sodium hydroxide in the drain cleaner in % m/m.



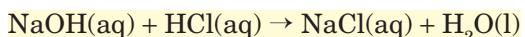
WORKSHEET 3.1
Revision of acids and bases



Figure 3.2.1 Volumetric analysis involves the use of special glassware to accurately measure volumes of solutions.

Sample pages

Step 1: Write a balanced equation.



Step 2: List all information.

$$c(\text{HCl}) = 0.205 \text{ M} \quad c(\text{NaOH}) = ? \% \text{ m/m}$$

$$V(\text{HCl}) = 21.02 \text{ mL} \quad m(\text{cleaner}) = 0.412 \text{ g}$$

Step 3: Calculate the amount (in mol) of the known substance.

$$n(\text{HCl}) = c \times V = 0.205 \times 21.02 \times 10^{-3} = 4.309 \times 10^{-3} \text{ mol}$$

Step 4: Determine the mole ratio of the unknown substance to the known substance.

$$n(\text{NaOH}) = n(\text{HCl}) = 4.309 \times 10^{-3} \text{ mol}$$

Step 5: Solve for the required quantity (in the required units).

$$m(\text{NaOH}) = n \times M = 4.309 \times 10^{-3} \times 40.0 = 0.172 \text{ g}$$

We have: 0.172 g of NaOH in 0.412 g of cleaner

$$\therefore \left(\frac{0.172}{0.412} \times 100 \right) \text{ g of NaOH in 100 g of cleaner}$$

$$\therefore 41.7\% \text{ m/m}$$

Glassware

The data used in the example above comes from a **titration** experiment. This is the procedure of adding one solution to another until the reaction between them is just complete. Usually in a titration, a measured volume of one solution is placed in a conical flask using a pipette. A few drops of an indicator are added to the flask. This indicator changes colour when the reaction is complete. The second solution is added drop-by-drop from a burette until the reaction is complete. Successful analysis therefore relies on the accurate measurement

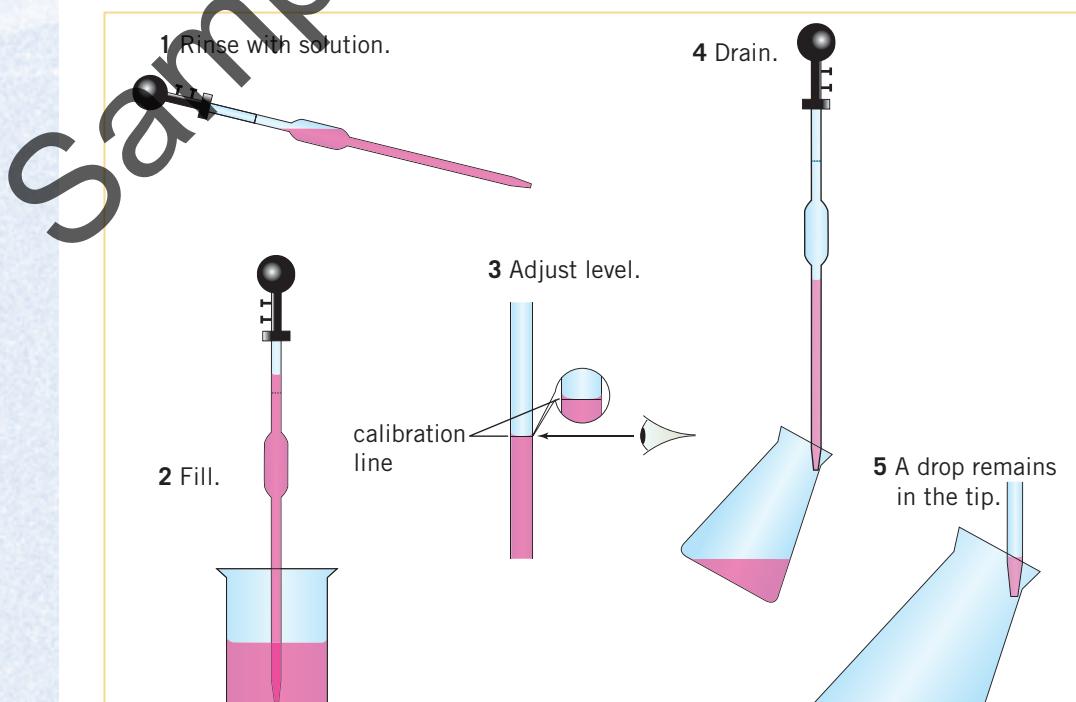


Figure 3.2.2 Correct use of a pipette ensures an exact volume of solution is delivered into the flask during a titration.

In the final case of a weak acid–weak base titration, the pH does not change rapidly at the equivalence point. Determining the equivalence point using an indicator is therefore difficult. In this case, the titration must be followed using a pH meter, and the titration curve used to determine the equivalence point.

Questions

19 For each of the following titrations identify:

- the species present at the equivalence point
- the pH of the reaction mixture at the equivalence point (7, above 7, below 7)
- an appropriate indicator.

- The titration of an NaOH solution with an HNO₃ solution.
- The titration of an Na₂CO₃ solution with an HCl solution.
- The titration of a KOH solution with a CH₃COOH solution.

20 The graph below shows titration curves for two experiments. A 25.0 mL aliquot of hydrochloric acid was titrated with a 0.100 M NaOH solution in one experiment. In the other, a 25.0 mL aliquot of ethanoic acid of the same concentration as the hydrochloric acid, was titrated with a 0.100 M NaOH solution.

- Which curve, X or Y, represents the experiment using the HCl solution?
- Why is the pH at the start of each curve different?
- Why are the pH values at the equivalence points different?
- What was the concentration of the acid solutions?

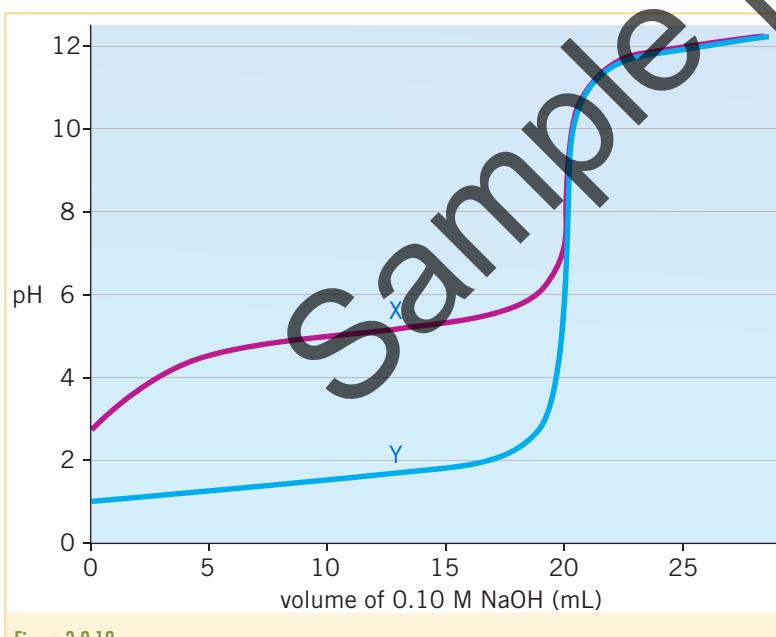


Figure 3.2.12

More complex titrations

Many substances to be analysed contain several components. This can make the analysis process appear complex. The technique is to concentrate on the chemistry of each component. Each component can then be analysed using an appropriate procedure. The following worked example illustrates this idea.



WORKSHEET 3.2
Acid–base titrations

Two components are present, but only one is acidic. In earlier examples, we have assumed that the only reacting substance was the one under analysis.

Worked example

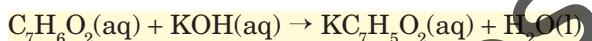
An environmental chemist analysed the waste from an industrial process. The waste was known to contain benzoic acid ($C_7H_6O_2$)—a weak, monoprotic acid—and carbon tetrachloride (CCl_4). A 0.293 g sample of waste was shaken vigorously in water to dissolve the benzoic acid. The aqueous solution was neutralised by 11.37 mL of 0.120 M KOH solution. Calculate the percentage by mass of benzoic acid in the waste sample.

Solution

Step 1: Write a balanced equation.

We know that $C_7H_6O_2$ is monoprotic.

We also know that CCl_4 is not acidic (there are no hydrogen ions to donate). The reaction is therefore:



Step 2: Calculate the amount (in mol) of the known substance.

$$n(KOH) = c \times V = 0.120 \times 11.37 \times 10^{-3} = 1.36 \times 10^{-3} \text{ mol}$$

Step 3: Determine the mole ratio of the unknown substance to the known substance.

$$n(C_7H_6O_2) = n(KOH) = 1.36 \times 10^{-3} \text{ mol}$$

Step 4: Solve for the required quantity (in the required units).

$$m(C_7H_6O_2) = n \times M = 1.36 \times 10^{-3} \times 122.1 = 0.166 \text{ g}$$

$$\% C_7H_6O_2 = \frac{m(C_7H_6O_2)}{m(\text{sample})} \times \frac{100}{1} = \frac{0.166}{0.293} \times \frac{100}{1} = 56.7\%$$

In some situations, it is not possible to conduct a volumetric analysis as described above. Where the substance to be analysed is insoluble, such as limestone ($CaCO_3$), direct titration is not possible. Titration is also not possible if the solution being analysed is volatile. In that case, as evaporation occurs, the titration method is not fast enough to carry out the analysis before the concentration of the solution changes. Weak acids and weak bases also present problems, as it is difficult to obtain sharp endpoints in these titrations. In each of these situations, the technique known as a **back titration** (or indirect titration) can be used. A back titration involves adding a measured excess of reagent to the sample being analysed. A reaction occurs completely and usually quickly, and an amount of unreacted reagent remains in the solution. This unreacted amount is then determined by direct titration. The determination of the $CaCO_3$ content of eggshells illustrates the procedures used in a back titration (see table 3.2.3).

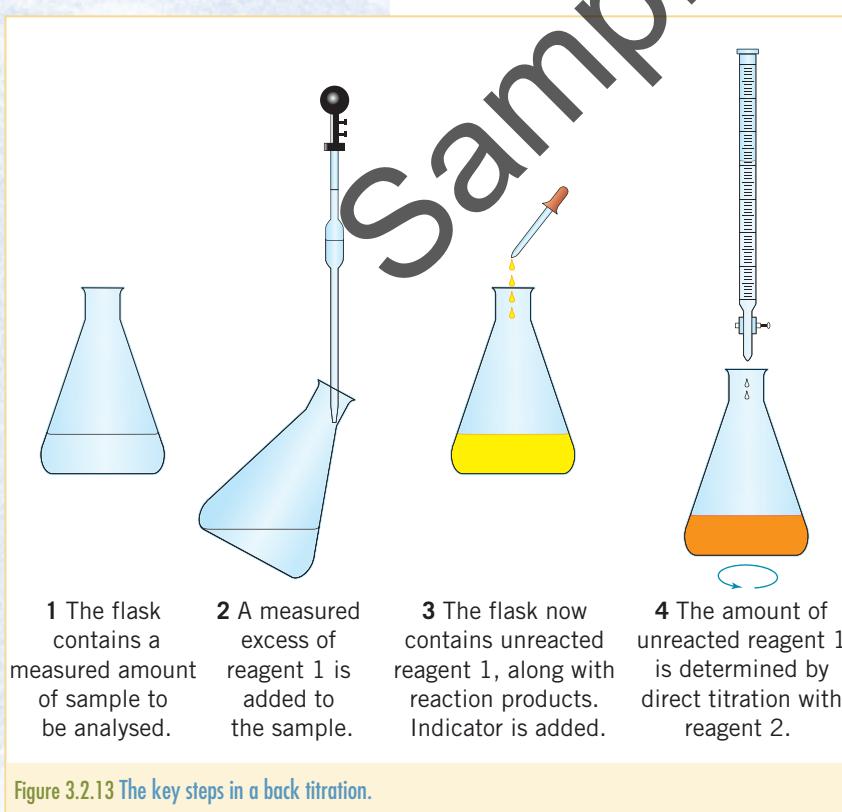


Figure 3.2.13 The key steps in a back titration.

TABLE 3.2.3 DETERMINING THE CaCO_3 CONTENT OF EGGSHELLS BY BACK TITRATION

Procedure	Explanation
1 Accurately weigh a sample of clean dry eggshells. Crush the shells and transfer to a conical flask.	Mass of the sample must be determined. The sample is crushed to allow faster, more complete reaction of the CaCO_3 in the shells with the hydrochloric acid.
2 Add an aliquot of standardised hydrochloric acid solution.	This is a measured excess of reactant. Reaction occurs according to: $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
3 Allow the mixture to stand until no more bubbles of CO_2 evolve.	This ensures the reaction is complete; that is, all the CaCO_3 has reacted. Unreacted HCl remains in the flask.
4 Rinse and fill a burette with standardised NaOH solution. Add several drops of methyl red indicator to the flask.	The unreacted acid is to be titrated with NaOH. The indicator changes colour when the reaction is complete. $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
5 Titrate the solution until the endpoint (colour change) is reached. Record the titre of NaOH used.	The amount of NaOH reacting is determined. This allows the amount of unreacted HCl to be determined, which in turn allows the amount of reacting HCl to be determined.

Worked example

The CaCO_3 content of an eggshell sample was determined by a back titration method as described in table 3.2.3. The results of the back titration were:

Mass of eggshell sample: 0.227 g

Concentration of HCl solution: 0.400 M

Volume of HCl solution added to sample: 20.00 mL

Concentration of NaOH solution: 0.152 M

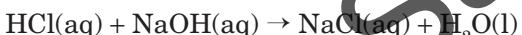
Titre of NaOH solution: 22.21 mL

Solution

Calculate the amount of HCl added initially:

$$n(\text{HCl})_{\text{initially}} = c \times V = 0.400 \times 20.00 \times 10^{-3} = 8.00 \times 10^{-3} \text{ mol}$$

Calculate the amount of HCl unreacted:



$$n(\text{NaOH}) = c \times V = 0.152 \times 22.21 \times 10^{-3} = 3.38 \times 10^{-3} \text{ mol}$$

$$n(\text{HCl})_{\text{unreacted}} = n(\text{NaOH}) = 3.38 \times 10^{-3} \text{ mol}$$

Calculate the amount of HCl reacting with the eggshells:

$$\begin{aligned} n(\text{HCl})_{\text{reacting}} &= n(\text{HCl})_{\text{initially}} - n(\text{HCl})_{\text{unreacted}} \\ &= 8.00 \times 10^{-3} - 3.38 \times 10^{-3} = 4.62 \times 10^{-3} \text{ mol} \end{aligned}$$

Calculate the amount of CaCO_3 reacting with HCl:



$$n(\text{CaCO}_3) = \frac{1}{2} \times n(\text{HCl})_{\text{reacting}} = \frac{1}{2} \times 4.62 \times 10^{-3} = 2.31 \times 10^{-3} \text{ mol}$$

Calculate the mass of CaCO_3 in the eggshells:

$$m(\text{CaCO}_3) = n \times M = 2.31 \times 10^{-3} \times 100.1 = 0.231 \text{ g}$$

$$\% \text{ CaCO}_3 \text{ in eggshells} = \frac{m(\text{CaCO}_3)}{m(\text{eggshells})} \times \frac{100}{1} = \frac{0.213}{0.227} \times \frac{100}{1} = 93.8\%$$



WORKSHEET 3.3
A back titration



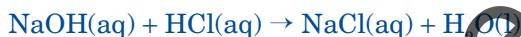
PRAC 3.5
Determining the nitrogen content of a fertiliser

Questions

- 21 Distinguish between the terms ‘direct titration’ and ‘back titration’.
- 22 40.0 mL of 0.10 M hydrochloric acid was mixed with 30.0 mL of 0.15 M sodium hydroxide solution. Calculate the volume of 0.10 M nitric acid needed to neutralise the resulting solution.
- 23 A 0.375 g sample of impure limestone was treated with 150.0 mL of 0.101 M hydrochloric acid. After reaction was complete, 19.84 mL of 0.200 M sodium carbonate solution was required to neutralise the unreacted acid. Calculate the percentage of calcium carbonate in the limestone sample.
- 24 A sample of lawn fertiliser was analysed by back titration to determine its ammonium ion (NH_4^+) content. The sample was boiled in NaOH solution. The reaction occurred according to the equation:



When evolution of the ammonia ceased, the solution was cooled and then titrated with HCl solution. The reaction occurred according to the equation:



The results of the analysis were:

- Mass of fertiliser sample 0.104 g
- Volume of NaOH solution 25.00 mL
- Concentration of NaOH solution 0.120 M
- Titre of HCl solution 16.13 mL
- Concentration of HCl solution 0.100 M

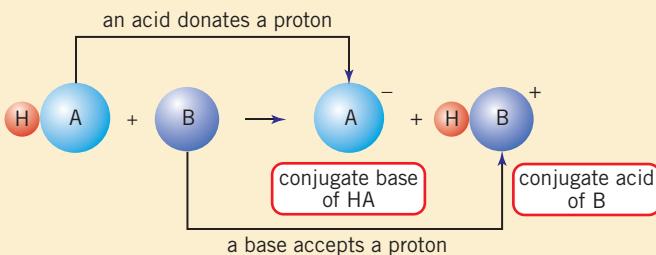
Calculate the NH_4^+ content of the fertiliser (as % m/m).



Figure 3.2.14 Volumetric analysis in industry uses equipment somewhat more sophisticated than the burette. Automatic titration assemblies carry out volumetric analyses with greater speed and accuracy than the school laboratory version.

Chapter summary

- Reactions typical of acids include:
 $\text{Acid} + \text{metal} \rightarrow \text{salt} + \text{hydrogen gas}$ (a redox reaction)
- $\text{Acid} + \text{metal hydroxide} \rightarrow \text{salt} + \text{water}$
- $\text{Acid} + \text{metal oxide} \rightarrow \text{salt} + \text{water}$
- $\text{Acid} + \text{metal carbonate} \rightarrow \text{salt} + \text{water} + \text{carbon dioxide}$
- Acids are proton donors, bases are proton acceptors. Acid–base reactions involve the transfer of protons.



- Acidic species may be described as monoprotic (donate one proton), diprotic (donate two protons), triprotic (donate three protons) or amphiprotic (both donate and accept protons).
- Acid–base strength is a measure of how readily protons are donated or accepted.
- pH is the scale used to measure the acidity or basicity of a solution, where $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$.
- Volumetric analysis is a quantitative technique that involves measuring volumes of solutions taking part in a chemical reaction. Volumetric analysis involves the process of titration.
- A titration involves adding one solution to another until the reaction between them is complete.
- Specialised glassware (pipettes, burettes and volumetric flasks) are used to perform titrations.

Glassware	Used for measuring:	Rinsed prior to use with:
Volumetric flask	a fixed, usually large, volume of solution, such as 250.0 mL	distilled water
Pipette	a fixed volume of solution (aliquot)	the solution it is to contain
Burette	a variable volume of solution (titre)	the solution it is to contain

- A typical titration proceeds according to the flowchart shown below.

1 Rinse and fill a burette with the standard solution. Record the initial volume.

2 Rinse and fill a pipette with the unknown solution. Transfer this aliquot to a conical flask.

3 Add several drops of suitable indicator to the conical flask.

4 Titrate the unknown solution with the standard solution until the endpoint (colour change) is reached.

5 Record the final burette reading and hence determine the titre (volume added).

6 Repeat steps 1 to 5 until three concordant titres have been obtained.

- A standard solution is one whose concentration is accurately known.

A primary standard is a substance which has the properties of: having a known formula, being able to be stored without deterioration or reaction with the atmosphere, and being obtainable in pure form. It is preferably of high molar mass and inexpensive. A primary standard may be weighed and made up into a standard solution.

1 Accurately weigh a sample of the primary standard.

2 Transfer the sample to a volumetric flask.

3 Ensure complete transfer by washing with water.

4 Dissolve the primary standard in water by shaking.

5 Add water to make the solution up to the calibration mark.

- An acid–base indicator is a substance that changes colour close to the equivalence point of a titration. A suitable indicator must change colour at a pH near the pH of the equivalence point of the titration.

- The equivalence point of a titration is the point at which chemically equivalent amounts of reactants have been mixed. The endpoint of a titration is the point at which an indicator changes colour to show that the reaction is complete.
- A titration curve is a graph showing the variation in pH of the solution in the flask as the solution is added slowly from a burette.

- A back titration is a technique that involves the addition of a measured excess of reagent to the analysis sample. The amount of unreacted reagent is determined by a titration. The key step in the calculations involved for a back titration is:

$$n(\text{reagent})_{\text{reacting}} = n(\text{reagent})_{\text{added initially}} - n(\text{reagent})_{\text{unreacted}}$$

Review questions

- Write balanced equations to illustrate the following reactions.
 - The first and second ionisations of sulfuric acid in aqueous solution.
 - Dilute hydrochloric acid added to solid sodium carbonate.
 - Dilute sulfuric acid added to magnesium oxide.
 - A hydrogen carbonate ion acting as a base when reacting with a hydrogen sulfate ion.
- Calculate the volume of 0.200 M NaOH solution needed to neutralise:
 - 20.00 mL of 0.115 M H_2SO_4 solution
 - 20.00 mL of 0.203 M CH_3COOH solution.
- Rank the following 0.10 M solutions in order of increasing pH.
 H_3PO_4 (a weak triprotic acid), H_2SO_4 , KOH, $\text{Ba}(\text{OH})_2$, H_2PO_4^- , NaNO_3
- Calculate the pH of each of the following at 25°C:
 - 0.010 M HCl solution.
 - 0.20 M $\text{Ba}(\text{OH})_2$ solution.
 - The solution resulting when 20.00 mL of 0.20 M HNO_3 is mixed with 25.00 mL of 0.10 M KOH.
 - The solution resulting when 20.00 mL of 0.10 M H_2SO_4 is added to 20.00 mL of 0.10 M NaOH.
- What mass of sodium hydroxide is needed to prepare 1.0 L of a cleaning solution with a concentration of 10.0 M?

- Match each term to an appropriate description.

Terms	Descriptions
Burette	Solid used to prepare a solution of known concentration.
Aliquot	The point at which an indicator changes colour.
Standard solution	Volume delivered from a burette.
Titre	Graduated glassware used to deliver a variable volume.
Equivalence point	A solution of accurately known concentration.
Pipette	Volume delivered from a pipette.
Primary standard	Graduated glassware used to deliver a fixed volume.
Endpoint	The point where stoichiometrically equivalent amounts of reactants have reacted.
7 Distinguish between a standard solution and a standardised solution.	
8 a Suggest how a neutralisation reaction could be used to minimise the damage when 10 M H_2SO_4 is spilled on a laboratory bench.	
b Would the neutralisation procedure described in part a be useful if the H_2SO_4 was spilled on your skin? Explain.	
9 Draw a flowchart to show how the hydrochloric acid content of a brick-cleaning solution could be determined by titration with 0.50 M sodium hydroxide solution. (The brick-cleaning solution is approximately 10 M HCl.)	

- 10** A 20.00 mL sample of vinegar was titrated with a standardised 0.989 M sodium hydroxide solution. A titre of 20.45 mL was recorded.
- Calculate the concentration (in mol L⁻¹) of ethanoic acid in the vinegar.
 - During the titration, several pieces of glassware were used. State which liquid should be used to rinse each of the pieces of glassware below, immediately prior to its use.
 - Burette
 - Pipette
 - Conical flask
- 11** **a** Nitric acid may be used for etching designs on copper objects. A commercially available nitric acid has a concentration of 15 M. What volume of this concentrated acid is needed to prepare 500 mL of a 2.5 M solution used in copper etching?
- b** In order to check the concentration of the prepared 2.5 M solution, a 10.00 mL aliquot was titrated with a standardised 1.011 M NaOH solution. The average titre required was 25.28 mL. Calculate the concentration of the prepared nitric acid solution.
- 12** Two bottles of cloudy ammonia cleaner were being compared. One bottle (A) stated that it contained 41 g L⁻¹ of NH₃ as NH₄OH. Another bottle (B) claimed to contain 21 g L⁻¹ NH₃. Which bottle had the higher concentration of NH₃? Explain your choice.
- 13** Oxalic acid is a diprotic acid (HOOOCOOH) that can be used as a rust remover. The following results were obtained during an analysis of a rust remover solution by titration with a sodium hydroxide solution.
- Volume of rust remover used: 5.00 mL
 Volume of diluted rust remover solution: 500.0 mL
 Aliquot of diluted rust remover solution: 10.00 mL
 Titre of 0.0200 M NaOH solution required: 13.45 mL
 Calculate the oxalic acid concentration in the rust remover (in % m/v).
- 14** Coal contains sulfur. When coal is burnt, the sulfur produces sulfur dioxide. This SO₂ may be analysed by reaction with hydrogen peroxide to produce sulfuric acid. The sulfuric acid is then titrated with a standardised sodium hydroxide solution.
- $$\text{H}_2\text{O}_2(\text{aq}) + \text{SO}_2(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$$
- When a 1.178 g sample of coal was burnt, the resulting SO₂ was collected in H₂O₂ to form H₂SO₄. This H₂SO₄ required 26.52 mL of 0.0953 M NaOH for neutralisation. Calculate the sulfur content of the coal sample (in % m/m).
- 15** **a** 1.342 g of anhydrous sodium carbonate was dissolved in water and made up to 250.0 mL. Calculate the concentration of the solution.
- b** This standard solution was used to standardise an approximately 0.1 M HCl solution. 20.00 mL of the Na₂CO₃ solution required 20.13 mL of HCl for neutralisation. Calculate the concentration of the HCl solution.
- c** The standardised HCl solution was used to standardise an approximately 0.1 M NaOH solution. 19.26 mL of HCl was needed to neutralise 20.00 mL of NaOH solution. Calculate the concentration of the NaOH solution.
- 16** The graph below shows the changes in the electrical conductivity of a reaction mixture that occurred as 20.00 mL of 0.0500 M Ba(OH)₂ solution was titrated with a sulfuric acid solution of unknown concentration.
-
- | Volume of sulfuric acid added (mL) | Conductivity (arbitrary units) |
|------------------------------------|--------------------------------|
| 0 | 85 |
| 2 | 75 |
| 4 | 68 |
| 6 | 62 |
| 8 | 56 |
| 10 | 50 |
| 12 | 44 |
| 14 | 38 |
| 16 | 32 |
| 18 | 26 |
| 20 | 20 |
| 22 | 14 |
| 24 | 85 |
- a** Write a balanced equation for the reaction.
- b** Explain why the electrical conductivity of the solution decreased as H₂SO₄ was added.
- c** Determine the volume of H₂SO₄ solution needed to neutralise the Ba(OH)₂ solution.
- d** Calculate the concentration of the H₂SO₄ solution.
- 17** An impure sample of solid KOH was dissolved in water and titrated with 0.100 M hydrochloric acid. 0.166 g of the solid required a titre of 26.23 mL of 0.100 M hydrochloric acid.

- a** Calculate the percentage by mass of KOH in the sample.
- b** State one assumption you have made in completing this calculation.
- 18** 0.0802 g of NaOH was dissolved in 20.0 mL of water in a conical flask. The resulting solution was titrated with 0.100 M HCl. A titre of 21.05 mL was required for neutralisation.
- a** Calculate the expected titre of 0.100 HCl required to neutralise 0.0802 g of NaOH.
- b** Which one or more of the following errors would account for the difference between the value calculated in part **a** and the result obtained in the experiment. Explain your choices.
- i** The NaOH solution was left exposed to the air for some time before the titration was performed.
- ii** The solid NaOH sample was damp.
- iii** The burette was rinsed with water immediately prior to use.
- iv** 25.00 mL of water was added to the conical flask by mistake.
- 19** Which of the following indicators would be most suitable for the titration of the weak base methylamine with hydrochloric acid—methyl red, which changes colour in the range pH 4.4–6.2, or bromothymol blue, which changes colour in the range pH 6.0–7.6? Explain your choice.
- 20** Aspirin tablets may be analysed using a back titration method. 0.425 g of aspirin tablets were heated gently in 40.00 mL of 0.243 M NaOH. When cooled, the solution was titrated with 0.250 M HCl. A titre of 22.23 mL was required for neutralisation. Given that aspirin ($C_9H_8O_4$) is a diprotic acid that reacts with sodium hydroxide in a 1:2 mole ratio, calculate the percentage by mass of aspirin in the tablets.

Examination questions

Multiple choice

- 1** Which of the following is *not* a property of a substance to be used as a primary standard?
- A** It has a known formula.
- B** It is highly soluble in the chosen solvent.
- C** It is able to be stored without reaction or deterioration.
- D** It preferably has a low molecular mass.
- 2** 20.00 mL of 0.20 M sodium hydroxide is added to 20.00 mL of 0.10 M sulfuric acid solution. The pH of the resulting solution is:
- A** 0.7
- B** 1.3
- C** 7.0
- D** 13

For more multiple-choice examination questions, connect to the *Chemistry Dimensions 2 Companion Website* at www.pearsoned.com.au/schools and select the chapter 3 Review Questions.

Extended response

- 1** The concentration of ethanoic acid (CH_3COOH) in a vinegar sample was determined by volumetric analysis. 20.00 mL of vinegar was transferred to a volumetric flask and water added to the total 250.0 mL volume. 20.00 mL aliquots of the diluted vinegar solution required an average titre of 19.82 mL of standardised 0.102 M NaOH solution for neutralisation.
- a** Write a balanced equation for the reaction.
- b** Calculate the molar concentration of ethanoic acid in the vinegar sample.
- c** The pH ranges for colour change of several indicators are shown in table 3.2.1 on page 46. Suggest a suitable indicator for use in the titration. Explain your choice.
- d** Why is the NaOH solution referred to as a ‘standardised’ solution?



- 2 During a practical class, the ammonia content of a window cleaning solution was determined using volumetric analysis. 20.0 mL of cleaner was pipetted into a volumetric flask and the volume made up to 250.0 mL using distilled water. A 25.00 mL aliquot of this diluted cleaner solution required 24.35 mL of 0.187 M hydrochloric acid for neutralisation. Methyl orange was used to indicate the endpoint.
- a Calculate the concentration (in mol L⁻¹) of ammonia in the window cleaner.
- b The value calculated in a was considerably less than the value given on the label of the window cleaner. Which one or more of the following

errors, if made during the analysis, would account for the lower than expected calculated value? Explain your choice or choices.

- i The 20.0 mL pipette was rinsed only with water prior to its use.
- ii The burette was rinsed only with water prior to its use.
- iii The volumetric flask was rinsed only with water prior to its use.
- iv Phenolphthalein indicator (colour change at approximately pH 9) was used during the titration instead of the specified methyl orange indicator.

Chapter 3 interactives

The following interactives support learning in this chapter. They are available on the *Student CD* and on the *Chemistry Dimensions 2 Companion Website*.

www.pearsoned.com.au/schools/secondary

Interactive animations

Classifying acids and bases

Neutralisation reactions

Titration curve for a weak acid with strong base

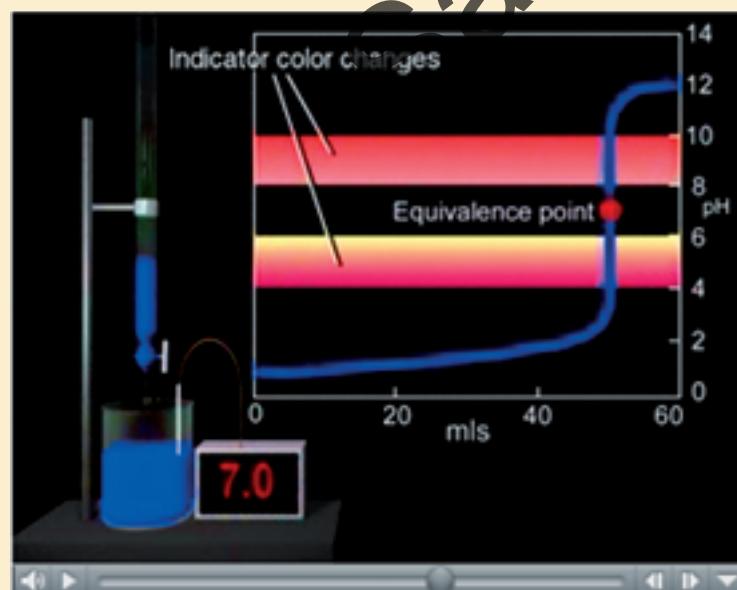


QuickTime video

Preparing a standard solution

Solution formation by dilution

Acid–base titration



Acid–base titration