

Chapter

9

THEORIES OF ACIDS AND VOLUMETRIC ANALYSIS



Figure 9.1

Accurate glassware is essential in volumetric analysis. A chemist must learn to manipulate the top of a burette so that fractions of drops can be dispensed into a conical flask during titration.

Introduction

In 1774, the element oxygen was discovered independently by Carl Scheele and Joseph Priestley. This discovery marked a turning point in our understanding of chemical reactions and, in particular, combustion reactions. In the history of acids, the discovery of oxygen led to new theories about the cause of acidity.

Antoine Lavoisier (often called the ‘father of modern chemistry’) developed more-accurate, quantitative methods for analysis, and proposed that oxygen was the cause of chemical acidity.

In this chapter

- | | |
|-------------------------|----------|
| 9.1 Theories of acids | page 177 |
| 9.2 Volumetric analysis | page 194 |

9.1 THEORIES OF ACIDS

Remember

Before beginning this section, you should be able to:

- define acids as proton donors and describe the ionisation of acids in water
- describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions.

Key content

By the end of this section, you should be able to:

- outline the historical development of ideas about acids, including those of Lavoisier, Davy and Arrhenius
- outline the Bronsted-Lowry theory of acids and bases
- describe the relationship between an acid and its conjugate base, and a base and its conjugate acid
- identify a range of salts which form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature
- identify conjugate acid-base pairs
- identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions
- qualitatively describe the effect of buffers with reference to a specific example in a natural system
- gather and process information from secondary sources to trace developments in understanding and describing acid-base reactions
- choose equipment and perform a first-hand investigation to identify the pH of a range of salt solutions.

Early theories of acids

The early experiments that chemists conducted on acids showed that they had a number of properties in common. In 1661, Robert Boyle summarised the known properties of acids and bases.

- Acids have a sour taste; bases (alkalis) have a bitter taste.
- Acids are corrosive.
- Acids and bases change the colour of vegetable dyes.
- Acids and bases neutralise one another on mixing.

These early observations demonstrated the properties of acids but did not explain the cause of acidity.

Antoine Lavoisier—The oxygen theory of acids

The first chemist to put forward a theory of acidity was the French chemist Antoine Lavoisier (1743–1794). He showed that many non-metal compounds containing oxygen produced acids when they dissolved in water. Thus the oxides of carbon, sulfur and phosphorus all produced acidic solutions. Lavoisier hypothesised in April 1776 that the presence of the oxygen in the compounds formed from these non-metals gave the compounds their acidic properties. It was Lavoisier who named the gas that Priestley and Scheele discovered. He coined the name ‘oxygen’, which literally means ‘acid former’.

Lavoisier’s theory of acids did not explain why oxides of metals were not acidic.

Humphry Davy — The hydrogen theory of acids

Humphry Davy (1778–1829) is best remembered for the discovery of many alkali metals (e.g. sodium), which he produced by electrolysis of their melted salts. In 1772, Joseph Priestley had generated hydro-

gen chloride gas by reacting sea salt with concentrated sulfuric acid; the gas dissolved readily in water to yield a very acidic solution which he called ‘marine acid’ after the sea salt he used in its preparation. Davy electrolysed samples of this acidic solution and showed that it produced hydrogen gas and chlorine gas when electrolysed. No oxygen was formed. Davy re-named this marine acid ‘hydrochloric acid’ and stated that it was a compound of hydrogen and chlorine only.

Later experiments by other chemists showed that other acids (e.g. prussic acid, HCN) also contained no oxygen but did contain hydrogen. Davy proposed that the presence of hydrogen in



Figure 9.2

Humphry Davy developed a theory of acids. He believed that all acids contained the element hydrogen.

acids gave them their acidic properties. Davy's theory did not explain why many compounds of hydrogen were not acidic (e.g. methane).

In 1838, the German chemist Justus von Liebig extended Davy's theory of acids. He stated that acids were substances that contained 'replaceable hydrogen'. Von Liebig reasoned that when acids attack metals, the metals replace the hydrogen in the acid to form a salt. Only compounds with replaceable hydrogen would attack these metals.



Von Liebig's ideas were a major step forward in our understanding of acids. His theory, however, failed to account for the production of gases such as nitrogen dioxide (rather than hydrogen) when concentrated nitric acid attacked metals.

Svante Arrhenius—the hydrogen ion theory of acids

Svante Arrhenius (1859–1927) developed a major new theory of acids and bases related to his extensive work on the theory of electrolytes, for which he won the 1903 Nobel Prize.

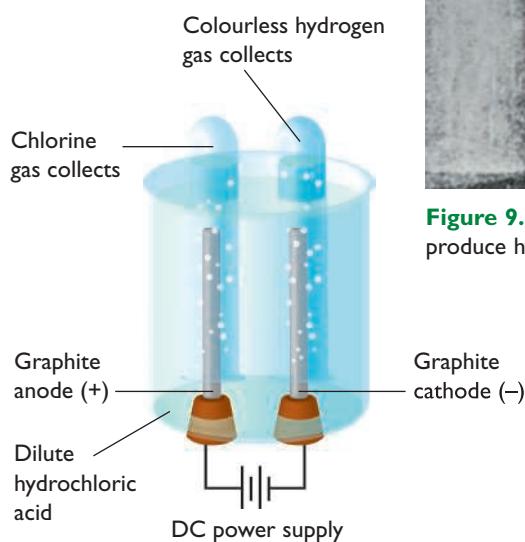


Figure 9.4

Arrhenius proposed that acid solutions contain hydrogen ions that are attracted to the negative electrode during electrolysis.

During the electrolysis of aqueous solutions of acids, hydrogen gas is produced at the cathode (negative electrode). This happens with all common acids. Arrhenius applied his theories of electrolytes to this observation and proposed that the cause of hydrogen gas evolution at the cathode was the conversion of hydrogen ions in the water into hydrogen molecules. Today we would express this original proposal as:



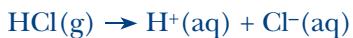
In 1884, Arrhenius stated that all acidic solutions are formed when acids ionise (Arrhenius used the word 'dissociate') into ions when they dissolve in the water.

Examples of Arrhenius acids:

Arrhenius acid: a substance that produces hydrogen ions in water solution

alkaline solution: a solution containing hydroxide ions and having a pH greater than 7

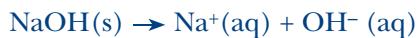
Arrhenius base: a substance that produces hydroxide ions in aqueous solution



Arrhenius recognised that some acids, such as acetic acid, were weaker than other acids. He proposed that they did not ionise as completely as the strong acids did in water. Arrhenius' theory was also important in the development of the pH scale, as it recognised the importance of the concentration of hydrogen ions in water solution.

Arrhenius also proposed the cause of basicity. He stated that a base is a substance that produces hydroxide ions (OH^-) when dissolved in water. It is an **alkaline solution** because of the presence of these hydroxide ions. Thus, substances such as sodium hydroxide and barium hydroxide are bases, as they dissociate in water to produce hydroxide ions in solution.

Examples of Arrhenius bases:



Arrhenius' theory and neutralisation

Arrhenius' theory of acids and bases also explains the process of neutralisation. He proposed that when an acid neutralises a base, it is the hydrogen ions and hydroxide ions that react to form neutral water.

Consider the following set of equations. The first equation is the whole formula equation; the second equation shows the ions that are present; the third equation is the net ionic equation, having eliminated the spectator ions (Na^+ and Cl^-).

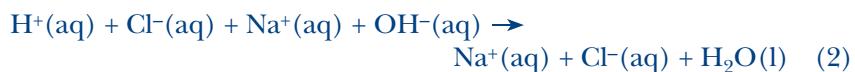


Figure 9.5



How does calcium carbonate neutralise the hydrochloric acid if there are no hydroxide ions present?

Problems with the Arrhenius' definition of acids and bases

Arrhenius' theory of acids and bases explains many properties of common acids and bases. It does fail, however, to account for all the observations made about the behaviour of these substances.

Problem 1. Why are metallic oxides and carbonates basic?

Chemists know that acids can be neutralised by metallic oxides and carbonates. These compounds contain no hydroxide ions that can dissociate into water. Many carbonates are insoluble and yet they do react with acids and neutralise them.



Arrhenius' theory could not explain these observations.



Figure 9.6

Testing a solution of zinc chloride with litmus paper shows that the solution is acidic.

Problem 2. Why are solutions of various salts acidic or basic rather than neutral? Even though a solution of sodium chloride is neutral, a solution of zinc chloride is acidic. A solution of sodium sulfide is basic. Arrhenius' theory could not explain these observations.

In order to solve these problems, new theories about acids and bases needed to be developed.

The Bronsted–Lowry theory of acids

In 1923, a Danish chemist, Johannes Bronsted (1879–1947), and an English chemist, Thomas Lowry (1874–1939), independently proposed a new theory of acids and bases. This theory is now called the Bronsted–Lowry theory. This theory helped to explain many of the problems of the Arrhenius theory. Bronsted and Lowry defined acids and bases as follows:

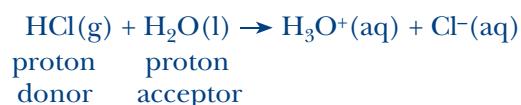
- Acids are proton donors.
- Bases are proton acceptors.

The Bronsted–Lowry theory recognised the importance of protons (hydrogen ions) in explaining acid–base behaviour. In other words, a substance cannot act as an acid without another behaving as a base. Acid–base behaviour should be thought of as proton exchange.

One major feature of this new theory was that it assigned a role to the solvent. The solvent was not just an inert liquid in which solutes dissolved. The theory focuses on the important role of water as an ionising solvent. Their theory, however, allowed chemists to venture outside aqueous chemistry and to apply these concepts in non-aqueous solvents or in gas-phase reactions.

Water as an ionising solvent

Molecular acids (e.g. HCl gas) dissolve in water to produce ions. According to the Bronsted–Lowry theory this occurs because a proton is donated from the molecular acid to the water molecule to produce the hydronium ion. The forward reaction is:



Thus the HCl is a Bronsted–Lowry acid (B–L acid) as it is the proton donor. Water is the Bronsted–Lowry base as it is the proton acceptor.

The presence of hydronium ions gives the solution its acidic properties. Water is not just behaving as a solvent, but as a Bronsted–Lowry base.

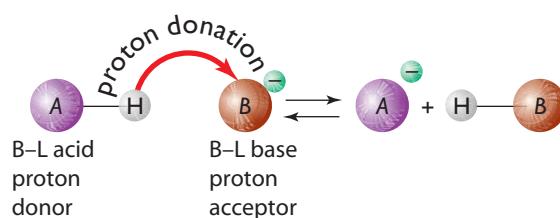
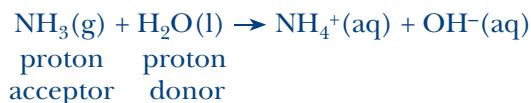


Figure 9.7

A Bronsted–Lowry acid donates a proton to a Bronsted–Lowry base. The base is the proton acceptor.

In similar fashion, molecular bases (e.g. NH₃ gas) dissolve in water to generate ions. In this example, however, the water behaves as a Bronsted–Lowry acid and donates a proton to the ammonia molecule to form the ammonium ion.





PROTON TRANSFER

Consequently, water is now seen to have a dual nature. It can behave as either a proton donor or a proton acceptor.

The self-ionisation of water can also be understood in terms of the Bronsted–Lowry theory. One water molecule behaves as a Bronsted–Lowry base and the other behaves as a Bronsted–Lowry acid.



proton proton
acceptor donor

Conjugate acids and bases

The Bronsted–Lowry theory develops the concept of acid–base pairs. When a Bronsted–Lowry acid donates its proton to the base, the anion of the acid is proton deficient. This species can act as a base as it could accept a proton and reform the original acid.

Example: HF/F[−] is an acid–base pair.

When HF donates a proton to a base, the fluoride ion (F[−]) is formed. The HF is a Bronsted–Lowry acid.

Fluoride ions can accept protons from an acid and form HF once again. The fluoride ion is acting as a base according to the Bronsted–Lowry definition.

As the water solvent is involved, let us examine the complete equilibrium reaction.



The reactants are classified as follows:

HF — Bronsted–Lowry acid

H₂O — Bronsted–Lowry base.

Looking at the reaction in reverse, we can see that the hydronium ion is an acid and the fluoride ion is a base. The hydronium ion donates a proton to the fluoride ion and water and HF are formed. In order to avoid confusion, the acids and bases on the right-hand side of the equation are called **conjugates**.

H₃O⁺ — conjugate acid

F[−] — conjugate base

The term *conjugate* means ‘coupled’ or ‘joined’. In the Bronsted–Lowry theory, each acid has its conjugate base and each base has its conjugate acid. In the example above:

HF = Bronsted–Lowry acid; F[−] = conjugate base of HF

H₂O = Bronsted–Lowry base; H₃O⁺ = conjugate acid of H₂O

SAMPLE PROBLEM 9.1

The hydrogen sulfate ion reacts with the acetate ion according to the following equilibrium reaction:



Classify each of the species in the equilibrium in terms of Bronsted–Lowry (B–L) acid–base pairs.

SOLUTION

Step 1. Identify the proton donor and proton acceptor in the forward reaction.

The HSO_4^- ion has donated a proton to the acetate ion.

Step 2. Classify the reactants as B–L acids and bases.

HSO_4^- = B–L acid

CH_3COO^- = B–L base

Step 3. Identify the conjugate acid and base.

The B–L acid will form the conjugate base (i.e. SO_4^{2-})

The B–L base will form the conjugate acid (i.e. CH_3COOH)

Step 4. Record the acid–base pairs.

HSO_4^- = B–L acid; SO_4^{2-} = conjugate base

CH_3COO^- = B–L base; CH_3COOH = conjugate acid

Comparative strength of conjugate acid–base pairs

Strong acids such as hydrochloric acid and nitric acid have very weak conjugate bases. The conjugate acids of strong bases such as the hydroxide ion are also very weak.

Examples:

(a) *Hydrochloric acid*

Hydrochloric acid is a strong Bronsted–Lowry acid. Its conjugate base (Cl^-) is a very weak base. It has a very poor ability to accept protons.

(b) *Acetic acid*

Acetic acid is a weak Bronsted–Lowry acid. The conjugate base (CH_3COO^-) is a stronger base than chloride ions.

(c) *Sodium hydroxide*

Hydroxide ions are strong Bronsted–Lowry bases. Their conjugate acid (H_2O) is a very weak acid.

(d) *Sodium hydrogen carbonate*

Hydrogen carbonate ions are weak Bronsted–Lowry bases. The conjugate acid (H_2CO_3) is a stronger acid than water.

Table 9.1 lists the conjugate acid–base pairs in decreasing order of their strength as acids or bases. Oxide ions and hydroxide ions are very strong bases, whereas acetate and fluoride ions are relatively weak bases.

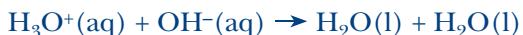
Table 9.1 Conjugate acid base pairs

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl^-	O^{2-}	OH^-
HNO_3	NO_3^-	OH^-	H_2O
H_3O^+	H_2O	S^{2-}	HS^-
HSO_4^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-
HF	F^-	NH_3	NH_4^+
HNO_2	NO_2	HCO_3^-	H_2CO_3
CH_3COOH	CH_3COO^-	HS^-	H_2S
H_2CO_3	HCO_3^-	CH_3OO^-	CH_3COOH
NH_4^+	NH_3	F^-	HF
HCO_3^-	CO_3^{2-}	SO_4^{2-}	HSO_4^-

When acids and bases are combined in aqueous solution the position of the equilibrium is determined by the relative strengths of the conjugate acid–base pairs.

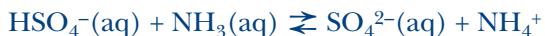
Example 1:

Strong acids react with strong bases to form weak conjugate bases and weak conjugate acids. The equilibrium lies so far to the right that we often write the equation as going to completion.



Example 2:

Reactions between a stronger acid and a weaker conjugate base (see columns 1 and 2 in Table 9.1) produce an equilibrium that lies to the right. In the following example, HSO_4^- is a stronger acid than NH_4^+ and NH_3 is a stronger base than SO_4^{2-} . Thus the equilibrium lies to the right.



Example 3:

Reactions between a weaker acid and a stronger conjugate base (see columns 1 and 2 in Table 9.1) produces an equilibrium that lies to the left. In the following example, HF is a stronger acid than CH_3COOH and CH_3COO^- is a stronger base than F^- . Thus the equilibrium lies to the left.



Example 4:

Reactions between a stronger base and a weaker conjugate acid (see columns 3 and 4 in Table 9.1) produce an equilibrium that lies to the right. In the following example, the sulfide ion is a stronger base than the hydrogen carbonate ion and carbonic acid is a stronger acid than the HS^- ion. Thus the equilibrium lies to the right.



SAMPLE PROBLEM 9.2

SOLUTION

Use Table 9.1 to predict the position of the equilibrium when sodium nitrate and nitrous acid solutions are mixed. Identify the Bronsted–Lowry conjugate acid–base pairs.

The sodium ions are spectators and can be ignored.

Table 9.1 shows that NO_3^- is a base and HNO_2 is an acid.

The reaction equilibrium is:



Using the table we can see that HNO_3 is a stronger acid than HNO_2 and that NO_2^- is a stronger base than NO_3^- . Thus the equilibrium lies to the left.

NO_3^- = B–L base; HNO_3 = conjugate acid

HNO_2 = B–L acid; NO_2^- = conjugate base

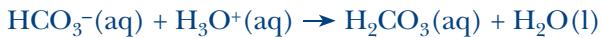
Amphiprotic species

Some of the chemical species listed in Table 9.1 appear as both acids and bases. This means that they can behave as either an acid or a base depending on the other chemical substances present. Such species that can behave as either proton donors or proton acceptors are called amphiprotic species. The term ‘amphiprotic’ should not be confused with the term ‘amphoteric’. Amphiprotism is a classification only within the Bronsted–Lowry theory.

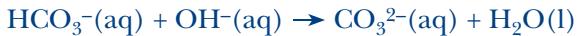
Example 1: HCO_3^-

The hydrogen carbonate ion is amphiprotic. When hydrogen carbonate ions are added to a solution of a strong acid, the hydronium ions react with the hydrogen carbonate ions to form carbonic acid which decomposes to form water and carbon dioxide. The hydrogen carbonate acts as a proton acceptor.

The presence of the strong acid and the loss of carbon dioxide drives the acid–base reaction to the right.



When hydrogen carbonate ions are added to a solution of sodium hydroxide, the hydrogen carbonate ions act as proton donors. Carbonate ions and water are formed. The presence of the strong base drives the reaction to the right.

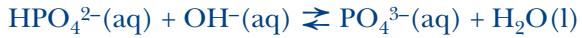


In water, hydrogen carbonate ions behave as Bronsted–Lowry acids. Carbonic acid (a weak acid) and hydroxide ions (a strong base) are formed. The final solution has a pH between 8 and 9.



Example 2: HPO_4^{2-}

The hydrogen phosphate ion is amphiprotic. It can accept a proton and form its conjugate acid (dihydrogen phosphate ion, H_2PO_4^-) or donate a proton to form its conjugate base (phosphate ion, PO_4^{3-}).



When hydrogen phosphate ions are added to water (e.g. as sodium hydrogen phosphate) the final solution is slightly basic. In this case the hydrogen phosphate ions act as weak Bronsted–Lowry acids.



Example 3: H_2O

Water itself is an amphiprotic species. We have already seen in many examples that in some Bronsted–Lowry acid–base reactions the water behaves as either a proton donor or a proton acceptor.

Water as a proton donor:



Water as a proton acceptor:



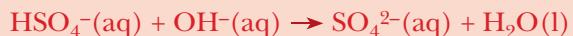
SAMPLE PROBLEM 9.3

SOLUTION

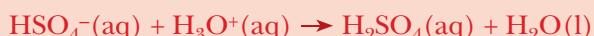
The hydrogen sulfate ion is amphiprotic.

- Write balanced equations to illustrate this behaviour.
- A solution of sodium hydrogen sulfate in water turns blue litmus red. Use an equation to explain this observation making reference to the Bronsted–Lowry theory of acid and bases.

- Choose a strong base to show the hydrogen sulfate ion acting as an acid. This drives the reaction towards completion.



Choose a strong acid to show the hydrogen sulfate ion acting as a base. This drives the reaction towards completion.



- The indicator tells us that the solution is acidic. Thus the hydrogen sulfate ion is behaving as a proton donor in the water. Water is behaving as a proton acceptor. The reaction is:



The production of hydronium ions makes the water acidic.

Hydrolysis of salts

One of the problems with the Arrhenius theory of acids and bases was its inability to explain why various salt solutions were acidic or basic. The Bronsted–Lowry theory provides an explanation for these observations. Some salt solutions are basic and some are acidic. We classify salts that form basic solutions as *basic salts*. Those that form acidic solutions are called *acidic salts*. Other salts are *neutral*.

The reaction of a salt with water to produce a change in pH is called *hydrolysis*.

Hydrolysis of basic salts

Let us look at a simple example involving sodium carbonate solution. When a 0.1 mol/L solution is tested with universal indicator, the indicator turns from green to violet (Figure 9.8). We can conclude that the solution is basic.

The basicity of the sodium carbonate solution can be explained by the carbonate ion's ability to act as a Bronsted–Lowry base. The water acts as a Bronsted–Lowry acid. The equation for the reaction is:



proton proton conjugate conjugate
acceptor donor acid base

The hydroxide ion is a stronger base than the carbonate ion. The hydrogen carbonate ion is a stronger acid than water and so this equilibrium lies to the left. There is sufficient hydroxide ions formed in the equilibrium, however, to produce a basic solution ($\text{pH} = 11.6$).

How do we know when a salt is a basic salt? Basic salts are the salts of strong bases (e.g. sodium hydroxide, potassium hydroxide) and weak acids (e.g. acetic acid, hydrofluoric acid, carbonic acid etc).



Figure 9.8

The universal indicator turns violet in sodium carbonate solution. This indicates that the solution is basic.

WEAK ACID + STRONG BASE → BASIC SALT + WATER

Example 1: Potassium fluoride (KF)

This is the salt formed from potassium hydroxide and hydrofluoric acid. The fluoride ion acts as a weak Bronsted–Lowry base when dissolved in water. This equilibrium lies to the left as the hydroxide ion is a stronger base than fluoride ions and HF is a stronger acid than water. The final solution is mildly basic due to the presence of the hydroxide ion.



Example 2: Sodium acetate (NaCH_3COO)

This is a salt formed from sodium hydroxide and acetic acid. The acetate ion acts as a weak Bronsted–Lowry base when dissolved in water. This equilibrium lies to the left as the hydroxide ion is a stronger base than acetate ions and acetic acid is a stronger acid than water. The final solution is mildly basic due to the presence of the hydroxide ion.



Hydrolysis of acidic salts

Let's look at an example of a salt of a transition metal such as copper. A 0.1 mol/L solution of copper (II) nitrate is deep blue. When a pH meter is used to test its acidity the pH is found to be 4.0. The Bronsted–Lowry theory can explain this acidic behaviour of the copper (II) nitrate solution.

The copper (II) ion in solution is surrounded by a primary hydration shell of four water molecules. These water molecules are bonded to the central copper ion by coordinate covalent bonds. These hydrated copper (II) ions act as Bronsted–Lowry acids in water. They donate a proton to the water molecule, which behaves as a Bronsted–Lowry base.

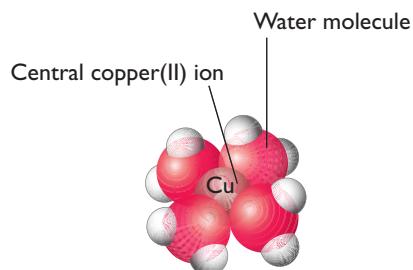


Figure 9.9

The copper (II) ion is surrounded by water molecules. The attraction of the copper ion for electrons weakens the O—H bond in the water molecules, and thus they are more readily donated to a base.

How do we know when a salt is an acidic salt? Acidic salts are the salts of strong acids (e.g. hydrochloric acid, nitric acid) and weak bases (e.g. ammonia, carbonate ions).

WEAK BASE + STRONG ACID → ACIDIC SALT + WATER

Example 1: Ammonium chloride (NH_4Cl)

This is the salt formed from ammonia (or ammonium hydroxide) and hydrochloric acid. The ammonium ion acts as a weak Bronsted–Lowry acid when dissolved in water. This equilibrium lies to the left as the

hydronium ion is a stronger acid than ammonium ions and NH_3 is a stronger base than water. The final solution is mildly acidic due to the presence of the hydronium ion.



Example 2: Zinc sulfate (ZnSO_4)

This is the salt formed from zinc hydroxide and sulfuric acid. The hydrated zinc ion acts as a weak Bronsted–Lowry acid when dissolved in water. This equilibrium lies to the left as the hydronium ion is a stronger acid than hydrated zinc ions and $\text{Zn}(\text{H}_2\text{O})_3\text{OH}^+$ is a stronger base than water. The final solution is mildly acidic due to the presence of the hydronium ion.



Neutral salts

Neutral salts are formed when strong bases neutralise strong acids.

STRONG ACID + STRONG BASE → NEUTRAL SALT + WATER

Neutral salts do not react with water to any appreciable extent. Consequently, the pH of the water remains unchanged. Salts such as NaCl , KBr and NaNO_3 are neutral salts.

The salts of weak bases and weak acids may also be neutral if the relative strengths of the acid and base are similar. This is difficult to achieve in practice.

Table 9.2 compares the pH of various 0.1 mol/L solutions of common laboratory acids and bases with various salt solutions. Note that the acidic salts are salts of weak bases and strong acids whereas the basic salts are formed from strong bases and weak acids.

Table 9.2 Approximate pH of some common laboratory acids, bases and salt solutions (0.10 mol/L)

Acid	pH	Base	pH
HCl	1.0	NaOH	13.0
NaHSO_4	1.4	Na_3PO_4	11.7
H_2SO_3	1.5	Na_2CO_3	11.5
H_3PO_4	1.5	NH_3	11.1
HF	2.1	Na_2SO_3	9.8
CH_3COOH	3.0	Na_2HPO_4	9.2
NaH_2PO_4	4.5	NaHCO_3	8.4
NH_4Cl	4.6	NaCH_3COO	8.4



HYDROLYSIS

9.1 PRACTICAL ACTIVITIES



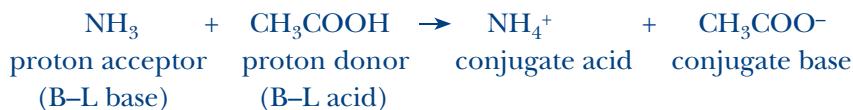
Hydrolysis of salts

Acid–base reactions in non-aqueous environments

The Bronsted–Lowry theory can be applied in non-aqueous systems.

Reactions in non-aqueous solvents

Liquid methanol can be used as a solvent rather than water. Solutions of ammonia and acetic acid can be made using methanol solvent. When these solutions are mixed, an acid–base reaction occurs in which a proton is donated from the acetic acid to the ammonia to form ammonium ions and acetate ions.



Liquid ammonia, like water, also undergoes a self-ionisation reaction. The equilibrium established is shown in the following equation. One ammonia molecule donates a proton to the other. The products are the ammonium ion and the amide ion.



Figure 9.10

When concentrated ammonia solution (adhering to a glass rod) is brought near a dish of concentrated hydrochloric acid, a smoke of ammonium chloride forms in the air. This is an example of a proton donation reaction.

Reactions in the gas phase

If ammonia gas and hydrogen chloride gas are mixed in a flask in the absence of water, a reaction is observed in which fine white crystals form as a fine smoke. The smoke particles consist of crystals of ammonium chloride. The reaction can be written as:



In this case the HCl is acting as a Bronsted–Lowry acid and donates a proton to the ammonia which is a Bronsted–Lowry base. The ammonium ion that forms is attracted to the negative chloride ion formed to produce a crystalline ionic solid.

Buffers

Our body fluids and secretions must be maintained in a narrow pH range in order for our biochemical processes to occur at an optimal rate. The pH of saliva, which is produced by our salivary glands, must be maintained in the range 6.4–7.0 or the amylase enzymes that catalyse the hydrolysis of complex carbohydrates will not function. Our stomach gastric juices must have a pH around 1.6 in order for enzymes such as pepsin and rennin to catalyse the breakdown of proteins into amino acids. Cells in the pancreas secrete pancreatic juice whose pH must be maintained around 8.5 in order for lipase enzymes to digest fats into fatty acids. The alkalinity of this fluid also neutralises gastric juices from the stomach as they enter the small intestine.

Solutions called *buffers* resist changes in pH when small quantities of an acid or base are added to them. By restricting the pH range of body fluids, these buffers ensure that biochemical reactions proceed at their required rate. Buffers keep our bodies in pH balance.

Buffers are also used in a chemical laboratory to calibrate pH meters, as well as providing a constant pH environment for chemical processes.

Theory of buffers

Buffer solutions usually contain a weak Bronsted–Lowry acid and its conjugate base or a weak Bronsted–Lowry base and its conjugate acid. By choosing the correct amounts of the weak acid and weak base in the solution, the pH of the solution can be fixed to within narrow limits.

Consider the weak acid HA and its conjugate base, A^- . If HA is added to water, the following equilibrium is established:



As the hydronium ion is a stronger acid than HA, and A^- is a stronger base than water, this equilibrium lies well to the left.

If A^- is added to water (e.g. as the sodium salt), then the following equilibrium is established.



As the hydroxide ion is a stronger base than A^- , and HA is a stronger acid than water, then this equilibrium also lies well to the left.

Now imagine what happens if we prepare a solution that contains both HA and A^- in approximately equal amounts. This solution is our buffer solution. The system reaches equilibrium quickly. Now we add a few drops of hydrochloric acid as a source of hydronium ions. The addition of hydronium ions will shift equilibrium (1) to the left to use up some of the added hydronium ions (Le Chatelier's principle). Because our solution contains a high concentration of A^- , they will be able to remove most of this excess acid and convert it into HA. The net result is very little change in pH as the added acid is converted mainly into an un-ionised molecular acid (HA).

Next, we try adding a few drops of sodium hydroxide solution to the HA/ A^- buffer solution. The increase in hydroxide ion concentration affects equilibrium (2) and causes it to shift to the left to use up the added OH^- . Because our solution has a high HA concentration, these molecules can combine with the added hydroxide ions to form A^- . The net result is very little change in pH as the added strong base is converted into a much weaker base (A^-).

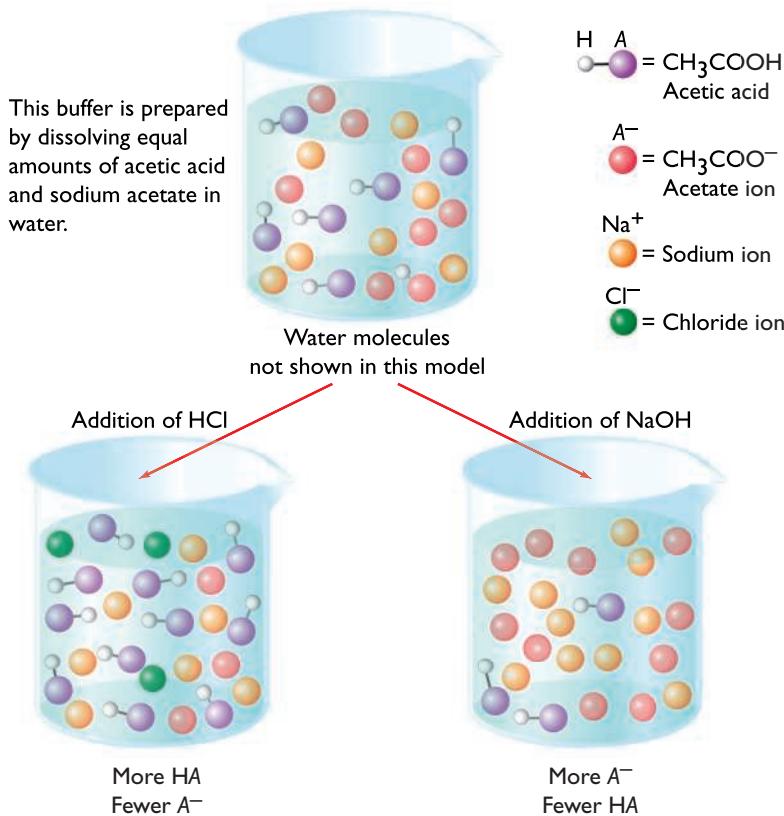


Figure 9.11

A buffer solution contains a weak acid and its conjugate base. The addition of small amounts of strong acids or bases causes little change in pH as the excess acid or base is removed by either the conjugate base or the B-L acid.

SYLLABUS FOCUS

19. LABORATORY BUFFERS

A simple buffer solution can be prepared in the laboratory using an equimolar mixture of acetic acid and sodium acetate, such that the concentration of each species is 0.1 mol/L. The equilibrium is:



This buffer has a pH of 4.7.

To demonstrate the buffering properties of this solution compared with a solution of acetic acid, a pH titration can be performed. A buffer solution is prepared by dissolving 0.10 moles of acetic acid and 0.10 moles of sodium acetate in 1 litre of water. A second 1-litre solution contains 0.10 moles of acetic acid only. Small amounts of solid sodium hydroxide are added to each solution and the mixtures stirred to allow the base to react. The pH is measured after each addition. Figure 9.12 shows the results of such an investigation.

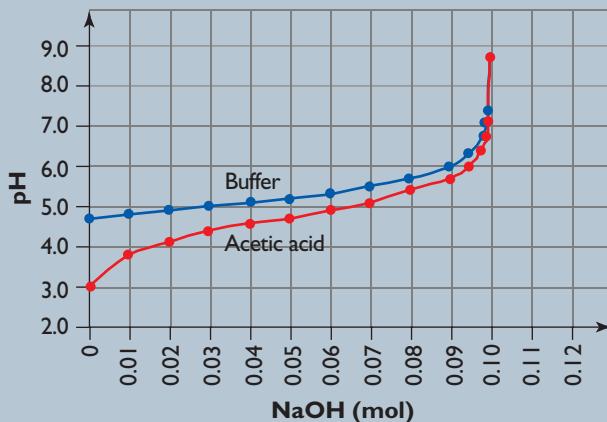


Figure 9.12

The addition of sodium hydroxide to the buffer solution does not produce as rapid a pH change as that observed with acetic acid alone.

Figure 9.12 shows that the pH does not rise as fast in the buffer solution as in the acetic acid solution as NaOH is slowly added.

Another buffer that is useful in the high pH range is the NaHCO_3 – Na_2CO_3 buffer. An equimolar (0.025 mol/L) solution of sodium hydrogen carbonate and sodium carbonate has a pH of 10.0. The equilibrium is:

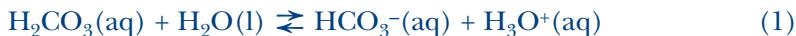


The effect of adding hydrochloric acid to this buffer can be followed with phenolphthalein indicator. The indicator is pink in the buffer, and the addition of acid leads to a very slow drop in pH compared with a control experiment using water.

Natural buffers

The maintenance of the pH of blood in the range 7.35 to 7.45 is a good example of a natural buffer system in operation. The system consists of a carbonic acid – hydrogen carbonate buffer linked to the haemoglobin-oxyhaemoglobin equilibrium that is used to maintain blood pH.

The relevant equilibrium for the carbonic acid – hydrogen carbonate buffer is:



Haemoglobin is the bluish-red iron-protein molecule that absorbs and transports oxygen in our blood. Haemoglobin is a complex molecule that contains four haem (Hb) groups bound to an iron (II) ion. Each haemoglobin molecule can bind four oxygen molecules. Haemoglobin is also a weak acid. It is a weak proton donor. The oxygenated form of haemoglobin is called *oxyhaemoglobin* which can be

represented by the symbol $\text{HHb}_4(4\text{O}_2)$ or HHb_4O_8 . Oxyhaemoglobin is bright red in colour. The oxygenation of haemoglobin is a reversible equilibrium:



Inhalation and cellular respiration

When oxygen is drawn into the lungs during inhalation, the oxygen molecules diffuse through a film of moisture on the surface of the alveoli and into the bloodstream via a capillary.

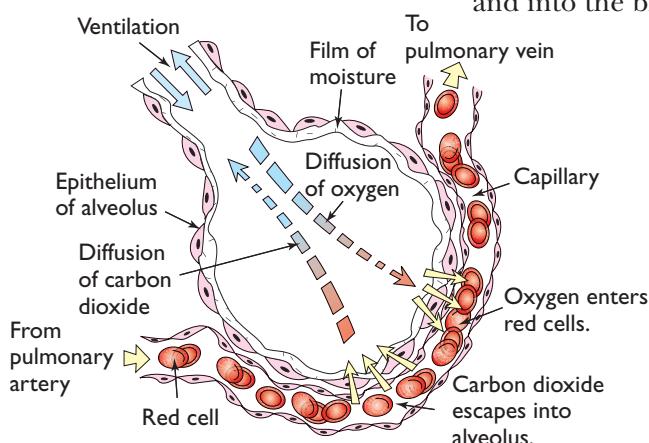


Figure 9.13

Oxygen gas and carbon dioxide gas are exchanged in the alveoli of the lungs. These gases dissolve in a thin film of moisture and then diffuse in and out of blood capillaries.

The haemoglobin molecules absorb the oxygen and are converted into oxyhaemoglobin. The blood now contains high levels of oxyhaemoglobin as it leaves the lungs. The increase in oxygen level in the blood causes equilibrium (2) to shift to the right to form oxyhaemoglobin and hydronium ions. Thus the blood acidity increases as hydronium ions are formed. To prevent the oxygenated blood becoming too acidic, the carbonic acid – hydrogen carbonate buffer system operates. The higher levels of hydronium ion cause equilibrium (1) to shift to the left in order to remove excess acid. The carbonic acid that forms breaks down to release carbon dioxide.

Cells need oxygen for cellular respiration. When oxygenated blood reaches oxygen-requiring cells in the body tissues, the oxygen diffuses from the blood into these cells. Equilibrium (2) responds to this loss of oxygen into the cells by shifting to the left to form haemoglobin. In this process hydronium ions are removed from the blood. At the same time, cells release carbon dioxide (a product of cellular respiration) back into the blood plasma. This increase in carbon dioxide in the blood leads to the formation of carbonic acid.



The increase in carbonic acid concentration causes equilibrium (1) to shift to the right and increase blood acidity.

Exhalation

The deoxygenated blood returns to the lungs, and carbon dioxide diffuses from the capillary into the alveoli. The partial pressure of carbon dioxide gas rises inside the lungs. As we exhale, the carbon dioxide is removed and equilibrium (4) is shifted to the right as carbon dioxide gas is lost.



The decrease in dissolved carbon dioxide in the blood as the result of exhalation affects equilibrium (3), which shifts to the left leading to a drop in carbonic acid levels in the blood. This drop in carbonic acid levels causes equilibrium (1) to shift to the left, and the blood pH rises as the concentration of hydronium ions decreases.

This complex system of interacting equilibria keeps the blood buffered over a narrow pH range. The blood buffering system is actually more complex than discussed here. Other buffering acid–base pairs also operate.

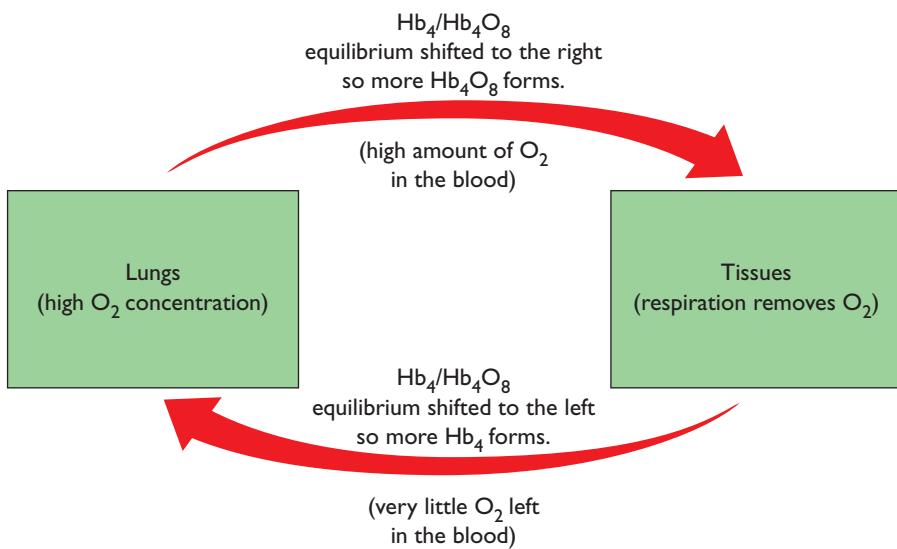


Figure 9.14

The transport of oxygen around the body relies on how the differing conditions in the lungs and in the tissues affect the haemoglobin–oxyhaemoglobin equilibrium.

Changing the balance

People who have a lung disease such as emphysema can suffer from low blood pH. This condition is called *acidosis*. If the carbon dioxide is not efficiently eliminated from the lungs, the carbonic acid concentration builds up in the blood. This drop in blood pH hinders the oxygen absorption process by the haemoglobin. In a healthy person, acidosis is quickly remedied by the production of hydrogen carbonate ions that cause an equilibrium shift, which restores the pH of the blood.

Some people may experience a condition called *hyperventilation* (breathing faster or deeper than necessary). This leads to a drop in carbon dioxide levels in the blood, so that the pH rises. This condition is called *alkalosis*. To restore the balance, more carbonic acid needs to form. To do this, the breathing rate can be slowed by re-breathing exhaled air from a paper bag. The increased carbon dioxide in the inhaled air raises the carbonic acid levels and leads the pH to return to normal.

9.1 Questions

1. Identify the Bronsted–Lowry acid and its conjugate base in the equilibrium reaction.



- A HF, F⁻
- B H₂O, H₃O⁺
- C HF, H₃O⁺
- D H₃O⁺, F⁻

2. Humphry Davy proposed that the presence of hydrogen in acids gave them their acidic properties. Identify the acid that he analysed to show that it contained hydrogen and no oxygen.

- A sulfuric acid
- B carbonic acid
- C nitric acid
- D hydrochloric acid

3. Identify the substance that could be classified as an Arrhenius base.
 - A water
 - B sodium carbonate
 - C potassium hydroxide
 - D calcium oxide
4. According to Arrhenius, the neutralisation of any base by any acid was the reaction between
 - A hydrochloric acid and calcium hydroxide.
 - B hydrogen ions and hydroxide ions.
 - C water molecules and salts.
 - D hydronium ions and any proton acceptor.
5. Lavoisier believed that the presence of the element oxygen in a compound made it
 - A basic.
 - B acidic.
 - C neutral.
 - D amphiprotic.

6. Write balanced whole formula equations for the following neutralisation reactions.
- nitric acid + calcium hydroxide solution
 - sulfuric acid + sodium carbonate solution
 - hydrobromic acid + barium oxide solid
7. Write net ionic equations for the following neutralisation reactions.
- hydriodic acid + potassium hydroxide solution
 - hydrochloric acid + lithium hydroxide solution
8. For each of the following reactions name the Bronsted–Lowry acid and the Bronsted–Lowry base for the forward reaction.
- $\text{N}^3\text{-}(aq) + 3\text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_3(aq) + 3\text{OH}^-(aq)$
 - $\text{CH}_3\text{COOH}(aq) + \text{NH}_2^-(aq) \rightleftharpoons \text{CH}_3\text{COO}^- + \text{NH}_3(aq)$
 - $\text{CN}^-(aq) + \text{HF}(aq) \rightleftharpoons \text{HCN (aq)} + \text{F}^-(aq)$
9. Write the formula for the conjugate base for each of the following Bronsted–Lowry acids.
- H_2S
 - H_2SeO_3
 - HOBr
 - PH_4^+
 - HSO_4^-
10. Write the formula of the conjugate acid for each of the following Bronsted–Lowry bases.
- HPO_4^{2-}
 - HCO_3^-
 - CO_3^{2-}
 - HO_2^-
 - HSO_3^-
11. Use appropriate equations to demonstrate the amphiprotic nature of the dihydrogen phosphate ion.
12. Classify the following salts as acidic, basic or neutral.
- NH_4I
 - Na_3PO_4
 - KBr
 - KF
 - $\text{Al}_2(\text{SO}_4)_3$
13. Use an appropriate equation to explain why a solution of sodium sulfite turns universal indicator blue-violet.
14. Explain how an equimolar solution of sulfurous acid and potassium sulfite can act as a buffer.
15. A hyperventilating patient has a blood pH of 7.6. Explain why, if she breathes in her exhaled air, she will eventually stop hyperventilating.
16. A patient has untreated diabetes. She has a rapid pulse. Her blood pH is 7.1.
- Her body reacts to the condition by hyperventilating. Why does this happen?
 - Her treatment involves an injection of hydrogen carbonate ions into the blood. Explain how this treatment will help her condition.
17. Identify which of the following acid-base pairs would make an effective buffer. Justify your choices.
- sulfuric acid—sodium hydrogen sulfate
 - nitrous acid—potassium nitrite
 - ammonium chloride—ammonia
 - sulfurous acid—potassium hydroxide
18. Potassium hydrogen phosphate is dissolved in water. A pH meter shows that the solution is slightly alkaline.
- Write an equation for the equilibrium that is established in the water.
 - Identify another salt that can be added to the potassium hydrogen phosphate solution to produce a buffer solution.
 - Explain how the addition of the salt named in (b) will change the pH of the original potassium hydrogen phosphate solution.
 - Having established this buffer, explain how the buffer prevents a large change in pH when drops of potassium hydroxide solution are added.
19. Sulfurous acid ionises in two steps in water.
- Write balanced ionic equations for this step-wise ionisation.
 - Compare the concentrations of the sulfurous acid, hydrogen sulfite ion and the sulfite ion in the final equilibrium mixture.
 - Identify a salt that could be dissolved in the sulfurous acid solution, and which will produce an effective buffer.
20. Explain the importance of the role of the solvent in the Bronsted–Lowry theory of acids and bases.
21. Assess how our understanding of acids and bases has expanded over the last two hundred years.

9.2 VOLUMETRIC ANALYSIS

Remember

Before beginning this section, you should be able to:

- describe the use of the pH scale in comparing acids and bases
- identify pH as $-\log_{10} [\text{H}^+]$ and explain that a change in pH of 1 means a ten-fold change in $[\text{H}^+]$
- identify conjugate acid–base pairs
- identify that indicators such as litmus, phenolphthalein, methyl orange and bromothymol blue can be used to determine the acidic or basic nature of a material over a range, and that the range is identified by change in indicator colour.

Key content

By the end of this section, you should be able to:

- describe the correct technique for conducting titrations and preparation of standard solutions
- identify neutralisation as a proton transfer reaction which is exothermic
- perform a first-hand investigation and solve problems using titrations and the preparation of standard solutions, and use available evidence to quantitatively and qualitatively describe reactions between selected acids and bases
- perform a first-hand investigation to determine the concentration of a domestic acidic substance using computer-based technologies
- analyse information from secondary sources to assess the use of neutralisation reactions as a safety measure or to minimise damage in accidents or chemical spills.

primary standard: a substance used in volumetric analysis that is of such high purity and stability that it can be used to prepare a solution of accurately known concentration

titration: a technique used in volumetric analysis in which one reactant (dissolved in a solvent) is added to another (also dissolved in a solvent) from a burette until an end-point is reached

Standards and unknowns

Volumetric analysis is a quantitative technique that involves reactions in solution. It involves the determination of the volume of a standardised solution that is required to react with the substance (or ‘unknown’) being analysed. Volumetric analysis is sometimes called titrimetric analysis after the technique called **titration**, which is used in the analysis. In acid–base analysis the reaction involves a neutralisation reaction.

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



Figure 9.15

During a titration, one reactant is placed in a conical flask with several drops of indicator. The other reactant, the titrant, is slowly added to the flask from a burette until the indicator just changes colour.

Primary standards

A primary standard is prepared using chemicals that are pure and which satisfy a special list of criteria. The properties of a primary standard are:

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

Many pure substances do not have all these properties. For example:

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

Anhydrous sodium carbonate, however, is a suitable primary standard. The white solid is dried in a drying oven and then allowed to cool in a desiccator. The final product is free of water; its exact composition is Na_2CO_3 .

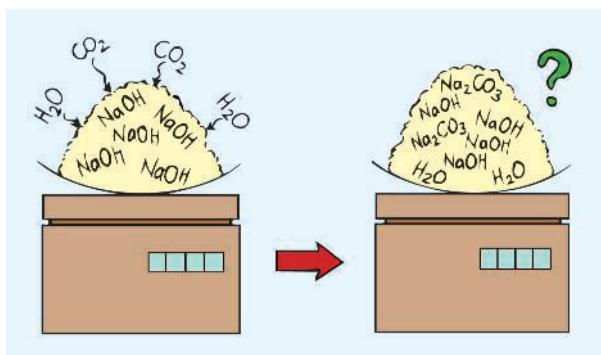


Figure 9.16

Sodium hydroxide is unsuitable as a primary standard as it is deliquescent.

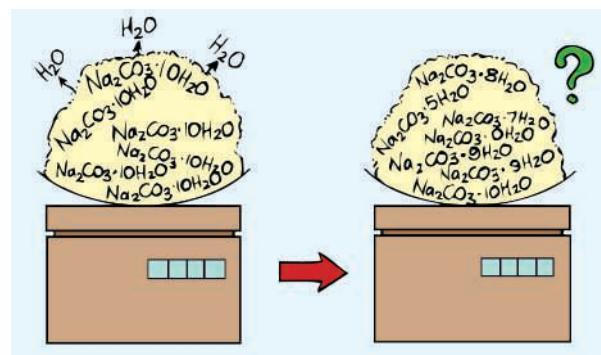


Figure 9.17

Hydrated sodium carbonate is unsuitable as a primary standard as it loses water to the atmosphere.

Table 9.3 lists some other primary standard acids and bases that chemists can use in their analyses.

Table 9.3 Primary standards

Acid standards	Base standards
potassium hydrogen phthalate (KHC ₈ H ₄ O ₄)	sodium carbonate (Na ₂ CO ₃)
benzoic acid (C ₇ H ₅ O ₂)	sodium hydrogen carbonate (NaHCO ₃)
oxalic acid (H ₂ C ₂ O ₄ ·2H ₂ O)	borax (Na ₂ B ₄ O ₇ ·10H ₂ O)

Secondary standards

Secondary standards are solutions whose concentrations have been determined using primary standards. Thus a hydrochloric acid solution can become a secondary standard by reacting it first with a known primary standard such as sodium carbonate solution. Sodium hydroxide can be used as a secondary standard after standardising against a standard acid such as potassium hydrogen phthalate solution.

Preparation of a standard sodium carbonate solution

We shall use the preparation of a standard solution of anhydrous sodium carbonate as a model of the techniques used to prepare a primary standard. The following steps describe the procedure to prepare 250 mL of 0.0500 mol/L sodium carbonate solution. The mass of sodium carbonate required can be calculated as follows:

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

$$\begin{aligned} n &= cV = (0.0500)(0.250) \\ &= 0.0125 \text{ mol Na}_2\text{CO}_3 \end{aligned}$$

$$\begin{aligned} m(\text{Na}_2\text{CO}_3) &= nM = (0.0125)(105.99) \\ &= 1.325 \text{ g} \end{aligned}$$

Step 1: Preparing and weighing the solid

Analytical grade (AR) anhydrous sodium carbonate is used. This solid has greater than 99.9% purity. The solid is dried at 150–180°C in a drying oven for 30 minutes and then allowed to cool in a desiccator containing drying crystals. The dry solid (1.325 g) is then weighed into a clean, dry 50 mL beaker on an electronic balance (3 decimal places).

Step 2: Dissolving the solid

Use a plastic wash bottle to add a little distilled water to the beaker, and use a fine, short glass rod to stir the mixture to dissolve the sodium carbonate. Keep the glass rod in the beaker at all times. Ensure the solid is completely dissolved.

Step 3: Transfer the solution to a clean 250 mL volumetric flask

The volumetric flask is an accurate piece of volumetric glassware. It should be pre-cleaned and rinsed with distilled water. The flask can be left wet as more water will be added later.

Transfer the sodium carbonate solution from the beaker into the volumetric flask with the aid of a small, clean glass funnel placed in the neck of the volumetric flask. Use the wash bottle to wash the beaker many times around the side and add these washings to the volumetric flask. The glass rod is a useful guide to pour the water from the beaker into the funnel as it prevents splashing. Rinse the rod and funnel with water from the wash bottle. All these washings go into the flask.

Step 4: Adding water to the mark

Add distilled water until the water level in the volumetric flask is about 1 cm below the engraved mark on the flask. Remove the funnel and add distilled water drop by drop until the bottom of the meniscus is aligned with the engraved line. Avoid parallax error. Stopper the flask and invert it to mix the contents thoroughly. The flask should be inverted and shaken four or five times.

Label the flask $0.0500 \text{ mol/L Na}_2\text{CO}_3$.

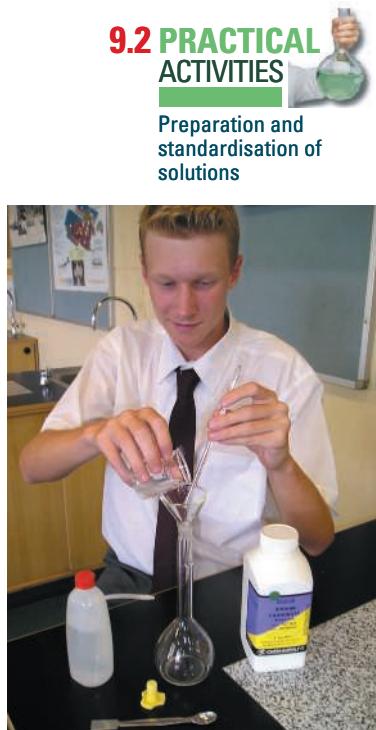


Figure 9.18

Accurate weighing of the primary standard and quantitative transfer of the solid into the volumetric flask is essential to achieve accuracy in the preparation of the standard solution.

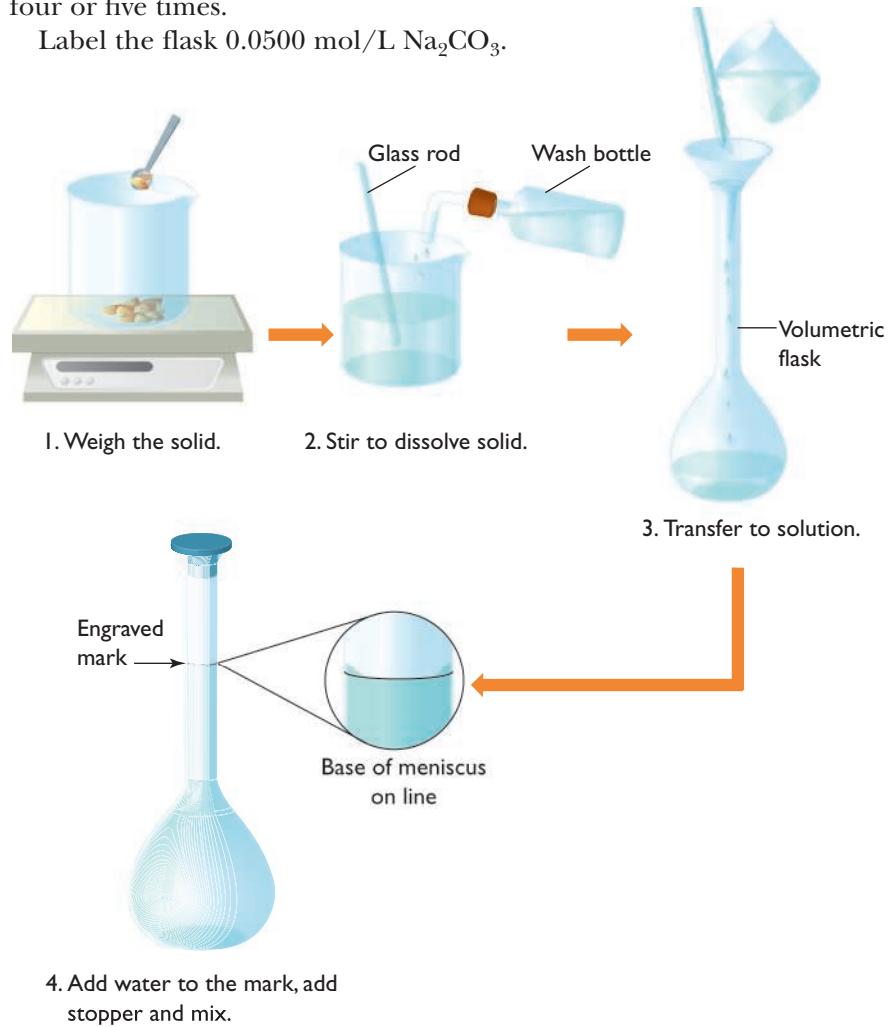




Figure 9.19

The burette must be cleaned with water and then rinsed with the solution (the titrant) before filling it to the zero mark.

titrant: the solution that is added from the burette

aliquot: a known volume of a liquid



Figure 9.20

The pipette must be cleaned with water and then rinsed with the solution before filling it to the mark. The solution in the pipette is transferred to the conical flask.

Titration techniques and calculations

The standard 0.0500 mol/L sodium carbonate solution that was prepared in the previous section can now be used to analyse unknown acids. This is done by titration.

Let us consider an example in which we analyse an unknown nitric acid solution whose concentration is about 0.1 mol/L.

The neutralisation reaction will be:



Before we perform the titration we need to carefully prepare the apparatus.

Step 1: Preparing the burette and filling it with the unknown acid

The burette is an accurate piece of volumetric glassware. It has markings from 0 to 50 mL with 0.1 mL divisions. The burette should be cleaned and rinsed several times with distilled water prior to use. The space below the tap must be cleaned as well. Small volumes of the unknown acid are then used to rinse the burette thoroughly. These washings are then discarded. The burette is clamped (using a burette clamp) to a retort stand. A small, clean glass funnel is used to fill the burette with the unknown acid to above the zero mark. The tap is then opened and the acid run into a waste beaker until the base of the meniscus is on the zero line. Ensure that the acid has filled the space below the tap and that there are no bubbles present. This liquid in the burette is called the **titrant**.

Step 2: Preparing the pipette and transferring the standard base into the conical flask

A bulb pipette is also an accurate piece of volumetric glassware. It has only one engraved line. Bulb pipettes come in different sizes, but the 25 mL pipette is common. A pipette filler is used to draw up some water to rinse the pipette several times. These washings are discarded. The pipette is then rinsed with small volumes of the standard base and these washings are also discarded. The pipette can then be filled with the standard base. This volume of base is called an **aliquot**. The bottom of the meniscus should be on the engraved line. Wipe the outside of the pipette with a tissue.

The conical flask is the reaction vessel. It must be thoroughly clean and rinsed several times with water. It can be left wet, as water will be added during the titration.

An **aliquot** of the standard base solution is now transferred from the pipette to the conical flask. The solution is allowed to drain under gravity into the conical flask. The tip of the pipette should rest against the inside glass wall of the flask so that adhesive forces ensure that the liquid is fully transferred into the flask. Do not shake out or blow out the remaining drop in the pipette, as this has been allowed for by the manufacturer.

Prepare a second conical flask of standard base to act as a reference.

Step 3: Performing the titration

The reaction involves the neutralisation of the sodium carbonate solution with nitric acid. As these solutions are colourless, a suitable indicator must be used. In this case a suitable indicator is methyl orange. The reasons for choosing methyl orange will be discussed later. Three drops of the indicator are added to each of the two conical flasks containing the base. The

titre: the volume of solution delivered from the burette that achieves an end-point

end-point: the stage in a titration at which the indicator just changes colour



Figure 9.21

The methyl orange indicator turns from yellow to orange or orange-red at the end point of the titration between sodium carbonate and nitric acid.



indicator turns yellow in the basic solution. Set one flask to the side on a white tile or white paper to act as a reference. Place the other flask on a white tile or filter paper under the burette.

Open the tap and add acid slowly. Use your other hand to swirl the flask to mix the solutions during addition. If any of the solution splashes up onto the sides of the flask, use the wash bottle to rinse the liquid down into the reaction mixture. Continue to add acid until a point is reached where the colour of the indicator in the flask just changes to orange compared with the yellow control. Record the volume of acid added from the burette. This volume is known as the **titre**. The first titration is called ‘rough’ titration as you will probably have missed the exact colour change or **end-point**. The rough titration allows you to locate the approximate end-point so that in subsequent titrations you can approach the end-point more slowly, and obtain a more accurate result. A skilled chemist can transfer fractions of drops from the burette tip into the reaction solution using a wash bottle. Accuracies of 0.05 mL can be achieved.

Step 4: Calculating the concentration of the unknown acid

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

Volume of sodium carbonate solution = 25.00 mL

Concentration of sodium carbonate solution = 0.0500 mol/L

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

(* Not used to calculate the mean)

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



Sample calculation:

Number of moles of base used:

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

From the reaction stoichiometry:

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

Concentration, *c*, of nitric acid:

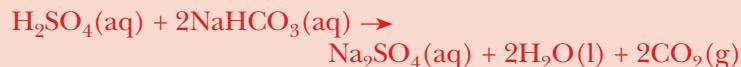
$$\begin{aligned} c &= n/V = (2.500 \times 10^{-3})/(22.38 \times 10^{-3}) \\ &= 0.112 \text{ mol/L} \end{aligned}$$

SAMPLE PROBLEM 9.4

SOLUTION

A standard solution of sodium hydrogen carbonate has a concentration of 0.100 mol/L. A 25.00 mL aliquot of the standard base was titrated against an unknown sulfuric acid solution using methyl orange indicator. The average titre at the end point was 28.35 mL. Calculate the concentration of the sulfuric acid solution.

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



Step 2. Identify the mole coefficients in the balanced equation for the acid A (mole coefficient a) and the base B (mole coefficient b).

$$a = 1, b = 2$$

Step 3. Tabulate the known and unknown data using the following table.

Acid (A)	H_2SO_4	Base (B)	NaHCO_3
c_A (mol/L)	?	c_B (mol/L)	0.100
V_A (L)	28.35×10^{-3}	V_B (L)	25.00×10^{-3}
a	1	b	2

Step 4. Substitute into the derived formula*.

$$c_A V_A / a = c_B V_B / b$$

$$c_A (28.35 \times 10^{-3}) / 1 = (0.100) (25.00 \times 10^{-3}) / 2$$

$$c_A = 0.0441 \text{ mol/L}$$

The concentration of the sulfuric acid unknown was 0.0441 mol/L. This derived formula is based on the general formula for concentration:

$$n = cV$$

The formula is based on the stoichiometric ratio ($a : b$) in the balanced general acid–base equation $aA + bB \rightarrow$ products.

$$a : b = n_A : n_B = c_A V_A : c_B V_B$$

which on rearranging gives: $c_A V_A / a = c_B V_B / b$.

Choosing a suitable indicator

The choice of a suitable indicator for an acid–base titration depends on the strength of the acid and base involved. There are four possibilities:

- strong-acid–strong-base titration
- strong-acid–weak-base titration
- weak-acid–strong-base titration
- weak-acid–weak-base titration.

The indicator is chosen such that the pH at the end-point matches as closely as possible the pH at the equivalence point of the titration.

It is important to distinguish between the end-point of a titration and the equivalence point.

End point — the point in the titration when the indicator just changes colour.

Equivalence point — the point where the acid has stoichiometrically reacted with the base (sometimes called the *stoichiometric end-point*).

Because indicators change colour over a narrow pH range rather than at an exact pH, it is important to achieve a close match of the equivalence point with the indicator's pH range. Table 9.4 shows the pH range of the three common indicators used in acid–base titrations.

Table 9.4 Indicator pH ranges

Indicator	pH range
methyl orange	3.1–4.4
bromothymol blue	6.0–7.6
phenolphthalein	8.3–10.0



Methyl orange indicates lower pH as red (left) and higher pH as yellow (right).



Bromothymol blue indicates lower pH as yellow (left) and higher pH as blue (right).



Phenolphthalein indicates lower pH as colourless (left) and higher pH as crimson (right).

Indicators are weak acids

Acid–base indicators are weak acids. They are weakly ionised in water solution. If we represent the un-ionised form of an indicator as HIn and its conjugate base as In^- , then the equilibrium is:



This indicator equilibrium is influenced by the pH of the solution. When the pH is low then the equilibrium shifts to the left. When the pH is high the equilibrium shifts to the right. The colour changes that we observe occur because the un-ionised molecule (HIn) has a different colour from that of the conjugate base (In^-). Table 9.5 shows the colour of the un-ionised acid and its conjugate base for the three indicators in Table 9.4.

Table 9.5 Colours of un-ionised indicator acid and conjugate base

Indicator	Colour of un-ionised molecule (HIn)	Colour of conjugate base (In^-)
methyl orange	red	yellow
bromothymol blue	yellow	blue
phenolphthalein	colourless	crimson

Matching pH graphs with indicator pH ranges

The following graphs show how the pH of the solution changes during four titrations involving strong and weak acids and bases. Each graph shows the colour-change pH range of the three indicators in Table 9.5.

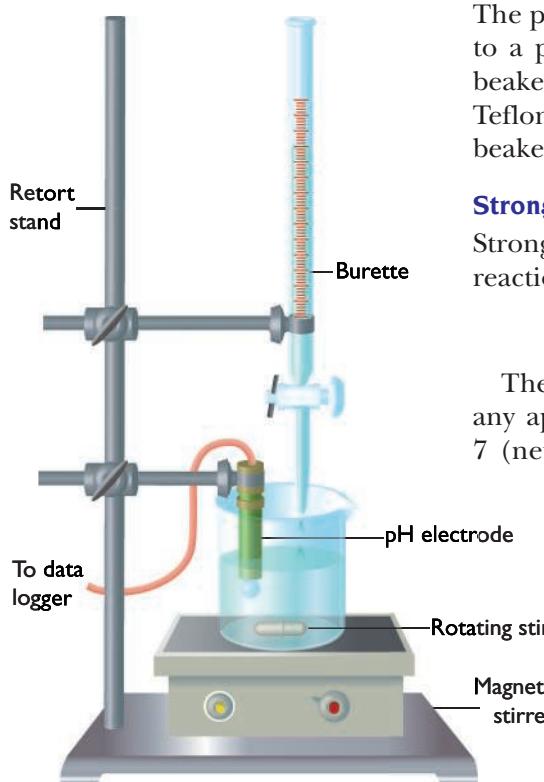


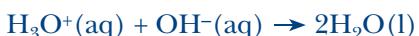
Figure 9.22

The pH titration is carried out in a beaker. The solution in the beaker is stirred magnetically. The base solution in the burette is added to the beaker of acid and the pH monitored.

The pH of the solution can be measured using a pH electrode connected to a pH meter/data logger. A pH titration is normally conducted in a beaker sitting on a magnetic stirrer. The solution is stirred by a spinning Teflon-coated steel rod. The burette can then be mounted above the beaker as shown in Figure 9.22.

Strong-acid – strong-base titration

Strong acids and strong bases are completely ionised, so the neutralisation reaction involves the hydronium ion and the hydroxide ion.



The salt that is formed in such neutralisations does not hydrolyse to any appreciable extent, so the pH at the equivalence point is equal to 7 (neutral). Figure 9.23 shows the change in pH as 0.1 mol/L NaOH is added to 10.00 mL of 0.1 mol/L hydrochloric acid during a titration. There is a rapid rise in pH from 3 to 10 on the addition of one drop of base. The equivalence point is at the centre of the inflection (pH = 7). All three indicators change colour within this steep portion of the pH curve. Although the bromothymol blue end-point most closely matches the pH at the equivalence point, we can use any of these three indicators for the titration, as their end-points are all within this steep portion of the pH curve. The accuracy of the technique is not sufficiently great to notice any difference in end point for the three indicators.

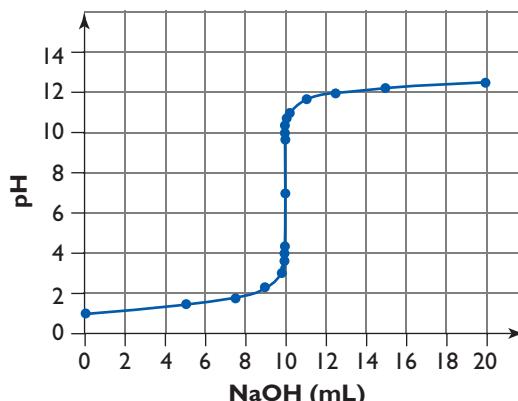


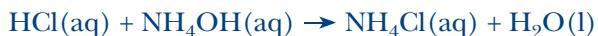
Figure 9.23

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

Strong-acid – weak-base titration

The pH at the equivalence point of a strong-acid – weak-base titration is less than 7 due to the hydrolysis of the acidic salt produced in the neutralisation reaction.

If 0.1 mol/L hydrochloric acid solution is titrated with a 0.1 mol/L ammonia solution (ammonium hydroxide), the salt that forms is ammonium chloride.



The ammonium ion is a weak Bronsted–Lowry acid and hydrolyses in water to produce hydronium ions:



The pH of the solution at the equivalence point is about 5.3. Figure 9.24 shows the pH graph for this titration in which 10.0 mL of 0.10 mol/L HCl

solution is titrated with 0.10 mol/L NH₃. Methyl orange or bromothymol blue are suitable indicators as their end-points closely match the steep portion of the pH graph (4.0–7.0). Phenolphthalein cannot be used as the end point is reached well after the equivalence point.

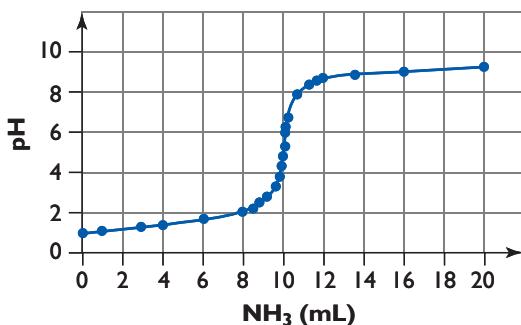


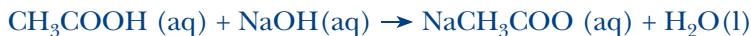
Figure 9.24

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

Weak-acid – strong-base titration

The pH at the equivalence point of a weak-acid – strong-base titration is greater than 7 due to the hydrolysis of the basic salt produced in the neutralisation reaction.

If 0.1 mol/L acetic acid is titrated with a 0.1 mol/L sodium hydroxide solution, the salt that forms is sodium acetate.



The acetate ion is a weak Bronsted–Lowry base and hydrolyses in water to produce hydroxide ions:



The pH of the solution at the equivalence point is about 8.7. Figure 9.25 shows the pH graph for this titration in which 10.0 mL of 0.10 mol/L acetic acid is titrated with 0.10 mol/L NaOH. Phenolphthalein is the only suitable indicator of the three listed, as the phenolphthalein end point closely matches the steep portion of the pH graph (7.5–10.0). Methyl orange cannot be used as the end point is reached well before the equivalence point.

You should note the buffering effect on pH as base is added to the acid. Well before the end point, the solution contains both the weak acid and its conjugate base. The pH rises only slowly in this region.

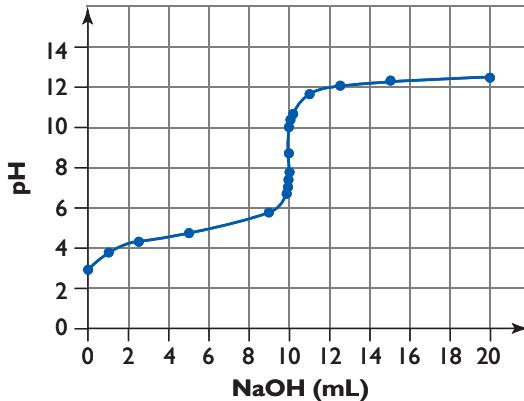


Figure 9.25

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

Weak-acid–weak-base titration

When a weak acid such as acetic acid is titrated with a weak base such as ammonia solution there is no rapid change in pH even at the equivalence point. The pH at the equivalence point is 7.0. As a consequence no single

indicator will achieve a sharp end point. Titrations of weak acids with weak bases are therefore best to avoid. The best strategy is to add a known excess of the standardised hydrochloric acid to a known volume of the weak base. The excess hydrochloric acid can then be back-titrated against a standardised strong base.

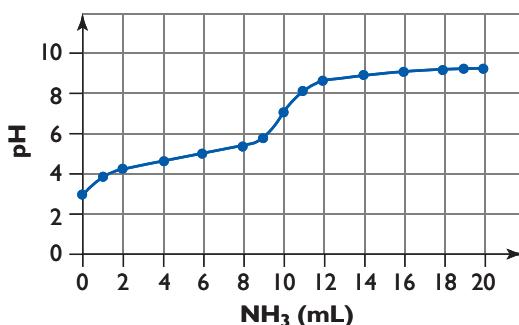


Figure 9.26

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

SAMPLE PROBLEM 9.5

SOLUTION

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

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

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

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



There is a 1 : 1 reaction stoichiometry.

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

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

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

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

Step 4. Calculate the concentration of the diluted ammonia solution

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

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

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

Step 6. Calculate the concentration in g/L

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

SYLLABUS FOCUS

20. USING INSTRUCTION TERMS CORRECTLY

When answering questions, it is important to know what the instruction terms ('verbs') require you to do. Here are some examples:

'Select'

This instruction word requires you to make the correct choice in preferences to other possible choices.

Example:

Select, from the following list, the pieces of equipment required to conduct an acid–base titration of a standard acid with an unknown base.

pipette, measuring cylinder, gas jar, 2 L beaker, Bunsen burner, conical flask, burette, burette clamp, tripod, gauze, pipette filler, retort stand, watch glass

Answer:

pipette, conical flask, burette, burette clamp, pipette filler, retort stand

9.3 PRACTICAL ACTIVITIES

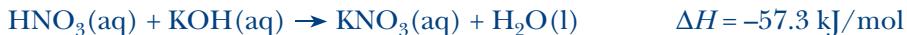


pH titration
of diluted
vinegar

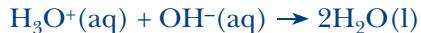
Safety issues related to acids and neutralisation reactions

Neutralisation reactions are exothermic. The amount of heat liberated per mole when a strong base is neutralised by a strong acid is almost the same no matter what acid or base is used.

Examples of 1 mol/L solutions:



This similarity is understandable as the same reaction occurs in each case; that is, the neutralisation of a hydronium ion and a hydroxide ion to form water.



The neutralisation reactions involving weak acids or bases, however, produce slightly less heat per mole.

Example of a 1 mol/L solution:



Diluting strong acids safely

Concentrated sulfuric acid is a dense, oily liquid. When a chemist prepares a dilute solution of sulfuric acid, it is important that only small quantities of the concentrated acid are added to a large volume of water with constant stirring. This process helps to dissipate the heat produced on dissolution. The reverse procedure of adding water to the concentrated acid should not be attempted, as the hydration process causes such a large generation of heat that the acid's temperature can quickly rise to boiling point. There is a danger that boiling acid could be ejected from the beaker. The use of safety glasses, gloves and laboratory coat (or rubber apron) is essential when any concentrated acid is diluted.

Acids and neutralisation reactions

The neutralising procedures appropriate in the laboratory may be different from those needed to treat large outdoor spillages.

In the laboratory

Neutralisation reactions can be used in laboratories to clean up after acids or bases have been accidentally spilled on the workbench or floor. Because of the exothermic nature of the neutralisation process, we should never use concentrated acids or bases in cleaning up spills. Not only is there the potential to cause boiling and the evolution of noxious fumes, but the strong base or acid will only cause further damage.

Consider the circumstances where an acid solution or concentrated acid has been accidentally spilled on the bench or floor. The spill area may need to be isolated, and people evacuated if fumes are present. If the acid has been spilled on a person's clothes or skin, then immediate first aid must be administered. This usually means flushing the skin or clothing with copious amounts of water to prevent damage.

The next step in the clean-up is to isolate the spill. This can be done with sand or vermiculite to prevent the acid flowing out to contaminate other areas. The acid-soaked sand or vermiculite can then be cleaned up and neutralised in a safe location. Some authorities suggest that a concentrated acid spill should be diluted with water before the acid is neutralised with a base. The reason is that a great amount of heat is released on neutralisation of a concentrated acid. This can be best achieved using an excess of a powdered base such as sodium carbonate or sodium hydrogen carbonate.

Sodium carbonate is commonly used as it is a stable solid that is safe to handle. It is also the cheapest of the bases commonly available. Sodium carbonate neutralises the acid; carbon dioxide and water, as well as the sodium salt of the acid, are formed. Excess sodium carbonate is easily cleaned up by dilution with water.



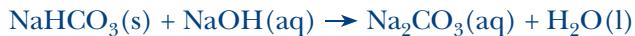
Sodium hydrogen carbonate is also commonly used to clean up acid spills. It is a weak base that is non-toxic.



Larger-scale neutralisations

If very large spills occur (e.g. a tanker carrying acid crashes and the acid spills onto the road), the best procedure is initially to prevent the acid escaping into the drains or off into the soil on the side of the road. This can quickly be done with large amounts of inert sand or vermiculite. Once the acid is absorbed, the highly acidic sand or vermiculite can be placed in a chemical waste container and removed for neutralisation off-site. Once the acidic solid is removed, sodium carbonate powder followed by copious quantities of water are used to neutralise and dilute any remaining acid.

If an alkaline material has been spilled, one option is to use sodium hydrogen carbonate, as it is amphotropic. That is, it can react with alkalis as well as acids and neutralise them.



Sodium hydrogen phosphate solid is also used in base spills. It is also amphotropic.

In many factory situations, alkaline wastes can be carefully neutralised with dilute hydrochloric acid followed by large volumes of water.

If the spillage of acids or bases occurs on a large scale in factories, it is important that once the acid or base has been neutralised, the products are diluted with copious quantities of water. This method prevents high concentrations of ions, or solutions with too high or too low a pH, from being discharged in the wastewater effluents.

9.2 Questions

1. Select the substance that can be used as a primary standard in volumetric analysis.
 - A Sodium hydrogen carbonate
 - B Sulfuric acid
 - C Hydrochloric acid
 - D Sodium hydroxide
2. The following steps are used in the preparation of a standard solution of sodium carbonate. The steps are listed in random order. Select the response in which the steps are placed in the correct order.
 - (i) Stopper the volumetric flask and invert it to mix the contents thoroughly.
 - (ii) Transfer the sodium carbonate solution from the beaker into the volumetric flask.
 - (iii) The dry solid is weighed into a clean, dry 50 mL beaker on an electronic balance.
 - (iv) Use a plastic wash bottle to add a little distilled water to the beaker; and use a fine, short, glass rod to stir the mixture to dissolve the sodium carbonate.
 - (v) The solid is dried at 150–180°C in a drying oven for 30 minutes and then allowed to cool in a desiccator containing drying crystals.
 - A (v), (iii), (iv), (ii), (i)
 - B (iii), (v), (ii), (iv), (i)
 - C (i), (ii), (iv), (iii), (v)
 - D (iv), (v), (iii), (i), (ii)
3. A solution of potassium hydrogen carbonate of unknown concentration is to be titrated with standardised hydrochloric acid. The acid is to be placed in the burette.
 - (a) Write a balanced equation for the neutralisation reaction that will occur during the titration.
 - (b) Describe how the potassium hydrogen carbonate solution is transferred quantitatively to the conical flask.
 - (c) Explain why the burette is rinsed with water and then HCl before filling it with acid.
 - (d) Identify a suitable indicator for this titration. Justify your choice.
4. A 50 mL burette is to be used in a titration. Identify the procedure that is used to prepare the burette for use.
 - A Rinse the burette with tap water several times and leave it wet.
 - B Rinse the burette with distilled water several times and then with the solution to be used several times.
 - C Rinse the burette, using only the solution to be used in it.
 - D Dry the burette in a low temperature drying oven prior to use.
5. Select the correct procedures to be used in preparing a pipette and conical flask for use in a titration.
 - A Rinse both the pipette and flask with water several times prior to use.
 - B Rinse the pipette with water, but dry the flask in the drying oven.
 - C Rinse both the conical flask and pipette with water and then rinse the pipette several times with the solution to be placed in it.
 - D Wash the flask and pipette, using only the solution to be placed in them.
6. A suitable indicator for the titration of ammonia solution with nitric acid is
 - A phenolphthalein.
 - B litmus.
 - C universal indicator.
 - D methyl orange.
7. Bromothymol blue indicator is a weak organic acid. If we represent the molecule as HB , then the following equilibrium exists in water solution.
$$\text{HB}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{B}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$
 - (a) Identify the Bronsted–Lowry acid and its conjugate base in the forward reaction.
 - (b) Identify the colour of (i) HB and (ii) B^- .
 - (c) Explain the effect on the above equilibrium of the addition of sulfuric acid to the solution of bromothymol blue indicator in water.
 - (d) Explain why bromothymol blue is a suitable indicator for the titration of sulfuric acid and sodium hydroxide.

8. A standard solution of sodium carbonate has a concentration of 0.0500 mol/L. This solution is used to standardise a solution of hydrochloric acid. A sample of 25.00 mL of the base is titrated with the acid, and the average acid titre is 17.25 mL. Calculate the concentration of the hydrochloric acid solution.
9. Phosphoric acid is a weak triprotic acid (H_3PO_4).
- Write three equations to show the stepwise neutralisation of this acid by sodium hydroxide solution.
 - Write the overall equation for the neutralisation of the phosphoric acid by sodium hydroxide solution.
 - Identify a suitable indicator for the titration of phosphoric acid by sodium hydroxide.
 - A sample of 20.0 mL of a phosphoric acid solution is completely neutralised by 16.5 mL of a 0.120 mol/L sodium hydroxide solution. Calculate the concentration of the phosphoric acid solution.
 - The titration was repeated using methyl orange indicator. An end-point was observed at 5.5 mL. Explain this observation.
10. The following set of pH data was collected for the titration of 100 mL of 0.10 mol/L nitric acid with 0.10 mol/L potassium hydroxide solution.

Volume of NaOH (mL)	pH
0	1.0
50	1.5
75	1.8
90	2.3
99	3.3
99.5	3.6
99.8	4.0
99.9	4.3
100.0	7.0
100.1	9.7
100.2	10.0
100.5	10.4
101	10.7
102	11.0
110	11.7
150	12.3
200	12.5

- Plot this data as a line graph. Plot pH on the vertical axis.
- Identify the pH at the equivalence point.
- The solutions used in the titration were carbon-dioxide-free. Explain how the presence of dissolved carbon dioxide would affect the titration.
- Identify the increase in pH between 99.9 and 100.1 mL of added base.
- The following table lists some indicators and their pH ranges. Identify the indicator(s) that would be suitable for this titration. Justify your response.

Indicator	pH range
meta-cresol purple	1.2–2.8
bromophenol red	5.2–6.8
neutral red	6.8–8.0
thymol blue	8.0–9.6
alizarin yellow R	10.1–12.0

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

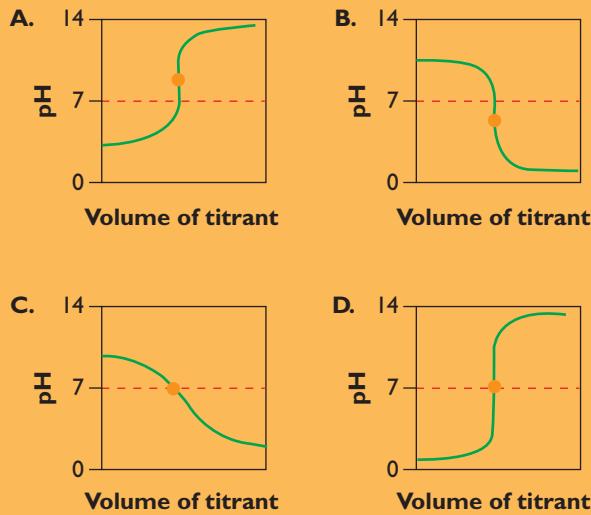


Figure 9.27 Use these pH graphs to answer the following question.

Identify the:

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

12. Kylie analysed the acetic acid content of vinegar using a titration. She took 20 mL of the white vinegar and diluted it systematically to 100 mL.
- Kylie transferred 25.00 mL of the diluted vinegar to a conical flask. Name the piece of glassware she used for this procedure.
 - The diluted vinegar was titrated with 0.105 mol/L potassium hydroxide solution and the end point was reached with an average titre of 31.8 mL of the base.
 - Identify from the following table suitable indicators for Kylie's titration.

Indicator	pH range
meta-cresol purple	1.2–2.8
bromophenol blue	3.0–4.6
congo red	3.0–5.0
bromophenol red	5.2–6.8
neutral red	6.8–8.0
thymol blue	8.0–9.6

 - Calculate the concentration of acetic acid in the diluted vinegar.
 - Calculate the concentration of acetic acid in the white vinegar in
 - mol/L and (ii) g/100 mL.
13. Assess the use of neutralisation reactions to minimise damage in accidents or chemical spills.
14. Oxalic acid crystals, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, can be used to prepare a primary standard acid solution.
- Identify three properties of oxalic acid that make it suitable as a primary standard.
 - Calculate the mass of oxalic acid crystals that need to be weighed out to prepare 500 mL of 0.0250 mol/L oxalic acid.
15. In his student workbook, Justin wrote the following method for the preparation of 100 mL of a 0.100 mol/L sodium hydrogen carbonate standard solution.
- Weigh 0.100 g of sodium hydrogen carbonate into a beaker using an electronic balance.
 - Measure 100 mL of water using a measuring cylinder.
 - Pour the water into the beaker and dissolve the crystals.
- Pour the solution into a 100 mL volumetric flask. Add a few drops of water if needed to bring the volume up to the 100 mL mark.
- Evaluate Justin's experimental procedure.
16. Sharee titrated 20.00 mL of hydrobromic acid with 0.200 mol/L standard potassium hydroxide solution.
- Explain why she chose bromothymol blue as a suitable indicator for this titration.
 - Identify the colour change at the end point.
 - If Sharee's average titre was 18.55 mL, calculate the molarity of the hydrobromic acid.
17. Potassium hydrogen phthalate, $\text{KH}(\text{C}_8\text{H}_8\text{O}_4)$, or KHP, is a primary standard monoprotic acid. A 0.100 mol/L solution of potassium hydrogen phthalate is prepared. It is then used to titrate a 15.00 mL aliquot of sodium hydroxide solution. The average titre using phenolphthalein indicator was 22.75 mL.
- Classify the hydrogen phthalate ion as a strong or weak Bronsted-Lowry acid. Justify your classification.
 - Calculate the concentration of the sodium hydroxide solution.
 - The standardised sodium hydroxide solution is then used to determine the concentration of an unknown hydrofluoric acid solution. A 25.00 mL aliquot of hydrofluoric acid was found to be neutralised by 18.35 mL of the sodium hydroxide solution. Calculate the concentration of the hydrofluoric acid solution.
18. Figure 9.28 shows the pH graph of a titration in which a monoprotic acid (HA) reacts with a base (BOH).

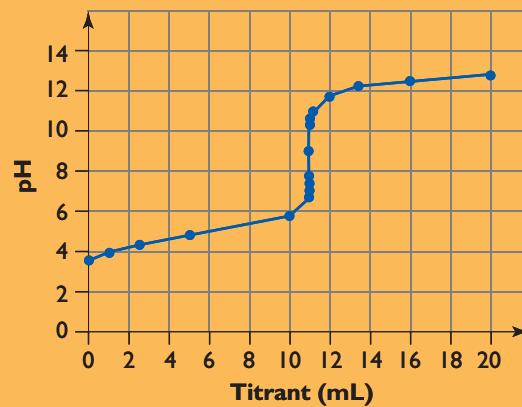


Figure 9.28

- (a) Identify which solution was present in the conical flask.
- (b) Classify the acid and the base as weak or strong.
- (c) Identify the pH of the solution at the equivalence point.
- (d) Write a balanced equation for the neutralisation reaction.
- (e) Determine from the graph the volume of titrant from the burette that was required to reach the equivalence point.
- (f) If 10.0 mL of solution was initially present in the flask and the concentration of BOH is 0.135 mol/L, calculate the concentration of HA.



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SUMMARY

- Antoine Lavoisier proposed the oxygen theory of acids. He believed that the presence of oxygen in non-metal oxides caused acidity.
- Humphry Davy proposed the hydrogen theory of acids. He showed that oxygen was not present in hydrochloric acid.
- Justus von Liebig improved on Humphry Davy's concept by stating that acids contained replaceable acids. When a metal reacted with an acid, the metal replaced the hydrogen in the acid. This theory did not account for oxidising acids that released other gases.
- Svante Arrhenius proposed the hydrogen ion theory of acids. An Arrhenius acid is one that released hydrogen ions in water. An Arrhenius base releases hydroxide ions in water.
- The Arrhenius theory of acids and bases could not account for many observations such as why some salts were acidic or basic.
- The Bronsted–Lowry theory states that acids are proton donors and bases are proton acceptors. The Bronsted–Lowry theory emphasises the importance of the solvent. It also applies to non-aqueous solvents.
- The Bronsted–Lowry theory states that acids and bases come in conjugate pairs. The stronger the B–L acid, the weaker its conjugate base. The stronger the B–L base, the weaker its conjugate acid.
- The Bronsted–Lowry theory explains why salts can be acidic and basic. Basic salts are the salts of weak acids and acidic salts are the salts of weak bases.
- Buffers are solutions that contain a weak acid and its conjugate base. Buffers are solutions that resist a change in pH on the addition of small amounts of strong acids or bases.
- The hydrogen carbonate–carbonic acid buffer is important in controlling blood pH.
- Volumetric analysis is an important technique used to determine the concentrations of acids and bases.

- Standard solutions are solutions of accurately known concentration. Primary standard solutions are prepared from high purity, stable solid acids or bases. These standards must be free of moisture and not react with the air.
- Standard solutions are prepared in volumetric flasks.
- Pipettes are used to transfer known volumes of solution into a conical flask. Pipettes should be rinsed with water and then rinsed with the solution to be placed in them.
- Burettes are accurate pieces of volumetric glassware that are used to deliver the titrant in a titration. The burette must be cleaned with water and then with the solution that will be used in it. The burette must be filled so that no bubbles of air exist below the tap.
- Titrations can be used to analyse the acid or base content of solutions.
- Indicators must be selected according to the strength of acid and base used in the titration. The indicator's pH range must match as closely as possible the pH at the equivalence point.
- Titrations can also be performed using a pH meter and data logger.
- Neutralisation reactions are exothermic.
- Care must be taken when cleaning up acid and base spills after accidents. Neutralisation reactions using weak acids or bases, including sodium carbonate and sodium hydrogen carbonate, are used to clean up spills. Flushing with large amounts of water after neutralisation is also used.

PRACTICAL ACTIVITIES

9.1

PRACTICAL ACTIVITIES



HYDROLYSIS OF SALTS

Aim

To investigate the pH of a range of salt solutions

Materials

- dropper bottles of 0.1 mol/L solutions of sodium chloride, sodium acetate, ammonium chloride, sodium hydrogen carbonate; sodium carbonate; sodium hydrogen sulfate, ammonium nitrate; zinc sulfate, ammonium acetate
- dropper bottle of universal indicator solution
- universal indicator colour chart
- spot plate
- pH meter and buffers

Safety

- Wear safety glasses throughout this experiment.
- Do not ingest solutions.
- Identify the other safety precautions that are relevant to this experiment by reading the method.

Method

Part A. Indicator experiment

1. Each group of students should use a spot plate to test the colour of the universal indicator in each salt solution supplied.
2. Use the universal indicator colour chart to estimate the pH of each salt solution.
3. Measure the pH of distilled water as a control.
4. Tabulate your results.

Part B. pH meter measurements

1. Calibrate the pH meter probe with the buffers supplied.
2. Use the pH meter and probe to measure the pH of each of the supplied solutions. Recalibration of the pH meter with buffers will probably be required after measuring several salt solutions.
3. Tabulate your results.

Results and analysis

1. Classify the salts solutions as neutral, acidic or basic.
2. Acidic salts are salts of weak bases and strong acids.
 - (a) For each acidic salt, name a strong acid and a weak base that will produce this salt on neutralisation.
 - (b) For each acidic salt, identify the ion that acts as a weak Bronsted–Lowry acid in water.
 - (c) Write appropriate hydrolysis equations to explain the acidity of these acidic salts.
3. Basic salts are salts of weak acids and strong bases.
 - (a) For each basic salt, name a weak acid and a strong base that will produce this salt on neutralisation.
 - (b) For each basic salt, identify an ion that acts as a weak Bronsted–Lowry base in water.
 - (c) Write appropriate hydrolysis equations to explain the basicity of these basic salts.
4. Explain why ammonium acetate is a neutral salt (use appropriate equations).

Conclusion

Write an appropriate conclusion for your experiment.

PRACTICAL ACTIVITIES

9.2 PRACTICAL ACTIVITIES

PREPARATION AND STANDARDISATION OF A SOLUTION

Aim

To standardise a solution of sodium hydroxide using a primary standard

Materials

- sample of (approx) 0.1 mol/L sodium hydroxide solution to be standardised oxalic acid dihydrate crystals *or* potassium hydrogen phthalate crystals
- 250 mL volumetric flask
- burette
- pipette (25 mL)
- pipette filler
- burette clamp and stand
- electronic balance
- phenolphthalein
- white tile
- small funnel
- wash bottle
- beaker (50 mL)
- beaker (150 mL)
- short, fine glass rod
- spatula

Safety

- Wear safety glasses throughout this experiment.
- Sodium hydroxide is caustic and should not be ingested or be allowed to make skin contact.
- Oxalic acid is poisonous. Take care not to ingest it.
- Identify other safety precautions relevant to this experiment by reading the method.

Background and calculations

In this experiment you will be provided with either oxalic acid dihydrate crystals or potassium hydrogen phthalate crystals as your primary standard. Oxalic acid is a weak diprotic acid. The hydrogen phthalate ion is a weak monoprotic acid.

Calculate the mass of primary standard acid required, using the following data.

Oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)

Consider a 0.0500 mol/L standard solution.

1. Calculate the molar weight (M) of oxalic acid dihydrate.
2. The volume (V) of the oxalic acid solution is 250 mL. Convert this volume to litres.
3. The concentration (c) of the oxalic acid is to be exactly 0.0500 mol/L. Calculate the number of moles (n) of oxalic acid dihydrate that should be weighed out.

$$n = cV$$

4. Calculate the mass (m) of oxalic acid dihydrate that should be weighed out on the electronic balance.

$$m = nM$$

Potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$)

Consider a 0.100 mol/L standard solution.

1. Calculate the molar weight (M) of potassium hydrogen phthalate.
2. The volume (V) of the potassium hydrogen phthalate solution is 250 mL. Convert this volume to litres.
3. The concentration (c) of the potassium hydrogen phthalate is to be exactly 0.100 mol/L. Calculate the number of moles (n) of potassium hydrogen phthalate that should be weighed out.

$$n = cV$$

4. Calculate the mass (m) of potassium hydrogen phthalate that should be weighed out on the electronic balance.

$$m = nM$$

Method

Preparation of primary standard solution

1. Use the calculation you have performed, to accurately weigh out the require mass (m) of your selected primary standard. Use a clean, dry 50 mL beaker as your weighing beaker.
2. Meanwhile, clean your 150 mL volumetric flask with water.
3. Use a wash bottle to add water to the beaker of crystals and use a short glass rod to dissolve them.

PRACTICAL ACTIVITIES

4. Use a small funnel to quantitatively transfer the acid solution into the volumetric flask with the aid of the glass rod and the wash bottle. Irrigate the beaker with water and add all the washings to the volumetric flask.
5. Add water slowly to the mark. Add drops of water until the base of the meniscus is on the line. Stopper the flask. Invert and mix thoroughly. Label the flask (either 0.0500 mol/L oxalic acid or 0.100 mol/L potassium hydrogen phthalate).

Standardisation of the unknown sodium hydroxide solution

1. Prepare the burette and stand. Rinse the burette with water to clean it. Discard the washings. Rinse the burette with small volumes of the unknown sodium hydroxide solution. Discard the washings into a waste beaker. Fill the burette above the zero mark with sodium hydroxide solution. Open the tap and run out the solution into a waste beaker so that the solution fills the space below the tap. Adjust the base of the meniscus to the zero mark.
2. Prepare the conical flask by rinsing it well with water.
3. Prepare the pipette by rinsing with small volumes of water. Discard the washings. Rinse the pipette several times with small volumes of your standard acid from the volumetric flask. Discard these washings.
4. Use your pipette and pipette filler to fill the pipette with standard acid solution.
5. Transfer the acid solution to the conical flask. Allow the solution to drain with the tip of the pipette against the glass wall for 10 seconds.
6. Place the conical flask on a white tile under the tip of the burette. Add 3 drops of phenolphthalein indicator.
7. Conduct a rough titration to locate the approximate end point. Add the base from the burette whilst swirling the contents of the flask to ensure complete mixing. The end point is reached when the first faint permanent pink (not crimson) colour appears. Note the volume of base added.
8. Rinse the conical flask thoroughly and repeat the titration accurately to obtain at least two

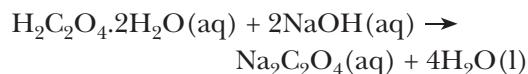
titres that agree within 0.05 mL (1 drop). To achieve this accuracy you will need to proceed drop by drop near the end point. The wash bottle is used to irrigate the internal walls of the flask to ensure all solution is at the bottom. The wash bottle also allows half-drops to be removed from the burette tip.

9. Tabulate your titres and take an average (not including the rough).

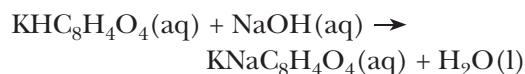
Results and analysis

Your calculations should be based on one of the following stoichiometric equations:

oxalic acid – sodium hydroxide



potassium hydrogen phthalate – sodium hydroxide



1. Convert the volume of standard acid (25.00 mL) to litres (V_A). Use this volume to calculate the number of moles (n_A) of standard acid (concentration c_A) used in the titration.

$$n_A = c_A V_A$$

2. Use the appropriate stoichiometric equation and the mole ratio to calculate the number of moles of sodium hydroxide (n_B) that reacted in the titration.

3. Convert the average titre volume (V_B) to litres. Calculate the concentration of the sodium hydroxide solution (c_B)

$$c_B = n_B / V_B$$

4. Express your answer to the number of decimal places justified by the accuracy of your experiment.

5. Explain why phenolphthalein was used as the indicator in this experiment.

6. Identify a reason that sodium hydroxide solution cannot be prepared as a primary standard.

7. Explain how reliability is improved in this experiment.

Conclusion

Write an appropriate conclusion for this experiment.

PRACTICAL ACTIVITIES

9.3 PRACTICAL ACTIVITIES

pH TITRATION OF DILUTED VINEGAR

Aim

To use phenolphthalein and a pH-probe/data-logger to monitor the neutralisation of a domestic acidic substance (dilute white vinegar) by a standardised sodium hydroxide solution

Materials

- standardised NaOH solution (from previous experiment 9.2; about 0.100 mol/L)
- diluted white vinegar (150 mL of white vinegar diluted to 1 litre with distilled water in a volumetric flask)
- phenolphthalein
- pH meter and data logger
- magnetic stirrer and Teflon-coated bar stirrer
- burette (with stand and clamp)
- beaker (250 mL)
- pipette and pipette filler
- 100 mL measuring cylinder

Safety

- Wear safety glasses throughout this experiment.
- Sodium hydroxide is caustic and should not be ingested or be allowed to make skin contact.
- Identify other safety precautions relevant to this experiment by reading the method.

Method

The apparatus for this titration is illustrated in Figure 9.22 on page 201.

1. Pre-calibrate the pH probe using the pH 4 and 7 buffers.
2. Pipette 25.0 mL (V_A) of the diluted vinegar into a clean 250 mL beaker. Add 100 mL of distilled water to increase the solution volume. Add 4–5 drops of phenolphthalein. Place the beaker on the magnetic stirrer plate. Insert the stirrer.

3. Gently place the pH probe into the acetic acid solution. Clamp the probe high enough so that it does not interfere with the rotating stirrer.
4. Mount the burette over the beaker.
5. Check that the pH probe and meter or data logger/display are working correctly before proceeding.

Methods of recording data

You may like to choose various display options on the pH meter or data logger. You can choose continuous measurement of pH versus time, which is then displayed on the computer screen or graphics calculator screen, or you can choose a single-point mode based on the 10-second measurement of pH after the addition of known aliquots of base during the titration. The equipment available at your school will determine your choice.

Continuous pH measurement mode

1. Open the tap of the burette and allow the sodium hydroxide solution to run into the beaker.
2. Monitor the pH on your computer screen. The pH will rise only gradually at first.
3. Reduce the addition rate as the end-point approaches. The pH begins to rise rapidly at the end point, where the indicator turns permanent pink. The sodium hydroxide will need to be added drop by drop to achieve an accurate titration volume. Record this titre. The wash bottle is helpful here. Continue the titration until the pH rises towards 12.
4. Repeat the experiment to obtain an accurate titre.

Single-point pH mode

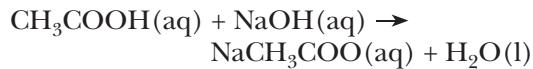
1. Add a known volume of NaOH solution (e.g. 5.0 mL). Measure the pH over a 10-second interval. In your book, record the volume of base added, the colour of the mixture and the pH.
2. Continue with the titration by adding known aliquots of the base to the beaker. At each step record the volume of base, pH and indicator colour.
3. Approach the end-point slowly and reduce the volume of base to drops. Measure the pH at the end point when the indicator is pale pink. Note the titre.

PRACTICAL ACTIVITIES

4. Continue to add base till the pH rises towards 12. Record the volume and pH at each point.
5. Repeat the experiment as time allows.

Results and analysis

1. Depending on your measurement method, you should produce a hard copy of the graph of pH versus volume of NaOH added.
2. Use the data to determine the average titre for the titration (V_B).
3. The neutralisation equation is:



- (i) Calculate the number of moles of base (n_B) that were required to reach the end point. ($n_B = cV_B$). Remember to convert your titre from 'mL' to 'L'.
- (ii) Thus calculate the concentration of acetic acid in the diluted vinegar.
- (iii) Calculate the concentration of acetic acid in the undiluted vinegar.

4. Explain why the vinegar was diluted for this analysis.
5. Discuss whether or not the use of a pH probe and data logger has produced a more accurate result than using an indicator alone.
6. Explain why the pH at the equivalence point was not equal to 7.

Conclusion

Write a suitable conclusion for your experiment.