

MODULE 2

The acidic environment

Acids have been known to chemists for well over 200 years. They are widely involved in natural processes such as the functioning of our respiratory and digestive systems, and the control of acidity is an important factor in creating hospitable environments for a wide range of living organisms.

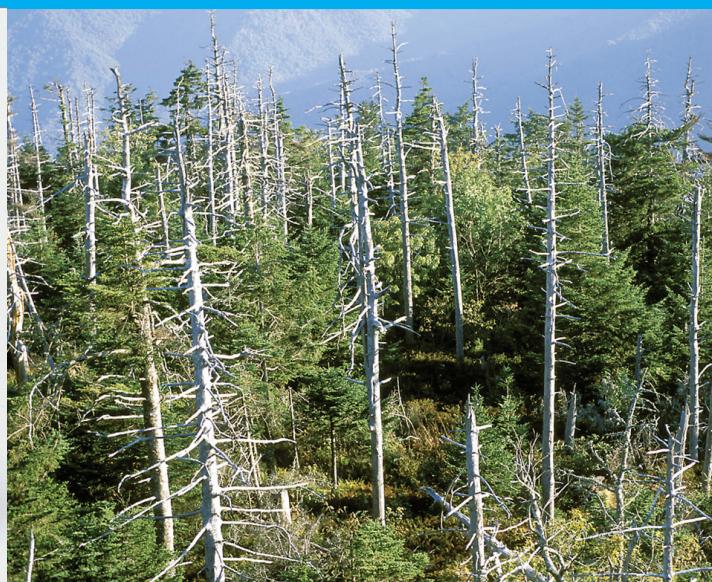
Acids and their partners in reactivity, bases, are widely used in industry. While we, as ordinary consumers, come into contact with some acids and bases—such as the products shown below—much larger quantities of acids and bases are used industrially to extract common metals and to manufacture other products that we are more familiar with, such as fertilisers, detergents, explosives, paints, plastics, synthetic fibres, glass, dyes, insecticides and pharmaceuticals. Apart from sulfuric acid in car batteries and sodium hydroxide in oven and drain cleaners, consumers have little contact with the major acids and bases of industry despite the fact that sulfuric and nitric acids, sodium hydroxide and calcium oxide rank in the top dozen manufactured chemicals in terms of quantities produced worldwide per year.

Because acids are involved in our natural environment and in the making of many of the products we use in our everyday lives, and because there is growing concern about the way that acidic and basic discharges are affecting the environment, we shall undertake a study of them in this module. This will help us handle these substances safely.



Chapter 4 will begin with a general introduction to acids, bases, neutralisation and salts then turn to acidic and basic oxides. This leads into a discussion of the equilibrium between carbon dioxide and its aqueous solution and to the introduction of an important chemical concept, Le Chatelier's principle. We then look at acidic oxides in the atmosphere—how they get there, their detrimental effects and how they are removed: this leads into a discussion of acid rain. Attention then turns to some common acids in everyday life, to the concept of pH, and to explanations of the terms weak and strong, concentrated and dilute. Calculations involving volumes of gases are also treated here.

In Chapter 5 we will look at the way that the concepts of acids and bases have developed over time, paying particular attention to the Brönsted–Lowry concept and its applications. This leads to an account of the use of acid–base reactions in volumetric analysis, and to a discussion of what are called buffers and how they control acidity, particularly in natural systems. The chapter will end with a discussion of alkanols and a particular type of acid called alkanoic acids and of the compounds (called esters) that form by reaction between alkanols and alkanoic acids.



ACIDS AND BASES AND THEIR EFFECTS ARE ALL AROUND US

Many everyday products such as the ones in these photographs are, or contain, acids and bases. We often determine acidity or basicity by using indicator solutions or papers. One detrimental effect of our discharge of acidic oxides such as nitrogen dioxide and sulfur dioxide into the atmosphere is acid rain which has caused damage to pine forests in parts of Europe and North America.



Acids and bases in everyday life

IN THIS CHAPTER

Simple definitions of acids and bases

Indicators for determining acidity and basicity of solutions

Acid-base reactions

Common acids and names for salts

Acidic and basic oxides

The carbon dioxide–water equilibrium

Le Chatelier's principle

Le Chatelier's principle and the CO_2 , H_2CO_3 equilibrium

Acidic oxides in the atmosphere

Properties of oxides of sulfur and nitrogen

The 'fate' of oxides of sulfur and nitrogen in the atmosphere

Acid rain

Calculations involving volumes of gases

Some common acids and bases

Meaning of pH

Self-ionisation of water

pH of alkaline solutions

Neutral, acidic and alkaline solutions

Measuring pH of solutions

Weak and strong acids

Many of the substances we deal with in our everyday lives are classed as acids or bases. Common substances that contain acids were shown on page 104: vinegar (contains acetic acid), lemon juice (contains citric acid), aspirin (acetyl salicylic acid) and vitamin C (ascorbic acid). In addition car batteries and rust converters contain sulfuric and phosphoric acids respectively.

Some household substances that contain bases were shown on page 105: cloudy ammonia, for cleaning, washing soda (sodium carbonate), antacid tablets (contain calcium carbonate and/or magnesium hydroxide) and oven and drain cleaners (contain sodium hydroxide). Others are lime for making mortar (calcium hydroxide) and garden lime (calcium carbonate).

This chapter will survey some of the ways that acids and bases impact upon our lives.

4.1 SIMPLE DEFINITIONS OF ACID AND BASE

In Chapter 5 we shall look at the way that the concepts of acids and bases have developed over the centuries. For present purposes we will use the following definitions.

An **acid** is a substance which in solution produces hydrogen ions, H^+ or more strictly H_3O^+ , sometimes called **hydronium ions**.

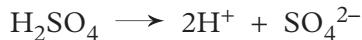
A **base** is a substance which either contains the oxide O^{2-} or hydroxide ion OH^- or which in solution produces the hydroxide ion.

A soluble base is called an **alkali**.

Compounds that contain the oxide ion are either insoluble in water (CuO , MgO , Fe_2O_3) or they react with water to form hydroxide ions (Na_2O , CaO). Therefore alkalis are compounds which contain, or in aqueous solution produce, hydroxide ions.

Common acids are hydrochloric acid, HCl , sulfuric acid, H_2SO_4 , and nitric acid, HNO_3 .

In solution, for example:



Other acids are shown in Table 4.2 (on page 114).

Common bases are sodium hydroxide, $NaOH$; barium hydroxide, $Ba(OH)_2$; potassium oxide, K_2O ; magnesium oxide, MgO ; iron(III) oxide, Fe_2O_3 ; copper hydroxide, $Cu(OH)_2$; ammonia, NH_3 . Of these seven substances only the first three and ammonia are alkalis (soluble in water).

Common properties of all acids

- 1 Acids have a *sour taste* (but you must *never* taste chemicals in the laboratory).
- 2 Acids *sting* or *burn* the skin.
- 3 In solution, acids *conduct electricity*.
- 4 Acids *turn blue litmus* (a vegetable dye) *red*. (Blue in Acid goes Red—BAR.)

These common properties arise because all acids produce hydrogen ions.

Common properties of alkalis

- 1 Alkalies have a *soapy feel*.
- 2 Alkalies have a *bitter taste* (though as with acids you should *never* taste them).
- 3 In solution, alkalies are *good conductors of electricity*.
- 4 Alkalies turn *red litmus blue*.

It was their effects upon vegetable dyes such as litmus that were first used to classify substances as acids or bases.

4.2 INDICATORS

Litmus is a dye that is extracted from lichens which are mixed algae-fungi organisms that grow on rocks and trees. In the eighteenth century it was discovered that certain substances could change the colour of litmus solution. Hence this colour change was used to classify substances as acids or bases. In addition if a substance did not change the colour of litmus (it left blue litmus blue, and red litmus red) it was classed as neutral: that is, it was neither an acid nor a base. The terms, **acidic**, **basic** (or **alkaline**)[†] and **neutral** are used to describe solutions that contain acid, base or neither respectively. We call litmus an indicator.

[†] Note that while the terms *base* and *alkali* have different meanings (alkalis are a sub-group of bases), the terms *basic* and *alkaline* when used to describe solutions have exactly the same meaning.

An **indicator** is a substance (usually a vegetable dye) that in solution changes colour depending on whether the solution is acidic or alkaline.

Many other vegetable dyes have this same property of changing colour when added to acidic or alkaline solutions. For example if red cabbage leaves are crushed up and extracted with methanol, the red solution obtained is an indicator. In acid solution it is red: as the hydrogen ion concentration is decreased, the colour changes to purple and then to green: if placed in a hydroxide ion solution this dye goes yellow.

The actual range of acidity or alkalinity over which indicators change colour varies from one indicator to another. Some indicators such as litmus and bromothymol blue have one colour in acid solution and a different one in alkaline solution. Others change colour as the solution changes from highly acidic to slightly acidic or from highly alkaline to slightly alkaline. Some common indicators and their colour changes are shown in Table 4.1 and illustrated in Figure 4.1.

TABLE 4.1 Common indicators and their acidity/alkalinity ranges

Indicator	Colour change				
	Highly acidic	Slightly acidic	Neutral	Slightly alkaline	Highly alkaline
methyl orange	red → yellow		yellow	yellow	yellow
bromothymol blue	yellow	yellow → blue		blue	blue
litmus	red → blue	red		blue	blue
phenolphthalein	colourless	colourless	colourless	colourless → red	

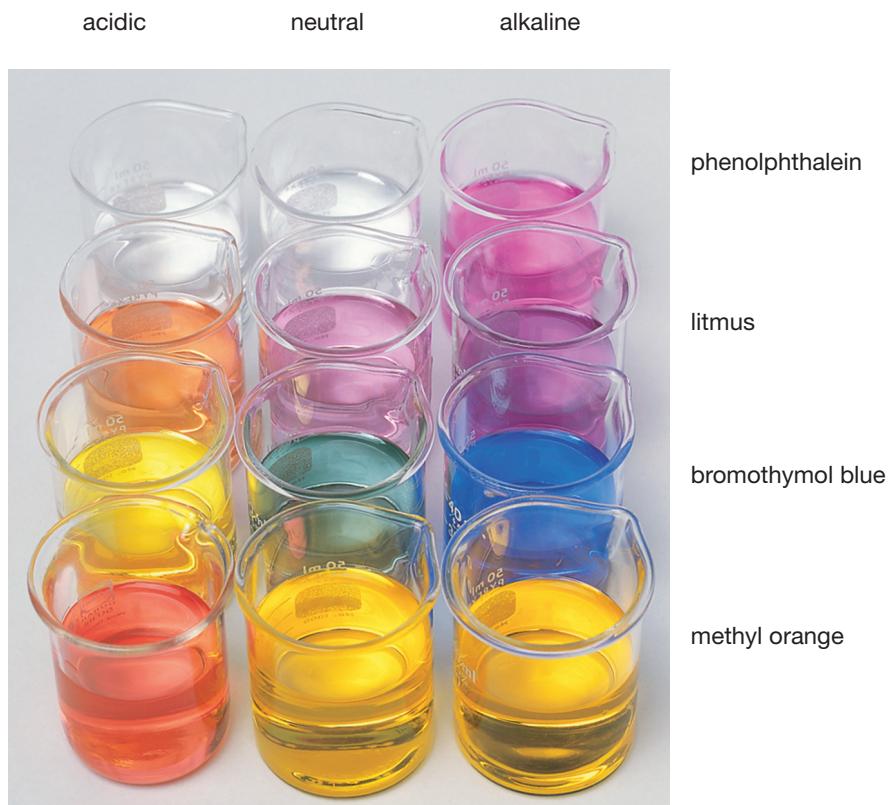


FIGURE 4.1
Common indicators in acidic, neutral and alkaline solutions



Example 1

Five solutions, A, B, C, D and E, were tested with indicators: the results are tabulated below. Using Table 4.1 deduce whether the solutions are acidic, neutral or alkaline, and if not neutral, decide whether they are highly or slightly acidic or alkaline. For Solution E describe any further test you would need to perform to answer these questions completely.

	A	B	C	D	E
litmus		purple ^a	red		
bromothymol blue		yellow			blue
methyl orange	red		yellow	yellow	
phenolphthalein				red	colourless

a Purple is an equal mixture of blue and red.

Solution A: The yellow colour of bromothymol blue tells us that this solution is acidic; the red colour with methyl orange tells us that it is *highly acidic*.

Solution B: The litmus colour is halfway between red and blue: this means that the solution is *neutral*. The methyl orange colour shows that this solution is not highly acidic which is consistent with the litmus result.

Solution C: The red litmus colour shows that this solution is acidic; the yellow colour with methyl orange shows that it is only *slightly acidic*.

Solution D: The blue colour with bromothymol blue shows that this solution is alkaline; the red phenolphthalein colour tells us that it is *highly alkaline*.

Solution E: All the phenolphthalein test tells us is that this solution is not highly alkaline. If we tested this solution with litmus, a blue colour would tell us that it is alkaline (and therefore slightly alkaline since it cannot be highly alkaline), a purple colour (mixed blue and red) would mean that it was neutral, and a red colour would show that it was acidic. In this last case we would then need to use methyl orange to decide whether it was highly or slightly acidic.

We can use litmus or bromothymol blue to decide whether a solution is acidic, neutral or basic (alkaline) and then we can use methyl orange or phenolphthalein to decide whether the solution is highly or slightly acidic or alkaline respectively.

Practical uses of indicators

Indicators provide a cheap and convenient way of determining the acidity or alkalinity of substances. Some everyday uses of indicators are:

- testing the acidity or alkalinity of soils (because some plants need an acidic soil—azaleas and camellias—while others need an alkaline or near neutral soil—most annual flowers and vegetables)
- testing home swimming pools (these need to be approximately neutral, though adding chemicals to sanitise the water can change its acid–alkali balance)
- monitoring wastes from laboratories that process photographic film (discharges to the sewerage system must be nearly neutral: photographic solutions are often highly alkaline).



A simple kit that is commercially available for measuring soil pH (using a universal indicator)

Exercises

- 1** Use Table 4.1 and the results in the table below to decide whether the solutions listed are acidic, neutral or alkaline (basic). If for any solution the result is inconclusive, describe what additional test you would perform and explain how this would clarify the uncertainty.



Solution	Z	Y	X	W	U	M	N
Indicator^a	btb	litmus	meth	btb	phth	litmus	meth
Colour	yellow	blue	red	green ^b	red	purple ^c	yellow

a *btb = bromothymol blue, meth = methyl orange, phth = phenolphthalein*

b *Green is an equal mixture of yellow and blue.*

c *Purple is an equal mixture of blue and red.*

- 2** The table below shows the results of some indicator tests on six different solutions. Decide whether the solutions are neutral or highly or slightly acidic or alkaline. If the results for any particular solution are not conclusive, describe any additional test(s) that you would perform and explain how it or they would resolve the situation.

	P	Q	R	S	T	V
litmus			blue			
bromothymol blue			yellow		green ^a	
methyl orange	red		yellow	yellow		yellow
phenolphthalein				red	colourless	colourless

a *Green is an equal mixture of yellow and blue.*

- 3** Which solute ions would be present in aqueous solutions of each of

- a** the following acids:
 - i** hydrobromic acid
 - ii** nitric acid
- b** the following alkalis:
 - i** barium hydroxide
 - ii** sodium oxide

4.3 ACID-BASE REACTIONS

Acids react with bases in what are called *neutralisation* reactions to form compounds called *salts*.

Typical acid-base reactions are:

- the reaction of the base (alkali) sodium hydroxide with hydrochloric acid to form the salt sodium chloride and water:



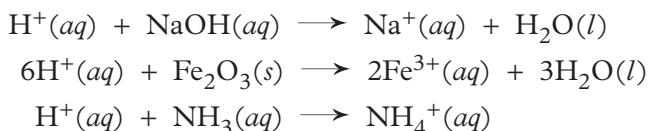
- the reaction of nitric acid with the base iron(III) oxide to form the salt iron(III) nitrate and water:



- the reaction of sulfuric acid with the alkali ammonia to form ammonium sulfate:

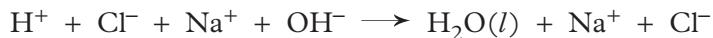


The aqueous acid solutions in the above three equations all contain H^+ ions (along with Cl^- , NO_3^- and SO_4^{2-} ions respectively). The bases actually react with these H^+ ions. The anions are still present in solution, unaltered, at the end of the reaction. Hence we often write these equations as:



Because the anions, Cl^- , NO_3^- and SO_4^{2-} , are not actually involved in the reactions, we call them *spectator ions* as we did in similar situations on p. 117 CCPC.

Equation 4.2 can be written in a complete ionic form (as on pp. 116–17 CCPC):



This shows that Na^+ as well as Cl^- is a spectator ion. The net ionic equation is therefore just

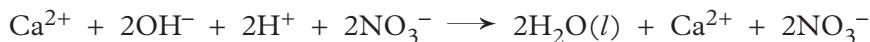


This is the net ionic equation for many acid–alkali reactions: for example for the reaction between calcium hydroxide solution and nitric acid:

Neutral species equation:



Complete ionic equation:



Net ionic equation:



To define terms:

Neutralisation is the reaction of an acid with a base.

A **salt** is an ionic compound formed when a base (alkali) reacts with an acid.

Or a salt is a compound formed when the hydrogen of an acid is replaced by a metal ion. In general:



Neutralisation reactions generally produce water as well as salts, but there are exceptions: see Reaction 4.3 above.

The salts sodium chloride, iron(III) nitrate, ammonium sulfate and calcium nitrate were formed in the reactions above. Other common salts are:

potassium nitrate	KNO_3	$(\text{K}^+ \text{NO}_3^-)$
copper sulfate	CuSO_4	$(\text{Cu}^{2+} \text{SO}_4^{2-})$
zinc chloride	ZnCl_2	$(\text{Zn}^{2+} 2\text{Cl}^-)$
aluminium nitrate	$\text{Al}(\text{NO}_3)_3$	$(\text{Al}^{3+} 3\text{NO}_3^-)$
ammonium phosphate	$(\text{NH}_4)_3\text{PO}_4$	$(3\text{NH}_4^+ \text{PO}_4^{3-})$

4.4 COMMON ACIDS AND NAMES FOR SALTS

Salts are named in a similar way to that used for binary ionic compounds on pp. 77–8 CCPC: several salts were named on p. 79 CCPC.

The metal ion (or cation) is named first with the name for the anion being derived from the name of the acid.

The hydrohalic acids—hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI)—lead to salts called **halides**—chlorides, bromides and iodides. Hence we have the salts magnesium chloride, MgCl_2 ; potassium bromide, KBr ; silver iodide, AgI . These names follow from the way we named binary compounds on pp. 77–8 CCPC.

Most of our common acids are what are called **oxyacids**: they have oxygen attached to an element such as sulfur, nitrogen, phosphorus, chlorine or carbon. When the name of the oxyacid ends in ‘-ic’, the salt takes a similar name but with the ending ‘-ate’. Sulfuric acid forms sulfates; nitric acid forms nitrates; phosphoric acid, phosphates; carbonic acid, carbonates. Hence we have the salts aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3$; lead nitrate, $\text{Pb}(\text{NO}_3)_2$; sodium phosphate, Na_3PO_4 ; and calcium carbonate, CaCO_3 .

Two other common acids are nitrous acid, HNO_2 , and sulfurous acid, H_2SO_3 . When the name of the acid ends in ‘-ous’, the name of the salt ends in ‘-ite’: nitrous acid forms nitrites such as sodium nitrite, NaNO_2 ; sulfurous acid forms sulfites such as potassium sulfite, K_2SO_3 .

Anions formed from oxyacids are called **oxyanions**. Nitrate, NO_3^- , sulfate, SO_4^{2-} , carbonate, CO_3^{2-} , nitrite, NO_2^- , are all oxyanions.

Names of common acids and of the salts they form are given in Table 4.2. It is essential that you know the names of the acids and anions in this table and are able to write formulae for salts formed from them.

The formulae of the acids should be memorised; the negative charge on the anion formed (that is, the valence of the anion) can be worked out from the number of H^+ ions lost. Knowing this and knowing the positive charge (valence) of the metal ion involved, we can deduce the formula of any salt. This is because, as on pp. 76–7 CCPC, the ions are present in ratios such that the total number of positive charges equals the total number of negative charges.

To deduce the formula of potassium sulfate, we start with the knowledge that potassium forms a singly charged ion, K^+ , and that sulfuric acid is H_2SO_4 , so sulfate is SO_4^{2-} . Hence potassium sulfate is K_2SO_4 , because $2 \times (1+)$ in magnitude equals $1 \times (2-)$. Similarly for aluminium nitrate: knowing that aluminium forms the Al^{3+} ion and that nitric acid is HNO_3 , we deduce that the nitrate ion is singly charged, NO_3^- , and so aluminium nitrate is $Al(NO_3)_3$, because $1 \times (3+)$ in magnitude equals $3 \times (1-)$.

TABLE 4.2 Common acids and the anions they form

Acid		Anion		Typical salt
hydrofluoric	HF	F^-	fluoride	CaF_2
hydrochloric	HCl	Cl^-	chloride	$NaCl$
hydrobromic	HBr	Br^-	bromide	KBr
hydroiodic	HI	I^-	iodide	Agl
sulfuric	H_2SO_4	SO_4^{2-}	sulfate	K_2SO_4
sulfurous	H_2SO_3	SO_3^{2-}	sulfite	Na_2SO_3
nitric	HNO_3	NO_3^-	nitrate	$Pb(NO_3)_2$
nitrous	HNO_2	NO_2^-	nitrite	$NaNO_2$
carbonic	H_2CO_3	CO_3^{2-}	carbonate	$CaCO_3$
phosphoric	H_3PO_4	PO_4^{3-}	phosphate	Na_3PO_4
formic (methanoic)	HCOOH	$HCOO^-$	formate (methanoate)	$Mg(HCOO)_2$
acetic (ethanoic)	CH_3COOH	CH_3COO^-	acetate (ethanoate)	$Ag(CH_3COO)$
hydrocyanic	HCN	CN^-	cyanide	KCN
hydrogen sulfide	H_2S	S^{2-}	sulfide	ZnS

As pointed out on p. 76 CCPC we need to memorise the charges of the common metal ions in Table 3.2 on p. 77 CCPC. There is no need to memorise formulae of individual salts—there are far too many of them for that—but we must be able to work out formulae for salts very quickly.

Exercises

- 4 Write equations for the reactions of each of:
- | | | |
|----------------------|------------------------|---------------------------|
| a nitric acid | b sulfuric acid | *c hydroiodic acid |
|----------------------|------------------------|---------------------------|
- with each of: **(i)** sodium hydroxide **(ii)** zinc oxide **(iii)** ammonia.
- 5 Write equations for the reaction of any acid (that is, of H^+) with:
- | | | |
|--------------------------|------------------------------|-------------------------------|
| a potassium oxide | c sodium hydroxide | *e iron(III) hydroxide |
| b aluminium oxide | d magnesium hydroxide | f ammonia |
- 6 Write equations for the reaction of the hydroxide ion with:
- | | | |
|----------------------|------------------------|--------------------------|
| a nitric acid | b carbonic acid | c phosphoric acid |
|----------------------|------------------------|--------------------------|

Name the anion formed in each case.

7 Give the formulae of:

- | | | |
|---------------------|----------------------|------------------------|
| a potassium iodide | e aluminium chloride | *i ammonium carbonate |
| b barium sulfate | f zinc nitrate | *j potassium phosphate |
| c sodium acetate | *g barium bromide | *k ammonium nitrite |
| d potassium sulfite | *h sodium sulfide | *l aluminium sulfate |

8 a Name the salts in the right-hand column of Table 4.2.

b Give the names of:

- | | | |
|--|-----------------------------------|--|
| i AgBr | iv MgF ₂ | *vii Al(NO ₃) ₃ |
| ii (NH ₄) ₂ CO ₃ | v KNO ₂ | *viii FeCl ₂ |
| iii Na ₂ SO ₃ | vi K ₃ PO ₄ | *ix Ca(CH ₃ COO) ₂ |

9 a Describe one method of preparing each of the salts in Exercise 7 (e) and (f) and in Exercise 8 (b) (iv) and (ix).

b For each of the reactions you used to prepare the salts in Exercises 7 (e) and 8 (b) (iv) write neutral species, complete ionic and net ionic equations.

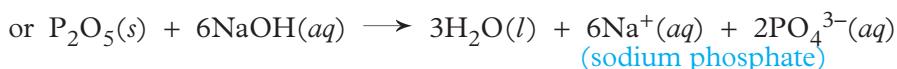
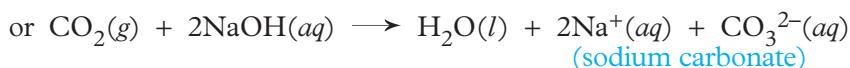
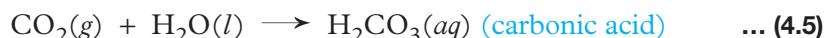
4.5 ACIDIC AND BASIC OXIDES

Oxides are a class of compound that often displays acidic or basic properties.

An **acidic oxide** is one which either:

- reacts with water to form an acid or
- reacts with bases to form salts (or does both).

Common acidic oxides are carbon dioxide, CO₂, and diphosphorous pentoxide, P₂O₅, because



A **basic oxide** is one that:

- reacts with acids to form salts but
- does not react with alkali solutions (such as NaOH or KOH).

Common basic oxides are copper oxide, CuO, and iron(III) oxide, Fe₂O₃, because:



There are some oxides, such as ZnO, PbO and Al₂O₃, that react with acids to form salts, but which also react with alkalis. These are called **amphoteric oxides**.

There is another group of oxides that do not react with either acids or bases. These are called **neutral oxides**. Common neutral oxides are carbon monoxide, CO, nitrous oxide, N₂O, and nitric oxide, NO.

Examples of the four types of oxide are listed in Table 4.3.

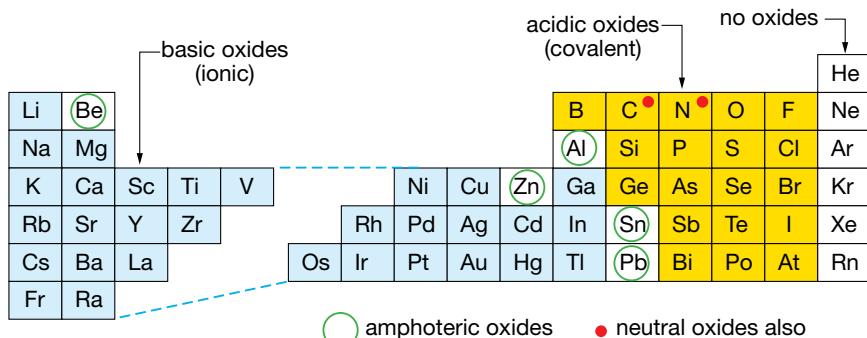
TABLE 4.3 Common acidic, basic, amphoteric and neutral oxides

Acidic oxides	Basic oxides	Amphoteric oxides	Neutral oxides
CO_2	Na_2O	ZnO	CO
NO_2	K_2O	Al_2O_3	NO
P_2O_3	MgO	PbO	N_2O
P_2O_5	CaO	SnO	
SO_2	CuO		
SO_3	Fe_2O_3		
Cl_2O	Ag_2O		

Acidic oxides are generally oxides of non-metals. They are all covalent compounds. Elements that have acidic oxides occur towards the right and top of the Periodic Table as shown in Figure 4.2.

Basic oxides are oxides of metals. They are ionic compounds. Elements that form basic oxides occur towards the left of the Periodic Table (Figure 4.2).

FIGURE 4.2
Location of different types of oxides in the Periodic Table



Exercises

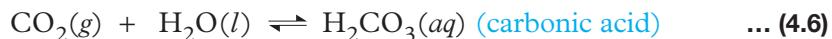
- 10 a** The following oxides are all acidic: B_2O_3 , N_2O_3 , P_2O_3 , SO_3 , Cl_2O . In water they form (respectively) boric acid, H_3BO_3 , nitrous acid, HNO_2 , phosphorous acid, H_3PO_3 , sulfuric acid, H_2SO_4 , and hypochlorous acid, HOCl . Write equations for these reactions.
- b** Write equations for the reaction of sodium hydroxide with carbon dioxide, sulfur trioxide and *dichlorine monoxide.
- 11** Acidic oxides react with basic oxides to form salts. Write equations for the reaction of:
- a** carbon dioxide with calcium oxide
 - b** sulfur dioxide with sodium oxide
 - *c** sulfur trioxide with copper oxide.

4.6 THE CARBON DIOXIDE-WATER EQUILIBRIUM

The reaction between carbon dioxide and water, Equation 4.5, is of great practical significance. It is involved in the removal of carbon dioxide from our

bodies, the transport of carbon dioxide in photosynthesis, the removal of carbon dioxide from the atmosphere and in the preparation of aerated drinks.

This reaction between carbon dioxide and water does not go to completion. Rather it is an equilibrium reaction: Equation 4.5 is more correctly written as:



The concept of chemical equilibrium was introduced on pp. 208–10 CCPC.

Another way of looking at this reaction is to regard it as the solubility of carbon dioxide in water. We find that this solubility increases as the pressure of carbon dioxide above the solution increases. If we maintain standard atmospheric pressure[†] of carbon dioxide above a solution of CO_2 in water at 25°C , the concentration of carbon dioxide (or of carbonic acid) in the solution is 0.033 mol/L. If we increase the pressure by a factor of three, the solubility increases to about 0.10 mol/L. If the pressure of CO_2 above the solution falls to the normal CO_2 pressure in the atmosphere (35 Pa^{\dagger}), the solubility falls to $1.2 \times 10^{-5} \text{ mol/L}$.

The solubility of carbon dioxide decreases as the temperature increases. This is shown in Figure 4.3. With solids and liquids solubility generally increases as temperature increases, but with gases solubility *decreases* as temperature increases.

These effects of changing pressure and temperature can be regarded as moving the position of equilibrium for Reaction 4.6. **Position of equilibrium**, or **equilibrium position**, means the extent to which the reaction has gone in the forward or reverse direction. If we say that the position of equilibrium lies well to the right, we mean that at equilibrium most of the reactant has been converted to product. If it lies well to the left, then at equilibrium most of the reactant is still present with only a small proportion of it having been converted to product.

There is a general principle that can be used to predict the effect on the position of equilibrium of changing the conditions.

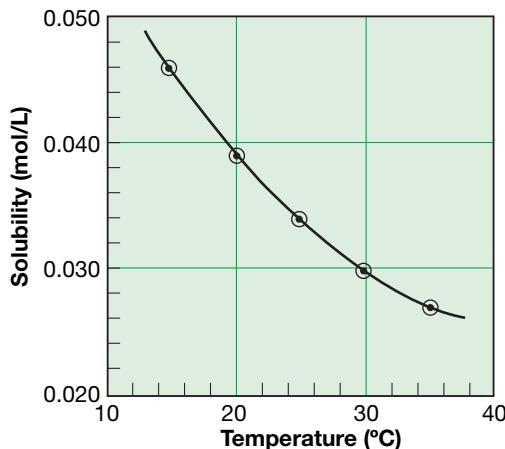


FIGURE 4.3
Solubility of carbon dioxide in water as a function of temperature (with 100 kPa pressure of CO_2 above the solution)

4.7 LE CHATELIER'S PRINCIPLE

In 1885, Le Chatelier formulated a simple generalisation for predicting how an equilibrium will respond to a disturbance; it is known as **Le Chatelier's principle**.

If a system at equilibrium is disturbed, then the system adjusts itself so as to minimise the disturbance.

[†] standard atmospheric pressure = 101.3 kPa; kPa is kilopascal; Pa, pascal, is the systematic unit of pressure

In this context, an equilibrium is ‘disturbed’:

- if the *concentration* (or *pressure*) of one or more of the species involved is changed
- if the *total pressure* acting upon a reaction that involves gases is changed, or
- if the *temperature* is altered.

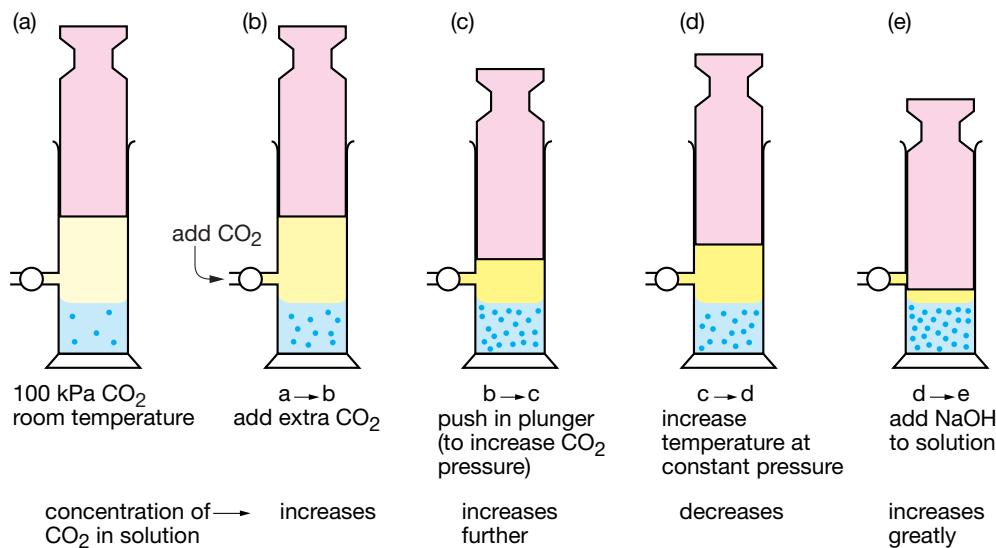
4.8 LE CHATELIER’S PRINCIPLE AND THE CO_2 , H_2CO_3 EQUILIBRIUM

We can illustrate the three ways of disturbing an equilibrium with our CO_2 , H_2CO_3 reaction:

- 1 If the pressure of CO_2 is increased (for example, by pumping more CO_2 into the reaction vessel, (b) in Fig. 4.4), then some CO_2 goes into solution as H_2CO_3 to try to counteract the increase; we say that the equilibrium, Equation 4.6, *moves to the right*. If the pressure of CO_2 is decreased (for example by sucking some of it out of the reaction vessel), then some H_2CO_3 decomposes to CO_2 and comes out of solution to try to counteract the decrease. We say that the equilibrium moves to the left.
- 2 If the total pressure on the reaction system is increased (for example by pushing in a plunger as in Fig. 4.4(c)), the equilibrium moves in the direction that tends to reduce pressure. That is, some CO_2 dissolves: the equilibrium moves to the right.
- 3 Reaction 4.6 is exothermic. This means that as it proceeds from left to right, heat is liberated, and conversely as it goes from right to left, heat is absorbed. If we increase the temperature of a CO_2 , H_2CO_3 equilibrium mixture at constant pressure, the equilibrium moves to the left, because that is the direction that absorbs heat and so tends to counteract the temperature increase. In Figure 4.4(d), in order to maintain a constant pressure we would need to draw the piston back as CO_2 came out of solution.

FIGURE 4.4

How the CO_2 , H_2CO_3 equilibrium changes as conditions are changed



A word of caution is needed about the effect of increasing the total pressure. If we had increased the total pressure by pumping some nitrogen or argon into the vessel (instead of decreasing the volume as in Figure 4.4(c)), this would have had no affect upon the equilibrium because it would not have changed the pressure of CO₂.

Another way of increasing the solubility of carbon dioxide in water is to make the solution alkaline. If there is OH⁻ in the solution, then carbonic acid reacts with it:



This effectively removes the product from Reaction 4.6. The equilibrium then moves to try to counteract this, so more CO₂ dissolves to form more H₂CO₃ which in turn reacts with OH⁻ and so on (Fig. 4.4(e)). This illustrates an effective method of forcing an equilibrium reaction to completion—remove the product as it forms.

The CO₂, H₂CO₃ equilibrium and aerated drinks

Aerated ('fizzy') drinks contain carbon dioxide. To make such drinks the solution is exposed to a high pressure of carbon dioxide. This causes a significant concentration of CO₂ to dissolve; the bottle or can is then sealed. The gas space above the solution (drink) still contains a high pressure of carbon dioxide. When the bottle or can is opened, the high pressure of CO₂ escapes. The reactant concentration (pressure) of Equation 4.6 has been greatly lowered and so the equilibrium moves to the left: CO₂ comes out of solution, forming the bubbles we see in the drink. If we leave the drink in a glass exposed to the atmosphere, then the pressure of CO₂ above the solution soon falls to normal carbon dioxide-in-air pressure (35 Pa) and the CO₂ concentration in the solution falls to about 1.2 × 10⁻⁵ mol/L. The drink has 'gone flat'.

If we open a warm container of fizzy drink, it produces bubbles more rapidly. This is partly because the equilibrium concentration of dissolved CO₂ at the higher temperature is lower and so more carbon dioxide has to escape, and partly because chemical reactions usually go faster at higher temperatures (p. 291 *CCPC*).

Shaking the bottle of drink when the cap is removed speeds up the release of carbon dioxide and so the drink froths up and shoots everywhere; equilibrium is reached more rapidly.

It is dangerous to put bottles of aerated drinks in a freezer, because as the temperature falls, pure ice freezes out of the drink. This means that all the CO₂ originally dissolved in the drink is forced as gas into the small gas space. This builds up an excessive pressure and the bottle may explode. In other words carbon dioxide has a very low solubility in solid ice.

Removing the cap from a bottle of lemonade causes CO₂ bubbles to be released





Exercises

12 The table below gives the solubility of carbon dioxide as a function of the pressure of carbon dioxide above the solution at 25°C.

- a Show graphically that solubility is proportional to the partial pressure of the gas above the solution. Hence calculate the constant k in the equation:

$$\text{Solubility} = k \times (\text{pressure of CO}_2)$$

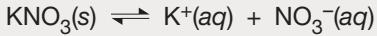
Pressure of CO ₂ (kPa)	10	30	50	80	130
Solubility (mol/L)	0.0031	0.0097	0.165	0.0260	0.042

- b From your graph calculate (i) the solubility when the pressure of CO₂ is 65 kPa, and (ii) the pressure of CO₂ needed to produce a solubility of 0.030 mol/L.
c Use either your graph or the equation in (a) to calculate (i) the solubility at a CO₂ pressure of 250 kPa, and (ii) the pressure of CO₂ needed to produce a solubility of 0.055 mol/L.

13 A bottle of soft drink is opened and half of the contents consumed, then the cap is screwed back on the bottle. Some time later the bottle is opened and the rest of the drink consumed. This portion of the drink tastes significantly ‘flatter’ than the original; that is, there is less ‘fizz’ in the drink. Explain why this is so.

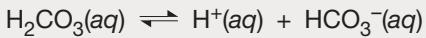
14 a The process liquid \rightleftharpoons vapour is reversible and is endothermic. Use Le Chatelier’s principle to decide whether vapour pressure increases or decreases as temperature increases. Explain your reasoning.

- *b Dissolution of potassium nitrate in water is a reversible process:



The solubility of KNO₃ increases as temperature increases. Use Le Chatelier’s principle to decide whether the process is exothermic or endothermic. Explain your reasoning.

15 a In home swimming pools one equilibrium reaction that occurs is:



Use Le Chatelier’s principle to determine the effect on hydrogen ion concentration of adding sodium hydrogen carbonate to the pool water.

b When home swimming pools are sterilised by adding so-called ‘solid’ chlorine (calcium hypochlorite, Ca(OCl)₂) or ‘liquid’ chlorine (solution of sodium hypochlorite, NaOCl), another equilibrium involved is:



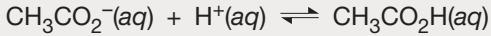
The species which is best at destroying bacteria and at resisting decomposition by sunlight is HOCl, not OCl⁻. How can you ‘force’ this equilibrium to the right?

16 The salt silver acetate, CH₃CO₂Ag, is sparingly soluble in water (almost insoluble).

- a Write the equation for the equilibrium involved.

b If sodium acetate solution was added to a silver nitrate solution to precipitate silver acetate, how would you maximise the amount of silver ion precipitated as acetate (i.e. how would you drive this equilibrium to the right)?

- c The acetate ion is also involved in the equilibrium:



This equilibrium lies well to the right. When hydrochloric acid is added to the mixture of precipitate and solution in (b), the precipitate redissolves. Use Le Chatelier’s principle along with the two equilibria involved to explain why this happens.

4.9 ACIDIC OXIDES IN THE ATMOSPHERE

Three acidic oxides are minor constituents of the atmosphere:

- carbon dioxide, CO_2 , 360 ppm
- sulfur dioxide, SO_2 , 0.001 ppm
- nitrogen dioxide, NO_2 , 0.001 ppm

ppm means parts per million. The values given are for unpolluted dry air.

Figure 4.5 shows models of these three oxides along with the two neutral oxides of nitrogen.

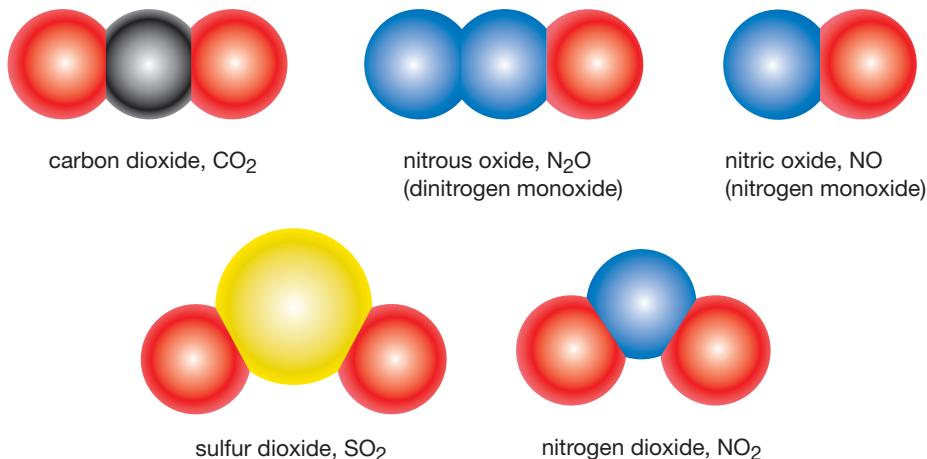


FIGURE 4.5
Models of some oxides of carbon, nitrogen and sulfur. Black is C, blue N, yellow S and red O. For N_2O and NO the systematic names are given in brackets, though these names are not widely used; for the other three oxides the common names are the systematic names (p. 81 CCPC)

In gaseous contexts **parts per million** has a different meaning from that in solution contexts (p. 213 CCPC). In gases parts per million means number of *molecules* of the particular species per million molecules of the mixture. As we will see in Section 4.12, this also means parts per million by *volume*. 360 ppm carbon dioxide means 360 CO_2 molecules per million molecules of air or 360 mL CO_2 in one million mL of air.

Carbon dioxide

Carbon dioxide in the atmosphere is part of the natural carbon cycle in which carbon moves through plants, animals, oceans and rivers, carbonate rocks and the atmosphere. However in the past 150 years human activity in the form of combustion of fossil fuels has led to a 30% increase in the concentration of carbon dioxide in the atmosphere—from about 280 ppm at the start of the industrial revolution to 360 ppm today.

This increase is of considerable concern because it is the major factor in the enhanced greenhouse effect (p. 288 CCPC).

Sulfur dioxide

About two-thirds of the sulfur dioxide released to the atmosphere worldwide comes from natural sources such as *geothermal hot springs* and *volcanoes*. Because volcanic activity varies greatly from year to year, atmospheric concentrations of sulfur dioxide also vary quite widely.

The main human activities that release sulfur dioxide to the atmosphere are:

- processing or burning fossil fuels
- extracting metals from sulfide ores.

Coal generally contains from 0.5 to 6% sulfur, mainly as metallic sulfides and sulfur in carbon-containing compounds. It is not practical to extract sulfur from coal before burning it, so in the combustion process most of the sulfur is converted to sulfur dioxide:



Although some coal-burning power stations remove most of the sulfur dioxide from their effluent gases (particularly in heavily industrialised parts of Europe and North America), the alternative of using low-sulfur coal (without any clean-up) is still widely favoured. Australian coals are generally low in sulfur (0.5 to 2%) which is why they are in strong demand.

Crude oil and sometimes natural gas contain a variety of sulfur compounds. Most of these are extracted at oil refineries or gas processing plants as elemental sulfur which is sold to sulfuric acid manufacturers. However there is some release of sulfur dioxide by refineries. In addition sometimes a small amount of sulfur remains (as compounds) in refined petrol and is also released to the atmosphere, generally as SO_2 but under some conditions as hydrogen sulfide.

Many metals occur as sulfides (e.g. copper, lead, zinc, silver, nickel) and the first step in extracting the metal is to roast the sulfide ore in air. This produces sulfur dioxide along with the metal or metal oxide. The extraction of copper was discussed on pp. 111–12 CCPC. For zinc the reaction is:



Depending on the location of the processing plant, the sulfur dioxide may be collected or just released to the atmosphere for dispersal over large tracts of sparsely populated land.

Oxides of nitrogen

There are three common oxides of nitrogen, nitrous oxide, N_2O , nitric oxide, NO , and nitrogen dioxide, NO_2 . NO_2 is acidic: the other two are neutral.

Nitric oxide and nitrogen dioxide

The major natural source of *nitric oxide* is *lightning*. At the very high localised temperatures generated by lightning, atmospheric oxygen and nitrogen gases combine to form nitric oxide:



Nitric oxide slowly reacts with oxygen to form *nitrogen dioxide*:



This is the major natural source of nitrogen dioxide.

The human activity that generates large amounts of nitric oxide and nitrogen dioxide is *combustion*, both in stationary sources (power stations) and moving ones (cars and trucks). At the high temperatures in the combustion chambers, oxygen and nitrogen from air combine to form nitric oxide (as they do in lightning, Equation 4.7). And again nitric oxide is slowly converted to nitrogen dioxide (Equation 4.8). Exhausts from power stations and vehicles generally have NO and NO_2 in the ratio of about 4:1, though additional reactions in the atmosphere gradually convert most of the NO to NO_2 .

The mixture, NO plus NO_2 , is often referred to as NO_x or NOx .

Combustion processes that use a high ratio of air to fuel (power stations and diesel engines) produce proportionately more NO_x than do petrol engines (which have a relatively low air to fuel ratio).

Nitrous oxide

Nitrous oxide is formed naturally by the action of certain *bacteria on nitrogenous material in soils*. Human activity has increased the release of nitrous oxide to the atmosphere through the increased use of nitrogenous fertiliser which provides more raw material for the bacteria. This is of considerable concern because nitrous oxide contributes to the enhanced greenhouse effect (p. 288 CCPC).

Health effects

Sulfur dioxide irritates the respiratory system and causes breathing difficulties at concentrations as low as 1 ppm. People suffering from asthma and emphysema are particularly susceptible. The effects of sulfur dioxide are magnified if particulates are present also.

Nitrogen dioxide irritates the respiratory tract and causes breathing discomfort at concentrations above about 3 to 5 ppm and at higher concentrations does extensive tissue damage. Concentrations above 3 ppm have rarely been reached even in heavily polluted cities. The main problem with NO_2 is that it leads to the formation of ozone in what is called **photochemical smog**. This is a form of air pollution in which sunlight acts upon nitrogen dioxide in the presence of hydrocarbons and oxygen to form ozone, other pollutants called peroxyacetyl nitrates (PANS) and haze, which is poor visibility due to small particles in the air. It will be discussed in Section 7.5. Ozone has harmful effects at concentrations as low as 0.1 ppm.

Environmental effects

The major environmental effects of emissions of oxides of sulfur and nitrogen to the atmosphere are those coming from the acid rain that these oxides eventually lead to (discussed in the next section).

Releases of sulfur dioxide to the atmosphere in industrialised cities up until the middle of the twentieth century and in mining and smelting areas until much more recently produced air that often had an unpleasant odour and which was detrimental to health, particularly for aged people and those with respiratory weaknesses.

Releases of oxides of nitrogen leads to formation of photochemical smog (above) which is both visually unattractive and a health hazard.

These matters will be considered further in the next section.

Information about the gaseous oxides discussed in this section is summarised in Table 4.4.

4.10 THE 'FATE' OF OXIDES OF SULFUR AND NITROGEN IN THE ATMOSPHERE

Sulfur dioxide and NO_x are pollutants that form in localised industrial areas such as big cities (with industry, power generation and many vehicles) and mining towns (SO_2 from roasting ores). They do not spread out globally because natural processes remove them from the air.

TABLE 4.4 Some gaseous oxides of atmospheric importance

	Carbon dioxide CO₂	Sulfur dioxide SO₂	Nitrous oxide N₂O	Nitric oxide NO	Nitrogen dioxide NO₂
colour	colourless	colourless	colourless	colourless	reddish-brown
odour	odourless	pungent odour	slightly sweet	cannot be smelt ^b	choking odour
solubility in water	soluble	soluble	insoluble	insoluble	soluble
adverse health effects	none ^c	respiratory problems	none ^d	converts to NO ₂	respiratory problems ^e
concentration in clean air ^a	360	0.001 ^f	0.31	<0.001	0.001
natural sources	carbon cycle	volcanoes, geothermal springs	bacteria in soils	lightning	from NO + O ₂
human activities that produce it	burning fossil fuels	extracting metals, burning fuels	use of nitrogen fertilisers	combustion	from NO from combustion
concentrations ^a in urban areas	same as global	0.01 ^g	same as global	0.01	0.01
changes to global concentrations	increasing (30% in last 150 years)	not changing	increasing (15% in last 150 years)	not changing	not changing
maximum allowed concentrations ^{a, h}	no limit set	0.02 (1 year) 0.08 (1 day)	no limit set		0.03 (1 year) 0.12 (1 hour)

a ppm

b because it is quickly converted to NO₂

c though it can cause suffocation at high concentrations

d used as an anaesthetic, so prolonged exposure is dangerous

e above 3 to 5 ppm, which is rarely reached in the atmosphere; tissue damage at even higher concentrations

f can fluctuate significantly with volcanic activity

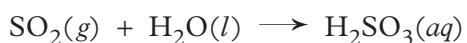
g but can be up to 1.0 ppm in some mining locations

h set by the National Environmental Protection Council in 1998

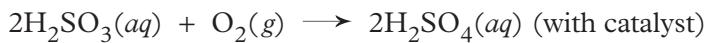
j means that the average over a year must not exceed 0.02 ppm, though a one-day average of up to 0.08 is acceptable

When these oxides disperse through larger volumes of air, they dissolve in water droplets (rain) and so are washed out of the atmosphere by rain.

Sulfur dioxide reacts to form sulfurous acid:



In water droplets various other impurities in air catalyse the conversion of sulfurous acid to sulfuric acid:

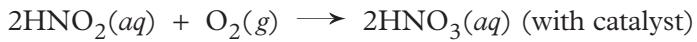


Sulfuric acid is also soluble in water and so it is removed from the atmosphere by rain.

Similarly, nitrogen dioxide reacts with water to form a mixture of nitrous and nitric acids:



Nitrous acid in solution is catalytically oxidised to nitric acid:



Again nitric acid is soluble in water and so is washed out of the atmosphere by rain.

SO₂ and NO_x concentrations in industrialised areas

After the Industrial Revolution of the early 1800s there was a great increase in emissions of sulfur dioxide (and particulates) to the air in the growing industrial cities (mainly from burning coal and extracting metals). Air quality deteriorated significantly until about the 1950s and '60s when a series of nasty pollution episodes in London and the north-east of the USA caused many deaths. This led to the introduction of regulations to control emissions from factories and these caused a dramatic improvement in air quality, particularly with respect to SO₂ and particulates. Today although the annual average concentration of sulfur dioxide in cities and mining areas is significantly greater than in 'pure' air, it is generally below the upper limits for safety recommended by health authorities.

Serious pollution from NO_x did not develop until the twentieth century as electricity generation and use of motor cars expanded dramatically (since it is high temperature combustion that produces NO). Photochemical smog (ozone in the air formed from NO_x and sunlight) first became a problem in the 1960s (first in Los Angeles, then in many other sunny cities). This led to the introduction of emission controls on motor cars (and some restrictions on power station emissions also). Consequently there was considerable improvement in air quality for about two decades.

However increasing city populations and increasing vehicle-kilometres being driven have to a large extent cancelled out further benefits of increasingly stringent emission controls. In most major cities air quality has probably not deteriorated in the past decade but it has not been improving either.

The annual average concentration of SO₂ and NO₂ in most large cities around the world is about 0.01 ppm for each gas. This is about ten times the value for clean air, though a concentration of 0.01 ppm of either gas is not harmful. Of more concern for the health of people is the number of days per year on which the concentration of one of these pollutants exceeds what health authorities generally regard as safe. In Sydney and Melbourne while the annual concentrations of these gases are suitably low, there is some concern about the number of days per year that safe levels are exceeded.

Ambient air quality standards are generally written in terms of both an annual average that should not be exceeded and a short-term average (over an hour or a few hours or a day) which also should not be exceeded more than a certain number of times per year. The last row in Table 4.4 shows the Australian standards: the short-term averages should not be exceeded more than once per year.

While the air quality in Australia's major cities generally meets the SO₂ and NO₂ standards, there are some mineral-processing areas which frequently exceed the sulfur dioxide limits, notably Port Pirie in SA, Mt Isa in Qld and Kalgoorlie in WA; these places process sulfide ores. Improved operating procedures, including trapping sulfur dioxide from flue gases, have resulted in steady improvement in air quality in these locations in recent years. High sulfur dioxide concentrations used to be regularly observed in the Port Kembla area (a copper smelter is there), but after the smelter was rebuilt in 2000 with the sulfur dioxide being trapped and used to make sulfuric acid, SO₂ levels have only rarely exceeded the safety standards.

SO₂ and NO_x concentrations in the atmosphere globally

Because SO₂ and NO₂ are washed out of the atmosphere by rain, there appears not to have been any significant build-up of their concentrations over the last century or so. This contrasts with the significant increases that have occurred for carbon dioxide and nitrous oxide. Carbon dioxide concentration has increased by about 30% over the last 150 years to about 360 ppm at the present, while nitrous oxide concentration has increased by about 15% over the same time period (to about 0.31 ppm). However it is difficult to be sure about SO₂ and NO₂, because there is a lack of reliable data for periods before about 1950. It has only been in the last few decades that we have been able to measure concentrations of these gases below 0.1 ppm with sufficient accuracy to follow changes in them.

4.11 ACID RAIN

High emissions of sulfur and nitrogen dioxides to the atmosphere lead to rain being somewhat acidic, because as we have just seen these pollutants are converted to sulfuric and nitric acids which dissolve in the rain.

Acid rain is rain that has a higher hydrogen ion concentration than normal—higher than about 10^{-5} mol/L.

The acids generally present in acid rain are sulfuric and nitric acids.

Rain that is unaffected by any pollutants is slightly acidic because of dissolved carbon dioxide which forms carbonic acid (Equation 4.6). This leads to the rain having a hydrogen ion concentration of between 10^{-5} and 10^{-6} mol/L. (We will see in Section 4.18 that in neutral solution the hydrogen ion concentration is 10^{-7} mol/L.) However when rain is affected by industrial emissions of sulfur and nitrogen dioxides, it can have a hydrogen ion concentration between 10^{-3} and 10^{-5} mol/L.

Effects of acid rain

Effects of acid rain include:

- *increasing acidity of lakes* which has a detrimental effect upon fish populations; such effects have been observed in many lakes of Scandinavia (partly from British and Central European emissions) and North America
- *damage to pine forests* in parts of Europe and North America (as shown in the photo on p. 105)
- *erosion of the marble and limestone of building surfaces and decorations*, because such materials contain carbonates, particularly calcium carbonate, and these readily react with acids; in parts of Europe acid rain over the past fifty years has done more damage to priceless statuary than the weathering of the previous 500 years.
- *severe damage to vegetation* around mine and smelter sites, particularly when they are located in high-rainfall areas such as Queenstown in Tasmania; this problem is less severe today than it was 50 to 150 years ago, when there were no controls on what could be released from mining and smelting operations.

While the last effect occurs quite close to the source of the pollution, the first three are often experienced in very diverse locations quite remote from the primary sources of the pollution.

The only way to prevent acid rain is to stop emitting SO_2 and NO_2 to the atmosphere. In most countries there are now legal limits on the amounts of these two pollutants that factories and power stations can emit.



This statue at St Alfege's Church, Greenwich, London has suffered more damage from acid rain in the past fifty years than from all atmospheric sources in the previous 500 years

Exercises

- 17 What are the systematic names for nitrous oxide, nitric oxide and nitrogen dioxide?
- 18 Some coals contain iron(II) sulfide. During combustion this is converted to iron(II) oxide and sulfur dioxide. Write an equation for the reaction.
- 19 A small proportion of the sulfur dioxide in polluted air is photolytically oxidised to sulfur trioxide in the gas phase with the sulfur trioxide so formed dissolving in water droplets. Write equations for these reactions.
- 20 In industrial areas a significant amount of ammonia is released to the atmosphere. This generally precipitates out as ammonium sulfate. Explain, with equations, how this substance forms. Could any ammonium carbonate be formed? If so, explain how.
- 21 One method of removing sulfur dioxide from the effluent gases from power stations is to pass the gas over calcium oxide. What would you expect to be the product of this reaction? Write an equation.
- 22 Write equations for the reactions of the main two components of acid rain with calcium carbonate, a major constituent of marble, and explain why this caused deterioration of marble statues.
- 23 1.00 L of air at 25°C and standard atmospheric pressure contains 0.041 moles of gas. If the concentrations of carbon dioxide and sulfur dioxide in this air are 360 ppm and 0.02 ppm respectively, what would be their concentrations in moles per litre?





WEBSITES

For air quality standards:

<http://www.ephc.gov.au>

(click on *NEPMs* then *Ambient Air Quality*; there is also other useful information about air quality on this site)

For SO₂ and NO_x in the atmosphere:

<http://www.deh.gov.au/soe/2001/atmosphere.html>

(click on *Key issues*, then on *Urban air quality* or *Regional air quality*; alternatively, scroll down the page to the relevant bits)

For acid rain:

<http://www.ausetute.com.au/acidrain.html> and <http://www.epa.gov/airmarkets/acidrain>

(both are good simple introductions to the topic)

4.12 CALCULATIONS INVOLVING VOLUMES OF GASES

We often want to calculate quantities of gases involved in chemical reactions. On pp. 142–5 *CCPC* we saw how to calculate masses in reactions. However with gases it is generally more convenient to work in terms of volumes. Let us see how this can be done.

On p. 150 *CCPC* Avogadro's hypothesis was stated as:

When measured at the same temperature and pressure, equal volumes of gases contain the same number of molecules.

This can be rearranged into:

Equal numbers of molecules of different gases occupy the same volume
(at the same temperature and pressure). ... (4.9)

Since a mole is a fixed number of molecules (6.02×10^{23}), a mole of any gas has the same volume as a mole of any other gas (at the same temperature and pressure). This volume is called the **molar volume** of a gas—the volume of one mole.

Because the volume of a gas changes quite significantly as its temperature and the pressure acting upon it change, we must always state the temperature and pressure when we give the volume of a gas. The two temperatures commonly used for the molar volume of a gas are 0°C and 25°C.

The common pressure used for both temperatures has been the *atmosphere*[†]. However the atmosphere is not part of the International System of Units (SI Units) and so its use is being phased out. The SI Unit for pressure is the pascal (Pa) which is a force of 1 newton per square metre, N m⁻². Standard atmospheric pressure (or 1 atmosphere) is 101.3 kPa (kilopascals). In nearly all chemistry books the molar volume of a gas is given for this pressure (101.3 kPa). However the NSW HSC examiners require that molar volume be given for a pressure of 100 kPa (more correctly 100.0 kPa, because it is not possible to tell whether 100 has one or three significant figures). Hence:

[†] As a unit of pressure the *atmosphere* is defined as being equal to standard atmospheric pressure, which is sea-level pressure averaged over time and space around the globe: it is 101.3 kPa. That is 1.000 atmosphere = 101.3 kPa. However, despite its convenience, we shall not be using the *atmosphere* as a unit of pressure in this book.

At 0°C and 100.0 kPa, the molar volume of all gases is 22.71 L. ... (4.10)

At 25°C and 100.0 kPa, the molar volume of all gases is 24.79 L. ... (4.11)

Figure 4.6 illustrates the size of a mole of gas. Examples will illustrate how to interconvert volumes and masses using the molar volume of a gas. In many ways the calculations are similar to the mass–mass calculations on pp. 143–5 CCP.

FIGURE 4.6
A mole of any gas at 25°C and 100 kPa has the volume of about twelve house bricks or of about twelve 2-litre milk bottles



Example 2

What mass of gas is present in a 515 mL flask containing carbon dioxide at 25°C and at a pressure of 100.0 kPa?

Using the molar volume of a gas at 25°C and 100.0 kPa:



$$\text{Number of moles of CO}_2 \text{ present} = \frac{0.515 \text{ L}}{24.79 \text{ L/mol}}$$
$$= 0.0208 \text{ mol}$$

$$\text{Molar mass of CO}_2 = 12.0 + 2 \times 16.0$$
$$= 44.0 \text{ g/mol}$$

$$\text{Mass of CO}_2 = 0.0208 \times 44.0$$
$$= \mathbf{0.914 \text{ g}}$$

Example 3

What volume is needed to store 3.11 g ethane at 100 kPa and 0°C?

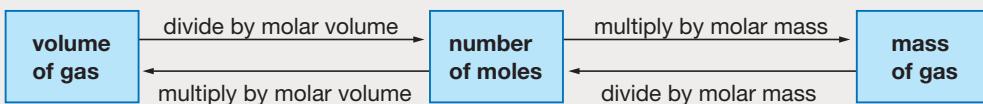


$$\text{Molar mass of ethane, C}_2\text{H}_6 = 2 \times 12.0 + 6 \times 1.01$$
$$= 30.1 \text{ g/mol}$$

$$\text{Number of moles of ethane} = \frac{3.11 \text{ g}}{30.1 \text{ g/mol}}$$
$$= 0.103 \text{ mol}$$

$$\text{Volume this will occupy} = 0.103 \times 22.71$$
$$= \mathbf{2.35 \text{ L}}$$

The method for doing these calculations can be shown schematically:



When a chemical reaction is involved, there is an additional step—using the chemical equation to convert from moles of given substance to moles of required substance. In many ways the calculations are similar to the mass–mass calculations on pp. 144–5 of *CCPC* as the following examples will illustrate.



Example 4

Calculate the volume of hydrogen produced at 0°C and 100.0 kPa when 2.5 g sodium reacts with excess water. The balanced equation is:



$$\text{Molar mass of Na} = 23 \text{ g/mol}$$

$$\therefore \text{number of moles of Na used} = \frac{2.5}{23} \\ = 0.109 \text{ mol}$$

From the chemical equation:

$$\frac{\text{number of moles of H}_2 \text{ produced}}{\text{number of moles of sodium used}} = \frac{1}{2}$$

$$\text{So number of moles of H}_2 \text{ produced} = \frac{1}{2} \times 0.109 \\ = 0.054 \text{ mol}$$

Molar volume of a gas

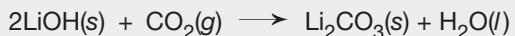
$$\text{at } 0^\circ\text{C and } 100.0 \text{ kPa} = 22.71 \text{ L}$$

$$\text{Hence volume of H}_2 \text{ produced} = 0.054 \times 22.7 \\ = \mathbf{1.2 \text{ L}}$$



Example 5

Lithium hydroxide has been commonly used in space craft to absorb carbon dioxide from the air. The reaction is:



Calculate the mass of lithium hydroxide needed to absorb 250.0 L carbon dioxide at 25°C and 100.0 kPa pressure.

The molar volume of a gas at 25°C and 100.0 kPa is 24.8 L.

$$\therefore \text{number of moles of CO}_2 \text{ to absorb} = \frac{250}{24.79} \\ = 10.1 \text{ mol}$$

From the chemical equation:

$$\frac{\text{number of moles of LiOH needed}}{\text{number of moles of CO}_2 \text{ to absorb}} = \frac{2}{1}$$

$$\text{So number of moles of LiOH needed} = 2 \times 10.1 \\ = 20.2 \text{ mol}$$

$$\text{Molar mass of LiOH} = 6.9 + 16.0 + 1.0 \\ = 23.9 \text{ g/mol}$$

$$\therefore \text{mass of LiOH needed} = 23.9 \times 20.2 \\ = \mathbf{483 \text{ g}}$$

Again the method for doing these calculations can be shown schematically as in Figure 4.7.

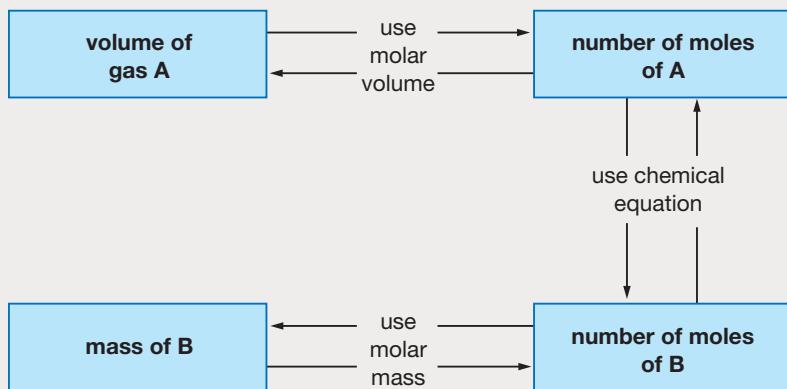


FIGURE 4.7
The method for doing mass–volume calculations involving chemical reactions

Exercises

- 24 a** A 2.042 L flask contains chlorine gas at 0°C and 100.0 kPa. What mass of gas is in the flask?
- b** What volume would 1.32 g carbon dioxide occupy at 25°C and 100.0 kPa pressure?
- 25** When 1.0 g magnesium is dissolved in excess hydrochloric acid, what volume of hydrogen (measured at 0°C and 100.0 kPa pressure) is formed?
- 26** What volume of carbon dioxide, measured at 25°C and 100.0 kPa, is formed when 0.33 g calcium carbonate is decomposed to form calcium oxide and carbon dioxide?
- 27** Sodium hydroxide reacts with carbon dioxide to form sodium carbonate and water. What volume of carbon dioxide (measured at 0°C and 100.0 kPa) will 100 mL of 1.35 mol/L solution of sodium hydroxide absorb?
- 28** As mentioned in Exercise 21, sulfur dioxide can be removed from the exhaust gas of power stations by reacting it with calcium oxide. What mass of calcium oxide is needed to absorb 1.00×10^3 L sulfur dioxide (at 25°C and 100.0 kPa)?



4.13 SOME COMMON ACIDS AND BASES

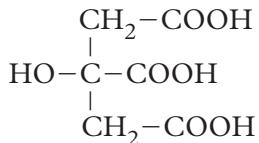
Some of the common acids that are involved in our everyday lives, either directly or indirectly, are the naturally occurring ones, hydrochloric, acetic and citric acids and the synthetic ones, sulfuric and nitric acids.

Naturally occurring acids

- **Hydrochloric acid, HCl.** This is produced by glands in the lining of our stomachs to form an acidic environment for the efficient operation of the enzymes that break some complex food molecules into easily transportable small molecules that are absorbed into the blood stream when they pass into the intestine.
Hydrochloric acid is also made commercially in very large quantities; it has many industrial uses such as cleaning metals before galvanising or soldering, cleaning brickwork, neutralising bases in manufacturing processes and adjusting acidity in swimming pools.
- **Acetic acid, $\text{CH}_3\text{—COOH}$** (systematic name ethanoic acid). The carboxylic acid functional group —COOH was introduced in Section 1.12 and will be discussed more fully in Section 5.19. Acetic acid is present in vinegar which is commonly made from wine by oxidation of the ethanol.

Acetic acid is also made industrially and used to make a wide range of organic chemicals.

- **Citric acid** (systematic name 2-hydroxypropane-1,2,3-tricarboxylic acid). This occurs in citrus fruit. It is also made industrially and widely used as a food additive (for flavour and as a preservative). The molecular formula of citric acid is $C_6H_8O_7$. Its structure is:



- **Vitamin C** (ascorbic acid). This acid occurs widely in fruit and vegetables and is essential to our health and wellbeing. Its molecular formula is $C_6H_8O_6$.

Synthetic acids

- **Sulfuric acid, H_2SO_4** . More sulfuric acid is manufactured worldwide than any other chemical. It is used to make fertilisers, synthetic fibres, industrial ethanol, detergents and car batteries. Its synthesis and uses are discussed in Chapter 9.
- **Nitric acid, HNO_3** . This acid is synthesised in huge quantities for the manufacture of fertilisers and explosives and numerous other chemicals.

Naturally occurring bases

- **Ammonia, NH_3** . This is present in the stale urine of humans and other animals. It has a sharp penetrating odour. Ammonia is also formed by *anaerobic decay* (decay without oxygen) of organic matter.
Ammonia is manufactured in huge quantities for the production of fertilisers, nitric acid and many other chemicals. It is often used in the home as a cleaning agent as it is good at removing waxes, particularly from floors.
- **Amines**. These are compounds with some other group such as an alkyl replacing one or more of the H atoms of ammonia (see Section 1.12). They have a strong fishy smell and are weak bases; they also are formed during the anaerobic decomposition of organic matter.
- **Metallic oxides** such as iron(III) oxide, copper oxide and titanium oxide. Metals are often extracted from such insoluble bases.
- **Carbonates** such as soluble sodium carbonate (in the mineral trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), and insoluble calcium carbonate (limestone) and magnesium carbonate. The insoluble carbonates do not conform to our interim definition of bases in Section 4.1, but are bases in terms of the broader definition to be introduced in Section 5.2.

Sodium carbonate is synthesised industrially in large quantities (Sections 10.17 to 10.19) for use in making glass, paper and soaps and detergents, for treating water and as a cheap base for neutralising acids.

Synthetic bases

- **Sodium hydroxide**. This is made from common salt (Sections 10.4 to 10.7). It is widely used for making soap and detergents, rayon and other synthetic fibres and for extracting alumina from bauxite (the first step in producing aluminium). Domestically it is used in oven cleaners and for clearing blocked

drains (though its extremely corrosive nature requires that it be handled very carefully).

■ **Calcium oxide, CaO** (quick lime) and **hydroxide Ca(OH)₂** (slaked lime).

Calcium oxide is made by heating limestone (calcium carbonate), and then hydroxide is made by reacting the oxide with water. Quicklime is used to make cement while slaked lime is used in some mortars and plasters and as whitewash. Agricultural lime is finely ground calcium carbonate.

Acids as food additives

Acids are frequently added to food in order to:

- *improve the taste*, by giving the food a certain tartness (for example in drinks and sweets)
- *preserve the food* by increasing its acidity (for example in canned fruits and vegetables and in pickles and chutneys), because many bacteria cannot survive in acid conditions.

The common acids added are acetic acid (vinegar) and citric acid, with phosphoric acid occasionally being used. Propanoic acid (propionic acid) is often used as a preservative in bread.

Ascorbic acid (vitamin C) is often added to foods but this is done because it is a vitamin (essential dietary ingredient), not specifically because it is an acid. Potassium hydrogen tartrate (cream of tartar) is often added to food along with sodium hydrogen carbonate as baking powder to make cakes rise as they cook.

WEBSITE

About food additives:

<http://www.foodstandards.gov.au/whatsinfood/foodadditives.cfm>

(scroll through the page for general information about additives; click on *Food Additives List—Alphabetical* to see a listing of allowed additives and their purposes)



4.14 ACIDS—A CLOSER LOOK

In Section 4.1 we said that an acid was a substance that in solution produces hydrogen ions, H⁺. As was explained on p. 198 CCPC, it is often convenient to write the hydrogen ion as H⁺, but it is more accurately described as H₃O⁺—an H⁺ attached to a water molecule. Free H⁺ does not exist in aqueous solution. When our common acids dissolve in water, they actually react with the water to form these H₃O⁺ ions. For nitric acid the reaction is:



This equation reads: liquid nitric acid reacts with liquid water to form an aqueous solution containing hydrogen ions and nitrate ions. We call this an **ionisation reaction**: the nitric acid has ionised to form H₃O⁺ and NO₃⁻. The H₃O⁺ ion is sometimes called the *hydronium ion*. Sometimes for brevity we write the ionisation reaction simply as:



Pure HCl is a covalent gas called hydrogen chloride. When it dissolves in water, it reacts with the water:



This aqueous solution of hydrogen and chloride ions is called hydrochloric acid. Again for convenience we often write this as:



A term that is often used in acid–base contexts is pH.

4.15 MEANING OF pH

Because hydrogen ion concentration is frequently referred to, and since its values can cover such a wide range—from 10 mol/L to 10^{-13} mol/L—chemists have introduced a more convenient scale for its measurement, called the pH scale.

The **pH** of a solution is defined as the negative of the logarithm (to base 10) of the hydrogen ion concentration:[†]

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] \quad \dots (4.12)$$

where square brackets around a species mean *concentration of*.

For a solution in which $[\text{H}_3\text{O}^+] = 0.01$ mol/L (that is, 10^{-2} mol/L), the pH is 2.0. If $[\text{H}_3\text{O}^+] = 10^{-7}$ mol/L, then pH = 7.0.

Most calculators have a ‘log to base ten’ key, usually labelled just ‘LOG’ (not to be confused with the ‘LN’ key which calculates the logarithm to the base e). Therefore, calculation of pH is a simple operation.

To calculate the pH

For a solution in which $[\text{H}_3\text{O}^+] = 0.042$ mol/L:

- use your calculator to find the LOG (to base 10) of this number: **-1.377**
- change the sign: **+1.377**
- adjust to the correct number of significant figures and write: **pH = 1.38**.

The *rule for significant figures* in converting between $[\text{H}_3\text{O}^+]$ and pH is this: the number of *decimal places* in the value for pH should equal the number of *significant figures* in the value for $[\text{H}_3\text{O}^+]$. In the above example $[\text{H}_3\text{O}^+]$ had two significant figures so pH had two decimal places, 1.38.

From Equation 4.12, it follows that:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \quad \dots (4.13)$$

Hence if a solution has a pH of 2.0, then $[\text{H}_3\text{O}^+] = 10^{-2}$ mol/L = 0.01 mol/L. If the pH is 5.0, then $[\text{H}_3\text{O}^+] = 10^{-5}$ mol/L.

To calculate $[\text{H}_3\text{O}^+]$ from pH when pH is not a whole number, we again need our calculators. Most calculators have a key labelled ‘SHIFT’, ‘INV’ or ‘2nd F’ (second function) which, when used with the LOG key, calculates 10 raised to the power keyed in. Generally the LOG key carries the secondary label, 10^x .

If the pH of a solution is 4.63, then to calculate the hydrogen ion concentration, we need to calculate $10^{-4.63}$.

[†] The logarithm to base 10 of a number is the power to which the base 10 must be raised to give the number. If $\log_{10} Z = Y$, then $Z = 10^Y$.

To calculate $[H_3O^+]$ from pH

When pH = 4.63:

- change the sign of the pH: **-4.63**
- use your calculator to find the ANTILOG of this number (SHIFT, LOG or INV, LOG or 2nd F, LOG): **0.00002344** or **2.344×10^{-5}**
- adjust to the correct number of significant figures and add units:
 $[H^+] = 2.3 \times 10^{-5}$ mol/L (two decimal places in pH give two significant figures in $[H^+]$).

Similarly, if pH = 8.95, $[H_3O^+] = 1.1 \times 10^{-9}$ mol/L by the same sequence (try it!).

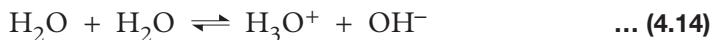
Because of the way that pH is defined,

a change in pH of one unit corresponds to a tenfold change in $[H_3O^+]$.

pH is also used for alkaline solutions. To see how this can be done we need to take a closer look at water.

4.16 SELF-IONISATION OF WATER

Although water is a covalent liquid, its electrical conductivity is significantly higher than that of other covalent liquids such as hexane or chloroform. This and other evidence shows that water undergoes a self-ionisation reaction to a small but significant extent:



This is called the **self-ionisation of water**. It is an equilibrium reaction that lies well to the left. At equilibrium in pure water only one molecule in four billion has ionised (formed a hydrogen ion). This self-ionisation of water occurs not just in pure water but in all aqueous solutions also.

In addition we find that there is always a relationship between the concentrations of hydrogen ions and hydroxide ions: the product of these concentrations is always constant at constant temperature; that is:

$$[H_3O^+][OH^-] = K_w \quad \dots (4.15)$$

where K_w is a constant at constant temperature. K_w is called the **ionic product constant for water**. At 298 K its value is 1.00×10^{-14} (mol/L)². Therefore:

$$\text{At 298 K} \quad [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ (mol/L)}^2 \quad \dots (4.16)$$

Although the more correct formula for the hydrogen ion (or hydronium ion) is H_3O^+ , it is often written as H^+ for convenience. It is acceptable to use H^+ provided you understand clearly that it is just an abbreviation for the more correct form, H_3O^+ .

Consequently you may see Equations 4.12, 4.14 and 4.16 written as:

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



$$\text{At 298 K} \quad [H^+][OH^-] = 1.00 \times 10^{-14} \text{ (mol/L)}^2$$

A consequence of Equation 4.15 (or 4.16) is that we can talk about the

hydrogen ion concentration in an alkaline solution and hence about the pH of an alkaline solution.

4.17 pH OF ALKALINE SOLUTIONS

If we know the hydroxide ion concentration in an alkaline solution at 298 K, we can use Equation 4.16 to calculate the hydrogen ion concentration and hence get pH. For example if $[\text{OH}^-]$ is 1×10^{-3} mol/L, then:

$$\begin{aligned}\text{from Equation 4.16} \quad [\text{H}_3\text{O}^+] &= \frac{1.00 \times 10^{-14}}{1 \times 10^{-3}} \\ &= 1 \times 10^{-11} \\ \text{and so} \quad \text{pH} &= -\log_{10}(1 \times 10^{-11}) \\ &= 11.0\end{aligned}$$

This means that we can use pH for alkaline solutions as well as for acidic ones. Table 4.5 shows the hydrogen and hydroxide ion concentrations corresponding to various pHs.

TABLE 4.5 Hydronium and hydroxide ion concentrations for various pHs

pH	1.0	3.0	5.0	7.0	9.0	11.0	13.0
$[\text{H}_3\text{O}^+]$	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}
$[\text{OH}^-]$	10^{-13}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}

In Section 4.1 we said that a neutral solution was one that was neither acidic nor alkaline. Let us review this in the light of the self-ionisation of water.

4.18 NEUTRAL, ACIDIC AND ALKALINE SOLUTIONS

A **neutral solution** is defined as one in which the concentrations of hydrogen ions and hydroxide ions are equal.

That is:

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

Putting this equality into Equation 4.16 gives at 25°C:

$$[\text{H}_3\text{O}^+]^2 = 1.00 \times 10^{-14} \text{ (mol/L)}^2$$

or

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-7} \text{ mol/L}$$

Hence at 25°C, a neutral solution is one in which the hydrogen ion concentration is 1.00×10^{-7} mol/L.

If $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, we say the solution is acidic. This means that at 25°C, a solution is acidic if $[\text{H}_3\text{O}^+]$ is greater than 10^{-7} mol/L.

If $[\text{H}_3\text{O}^+] < [\text{OH}^-]$, we say that the solution is alkaline (or basic). This means that at 25°C, a solution is alkaline if $[\text{H}_3\text{O}^+]$ is less than 10^{-7} mol/L. Alternatively, a solution is alkaline if $[\text{OH}^-] > 10^{-7}$ mol/L (since by Equation 4.16 the only way $[\text{H}_3\text{O}^+]$ can be less than 10^{-7} is if $[\text{OH}^-]$ is greater than 10^{-7} mol/L).

In terms of pH

- a neutral solution has pH = 7.00
- an acidic solution has pH < 7
- an alkaline solution has pH > 7

Table 4.6 shows the pH and hydrogen ion concentration of some common acidic and alkaline substances.

TABLE 4.6 pH of some common substances^a

[H ₃ O ⁺]	pH	Substance	
10	-1	concentrated hydrochloric acid,	ACID
1	0	car battery acid 1 mol/L hydrochloric acid	
10 ⁻¹	1	0.1 mol/L hydrochloric acid	
10 ⁻²	2	stomach acid	
10 ⁻³	3	vinegar lemon juice	
10 ⁻⁴	4	soft drinks soda water	
10 ⁻⁵	5	wine black coffee	
10 ⁻⁶	6	rain water milk, saliva	
10 ⁻⁷	7	very pure water	NEUTRAL
10 ⁻⁸	8	blood sea water	
10 ⁻⁹	9	bore water baking soda solution	
10 ⁻¹⁰	10	toilet soap	
10 ⁻¹¹	11	laundry detergents	ALKALINE
10 ⁻¹²	12	household ammonia dishwashing machine powders	
10 ⁻¹³	13	chlorine bleach solutions	
10 ⁻¹⁴	14	oven cleaners 1.0 mol/L sodium hydroxide	

^a The colour strip at the left shows the changes universal indicator undergoes as pH changes.



Exercises

29 Calculate the pH of solutions in which $[\text{H}_3\text{O}^+]$ is:

- | | | |
|----------------------------|-------------------------------|------------------------------|
| a 1×10^{-4} mol/L | c 0.00255 mol/L | e 5.8×10^{-5} mol/L |
| b 0.017 mol/L | d 4.33×10^{-4} mol/L | f 1.3 mol/L |

30 Calculate the hydrogen ion concentration in solutions having pHs of:

- | | | |
|---------|--------|---------|
| a 3.00 | d 1.44 | g 9.4 |
| b 3.86 | e 12.5 | h 0.35 |
| c 10.60 | f 5.82 | i -0.70 |

31 Show that a change in pH from 4.75 to 3.75 corresponds to a tenfold increase in hydrogen ion concentration.

4.19 MEASURING pH OF SOLUTIONS

pH meters are instruments that measure pH directly. The sensing device, shown in Figure 4.8, consists of a pair of electrodes (often mounted concentrically in the one unit). The measuring electrode, called a **glass electrode**, consists of a very thin and fragile membrane made out of a special kind of glass. This develops an electrical potential which depends upon pH. The other electrode is a reference electrode. When this sensing unit is immersed in the solution to be tested, it forms a galvanic cell (Section 2.5); the accompanying electronics unit simply measures the voltage (EMF) of this cell and converts it into a pH reading. A big advantage of a pH meter is that in measuring the pH of a solution, it does not alter the pH of the solution in any way; it does not disturb any chemical equilibria involved.

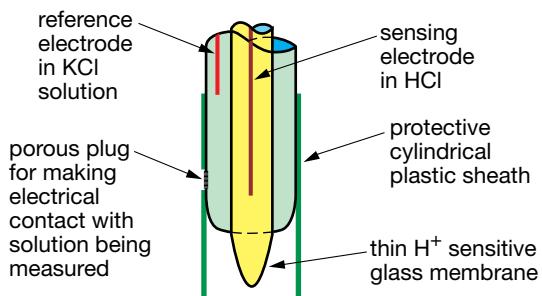


FIGURE 4.8
A pH meter in use. The diagram at the right shows the sensing (glass) electrode and the reference electrode mounted concentrically in one unit

pH meters give fairly accurate pH values, but they are relatively expensive. A cheaper way of estimating the pH of solutions is to use indicators. The use of a few indicators for determining whether solutions were acidic or basic was described in Section 4.2. Indicators change colours over fairly narrow pH ranges so they can be used to measure approximate pHs. Table 4.7 presents the ranges of pH over which several indicators change colour. Some of these changes are shown in Figure 4.9.

Using indicators to measure pH

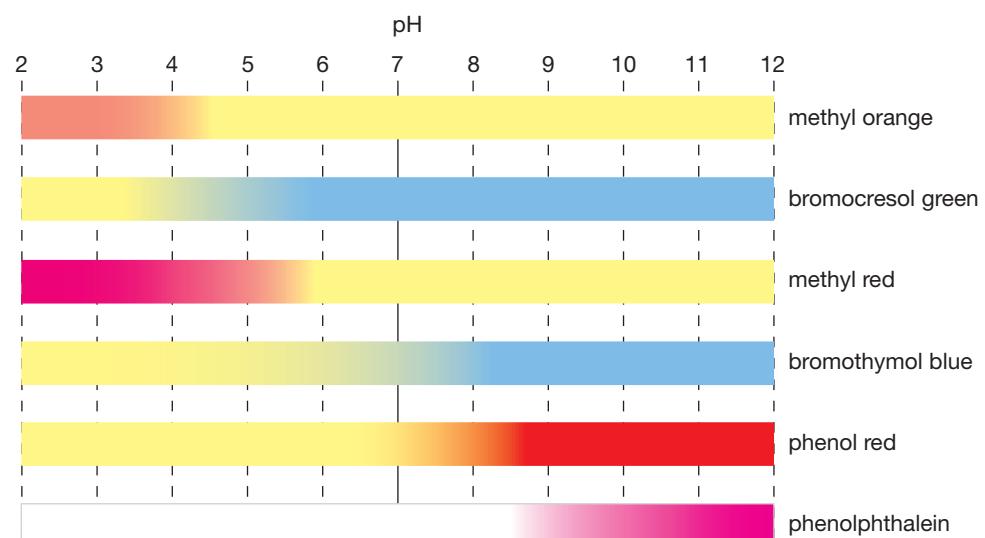
There are several ways of using indicators to estimate the pH of a solution.

TABLE 4.7 Common indicators and their pH ranges

Indicator	Colour change ^a	pH range
methyl orange	red – yellow	3.1–4.4
bromophenol blue	yellow – blue	3.0–4.6
bromocresol green	yellow – blue	3.8–5.4
methyl red	pink – yellow	4.4–6.0
litmus	red – blue	5.0–8.0
bromothymol blue	yellow – blue	6.2–7.6
phenol red	yellow – red	6.8–8.4
thymol blue	yellow – blue	8.0–9.6
phenolphthalein	colourless – red	8.3–10.0

a low pH colour – high pH colour

- 1 We can use the overall colour changes in Table 4.7 of two or more indicators to determine the approximate pH of a solution. Example 6 illustrates this.
- 2 We can use the changing colour of one indicator to estimate the pH over a narrow range. This can be done by preparing suitable standard solutions and comparing the colour of the unknown solution with these. However this is more commonly done by using indicator papers. An indicator paper is impregnated with one indicator; a piece of the paper is dipped into the solution to be tested and the pH is determined by comparing the colour of the paper with standard colours shown on the package the paper came in.
- 3 We can use what is called a **universal indicator**. This is indicator solution that passes through a variety of colours (shown in Table 4.6) as pH changes from about 1 to 11. Again by comparing the colour of the test solution with colours printed on the label of the bottle a quick estimate of pH can be obtained (to about ± 1 pH unit). Universal indicator is actually a mixture of several ordinary indicators. Universal indicator is also available as indicator paper.

**FIGURE 4.9**
Colours of common
indicators over ranges
of pH



Example 6

To estimate the pH of two solutions labelled A and B a student added drops of different indicators to separate samples of the solutions. The results were:

Solution A		Solution B	
Indicator	Colour	Indicator	Colour
methyl red	pink	thymol blue	yellow
methyl orange	yellow	bromothymol blue	blue

Using Table 4.6:

- For solution A, methyl red colour tells us that $\text{pH} \leq 4.4$ and methyl orange tells us that $\text{pH} \geq 4.4$. Therefore solution A has a pH of 4.4.
- For solution B, thymol blue tells us that $\text{pH} \leq 8.0$ and bromothymol blue tells us that $\text{pH} \geq 7.6$. Hence solution B has a pH of between 7.6 and 8.0.

4.20 WEAK AND STRONG ACIDS

Further insight into the nature of acids can be obtained by measuring the pH of solutions of equal concentration of several acids. Some such results are shown in Table 4.8.

TABLE 4.8 pH of 0.100 mol/L solutions of several acids

Acid	hydrochloric acid	acetic acid	citric acid	boric acid
pH	1.0	2.9	2.1	5.1

In the 0.10 mol/L hydrochloric acid solution, the pH value tells us that:

$$[\text{H}_3\text{O}^+] = 10^{-1.0} = 0.1 \text{ mol/L}$$

However the pH of the 0.10 mol/L acetic acid solution shows that:

$$[\text{H}_3\text{O}^+] = 10^{-2.9} = 1 \times 10^{-3} \text{ mol/L.}$$

These $[\text{H}_3\text{O}^+]$ values show that *all* the hydrochloric acid is present as ions but that in the acetic acid solution only *some* of the acetic acid molecules have ionised into hydrogen and acetate ions.

This leads us to the idea of weak and strong acids.

A **strong acid** is one in which all the acid present in solution has ionised to hydrogen ions: there are no neutral acid molecules present.

A **weak acid** is one in which only some of the acid molecules present in the solution have ionised to form hydrogen ions.

Hydrochloric acid is a strong acid. This means that when we dissolve hydrogen chloride gas in aqueous solution *all* the HCl molecules react with water to form hydrogen ions:



For a strong acid the ionisation reaction with water goes to completion.

On the other hand acetic acid is a weak acid, because when pure covalent acetic acid is dissolved in aqueous solution, only *some* of the acetic acid molecules actually react with water to form hydrogen ions; we write this as:



This reaction is an equilibrium one: it does not go to completion.

The pH measurement in Table 4.8 allows us to calculate the fraction of the acetic acid molecules that have ionised:

Total concentration of acetic acid in the solution = 0.10 mol/L

Concentration of hydrogen ions in the solution = 0.001 mol/L (from the pH value)

$$\begin{aligned}\text{So fraction of the molecules that have ionised} &= \frac{0.001}{0.10} \\ &= 0.01 \text{ (or } 1\%) \end{aligned}$$

The other 99% are still present as neutral CH_3COOH molecules.

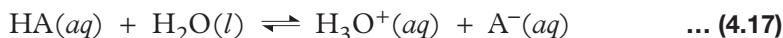
The fraction of the molecules that has ionised is called the **degree of ionisation**.

For the citric acid solution, $[\text{H}_3\text{O}^+] = 10^{-2.1} = 8 \times 10^{-3}$ mol/L so the degree of ionisation is $8 \times 10^{-3}/0.10 = 0.08$ or 8%. For boric acid the degree of ionisation is only 8×10^{-5} .

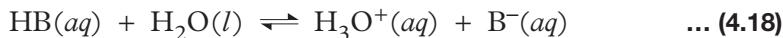
The pH measurements in Table 4.8 allow us to rank the weak acids in order of strength.

Relative strengths of weak acids

We say that acid HA is stronger than acid HB if the equilibrium



lies further to the right than does



That is, the *degree of ionisation* of HA is greater than that of HB. Figure 4.10 illustrates this.

Therefore if we use solutions of equal concentration, HA will be a stronger acid than HB if the $[\text{H}_3\text{O}^+]$ in the solution of HA is greater than in the HB solution, which means the pH of the HA solution is *less* than that of the HB solution.

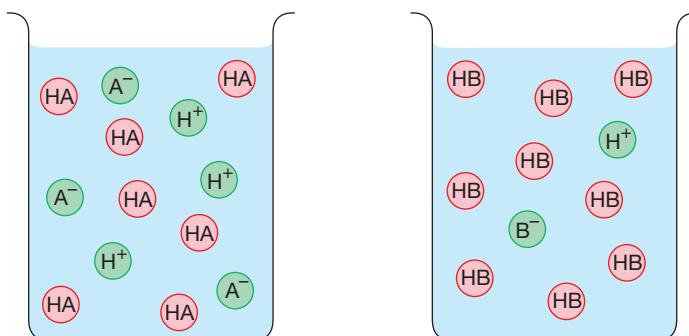


FIGURE 4.10
Illustrating the relative strengths of two weak acids: HB is a weaker acid than HA, because fewer HB molecules are ionised than HA molecules (one as opposed to three out of a total of ten molecules for each acid)

Hence from Table 4.8 we can deduce that the order of decreasing strength of the three weak acids is



because this is the order of *increasing* pH.

While we can talk about degrees of weakness of weak acids—moderately weak, extremely weak and the like—note carefully that:

there are no degrees of strongness for strong acids,

because if an acid is strong, it is completely ionised: end of story. If an acid is not completely ionised, it is not strong: it is weak.

In school laboratories the common strong acids are hydrochloric, hydrobromic, hydroiodic, nitric and the first step of sulfuric. All other common acids are weak.

Concentrated and dilute

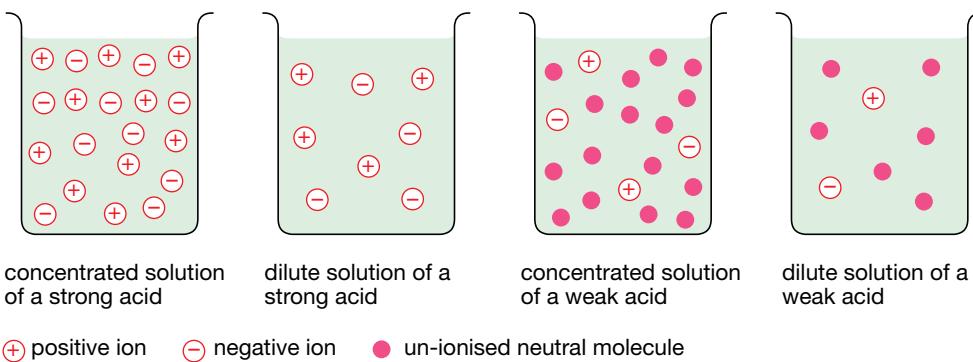
Concentrated and dilute are other terms that are used to describe acid and alkali solutions.

A **concentrated solution** is one in which the total concentration of solute species is high—say, above about 5 mol/L.

A **dilute solution** is one in which the total concentration of solute species is low—say, less than about 2 mol/L.

We can therefore have a concentrated solution of a weak acid or a dilute solution of a strong acid: the terms ‘strong’ and ‘weak’, and ‘concentrated’ and ‘dilute’, have completely independent meanings. Figure 4.11 illustrates this.

FIGURE 4.11
Concentrated and dilute
solutions of a weak and
strong acid



If we know the concentration of a strong acid solution, we can calculate its pH because the acid is completely ionised into hydrogen ions.

Exercises

- 32 When drops of indicators were added to samples of solutions A, B and C, the colours were as shown below. What is the pH of each solution? You may have to give a range within which the pH lies.

Solution	A	B	C
Indicator: colour	mr: yellow	bcg: yellow	btb: blue
	btb: yellow	bpb: green ^a	tb: yellow

^a green = yellow + blue

- 33** Estimate the pH of the solutions in Exercise 2, in terms such as less than or greater than a particular value or within a particular range.
- 34 a** Pure sulfuric acid is a covalent liquid; it dissolves in water to form a strong acid solution. Hydrogen fluoride is a covalent gas; it dissolves in water to form hydrofluoric acid, a weak acid. Write equations for the ionisation of these two substances.
- b** Perchloric acid, HClO_4 , is a strong acid, while chlorous acid, HClO_2 , is weak. For the ionisation reactions of these acids in water write equations that reflect these strengths.
- 35 a** Calculate the pH of a 0.065 mol/L solution of hydrobromic acid, a strong acid.
- b** The pH of a 0.037 mol/L solution of hydrofluoric acid is 2.32. Calculate the degree of ionisation of the acid in this solution.
- 36** 0.015 mol/L solutions of five acids, A, B, C, D and E, have pHs of 3.6, 2.5, 1.82, 5.8 and 4.3 respectively. Arrange them in order of increasing acid strength (weakest first, strongest last). Which, if any, would you class as a strong acid?
- 37 a** A 2.3×10^{-4} mol/L solution of sulfuric acid is completely dissociated. Calculate its pH.
- b** The pH of an 0.020 mol/L solution of sulfuric acid was 1.58. What can you deduce about the extent of ionisation of the HSO_4^- ion in this solution?

Important new terms

You should know the meaning of the following terms:

acid (p. 107)
acid rain (p. 126)
acidic (p. 108)
acidic oxide (p. 115)
alkali (p. 108)
alkaline (p. 108)
amphoteric oxide (p. 115)
base (p. 108)
basic (p. 108)
basic oxide (p. 115)
concentrated solution (p. 142)
degree of ionisation (p. 141)
dilute solution (p. 142)
equilibrium position (p. 117)
glass electrode (p. 138)
halide (p. 113)
hydronium ion (p. 107)
indicator (p. 109)

ionic product constant of water, K_w (p. 135)
ionisation reaction (p. 133)
Le Chatelier's principle (p. 117)
molar volume (p. 128)
neutral (p. 108)
neutral oxide (p. 115)
neutral solution (p. 136)
neutralisation (p. 112)
oxyacid (p. 113)
oxyanion (p. 113)
parts per million (ppm) in gases (p. 121)
pH (p. 134)
pH meter (p. 138)
photochemical smog (p. 123)
position of equilibrium (p. 117)
salt (p. 113)
self-ionisation of water (p. 135)
strong acid (p. 140)
universal indicator (p. 139)
weak acid (p. 140)

Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Give the names and formulae of five common acids.
- 3 List four common properties of acids.
- 4 Give names and formulae of three alkalis. Name three bases that are not alkalis.
- 5 List four common properties of alkalis.
- 6 Name four indicators that can be used to measure the acidity or alkalinity of solutions. Explain how you would use them to do this.
- 7 Write equations for three acid–base reactions.
- 8 Write the equation for the reaction between barium hydroxide and hydrochloric acid in three different ways—neutral species, complete ionic, and net ionic forms.
- 9 Write equations for two other neutralisation reactions. Give a general equation for neutralisation involving the hydroxide ion.
- 10 Name and give formulae for five salts.
- 11 Write a chemical equation that involves spectator ions.
- 12 Give the name and formula of an oxyacid of each of carbon, nitrogen, sulfur and phosphorus.
- 13 Give names and formulae for four acidic, four basic and two neutral oxides.
- 14 Name and give the formulae for two amphoteric oxides.
- 15 Write equations to demonstrate the acidic nature of the oxides you classed as acidic in Question 13.
- 16 Write an equation for a reaction between an acidic oxide and a basic oxide.
- 17 How do basic–acidic properties of oxides change in going across the Periodic Table from left to right?
- 18 How does the solubility of carbon dioxide in water depend upon the pressure of carbon dioxide above the solution and upon temperature? Write an equation for the dissolution reaction (which is exothermic) and show how Le Chatelier’s principle explains these solubility changes.
- 19 List three acidic oxides that are present in the atmosphere and explain how they get there.
- 20 Describe the detrimental effects (if any) of these oxides being in the atmosphere and explain how they are removed from the atmosphere.
- 21 What is acid rain and why is it detrimental to the environment? Name two pollutants which cause it. Give equations to illustrate.
- 22 What volume of hydrogen gas is produced at 100 kPa pressure and 25°C when 0.15 mol zinc reacts with excess hydrochloric acid?
- 23 Name three acids that are common food additives and give their formula or structure.
- 24 Many acids are covalent molecular substances which ionise when dissolved in water. Write two equations to illustrate this.
- 25 Write an equation which gives $[H_3O^+]$ in terms of pH.

- 26** What is $[\text{H}_3\text{O}^+]$ in solutions of pH 5 and 10?
- 27** What relation exists between $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in aqueous solution?
- 28** What is the numerical value of the ionic product constant of water at 298 K?
- 29** In terms of pH, what is:
- a** a neutral solution
 - b** an acidic solution
 - c** an alkaline solution?
- 30** How would you decide experimentally whether an acid was strong or weak?
- 31** Name the three most common strong acids.
- 32** Name three weak acids. Give formulae for them.
- 33** 0.1 mol/L solutions of acids HX and HY have pHs of 1.0 and 3.0 respectively. Are acids HX and HY strong or weak? Explain.
- 34** What is the difference between a *strong* acid and a *concentrated* acid?

CHAPTER 5

Acids—changing concepts, use in analysis and making esters from

IN THIS CHAPTER

Some history of the concept of acids	Preparing a standard solution
Brönsted–Lowry concept of acids and bases	Using volumetric glassware
Conjugates	Choice of indicator
Importance of each definition of acids	Buffer solutions
Mono-, di- and triprotic acids	Buffers in nature
Salts as acids and bases	Neutralisation and safety
Amphiprotic substances	Alkanols and alkanoic acids
Neutralisation	Their melting and boiling points
Volumetric analysis	Esters
Primary standards and standard solutions	Occurrence and uses of esters

The concept of an acid, like all concepts in science, has developed as our knowledge has increased. Let us briefly review this development.

5.1 SOME HISTORY

Originally, an acid was a substance that had a sour taste (vinegar, lemon juice) and which reacted with certain metals (such as zinc and iron).

Antoine Lavoisier, in about 1780, proposed that *acids were substances that contained oxygen*; in fact the name ‘oxygen’ derives from Greek words meaning ‘produces sour taste’. However this theory was soon disproved: many oxygen-containing substances were basic (such as sodium and calcium oxides) and some acidic substances (such as hydrochloric acid—called muriatic acid at that time) were distinctly acidic but contained no oxygen.

Humphry Davy in 1815 suggested that *acids were substances that contained replaceable hydrogen*—hydrogen that could be partly or totally replaced by metals. When acids reacted with metals they formed *salts* (such as ZnCl_2 , FeSO_4 , NaNO_3). *Bases* were substances that reacted with acids to form salts and water. These definitions worked quite well for most of that century.

Svante Arrhenius in 1884 proposed that *acids were substances that ionised in solution to produce hydrogen ions*: acids were strong if they ionised completely (hydrochloric, nitric), and weak if they ionised only slightly (acetic, formic). It was the Arrhenius definition of acids that was presented in Section 4.1. Arrhenius defined a base as a substance that in solution produced hydroxide



Antoine Lavoisier (1743–1794), centre, in black, was a great pioneering chemist, though he was wrong about acids

ions. This definition is somewhat narrow in that it excludes metallic oxides that are distinctly basic.

However there are some inadequacies with the Arrhenius definition of an acid. First, it does not give due recognition to the role of the solvent. Ionisation of an acid is not something the acid does in isolation: rather it is a reaction between the acid molecule and the solvent. Whether an acid is strong or weak depends not only upon the nature of the acid itself, but also upon the nature of the solvent it is dissolved in: hydrochloric acid in water is a strong acid, but when dissolved in diethyl ether it is quite weak. Second, acid–base reactions often occur in solvents in which the ‘acid’ is not ionised at all: hydrochloric acid, when dissolved in benzene, is not ionised yet it still reacts with ammonia to form ammonium chloride. Hydrochloric acid is still reacting with a base to form a salt, although the acid does not ionise in that solvent.

In 1923 two chemists, Brönsted from Denmark and Lowry from Britain, independently proposed new definitions for acids and bases in terms of proton donors and acceptors: these definitions overcome the difficulties, and are the most widely used definitions today.

Because of their relevance to chemical analysis, we shall consider the Brönsted–Lowry definitions and their consequences in detail.

5.2 THE BRÖNSTED–LOWRY CONCEPT OF ACIDS AND BASES

An **acid** is a substance that, in solution, tends to give up protons (hydrogen ions), and a **base** is a substance that tends to accept protons; or more briefly:

An acid is a proton donor.

A base is a proton acceptor.



Humphry Davy (1778–1829), among many scientific achievements, including the Davy safety lamp for miners, provided the first successful working definition of an acid

If a substance, HA, has a greater tendency to give up protons than the solvent, then that substance in that solvent will be an acid. If the solvent is water, then:



Remember from p. 198 *CCPC* and Section 4.14 of this book the hydrogen ion is more correctly written as H_3O^+ rather than just H^+ .

Similarly, if substance B has a greater tendency to accept protons than the solvent has, then B will be a base in that solvent. If the solvent is water, then:

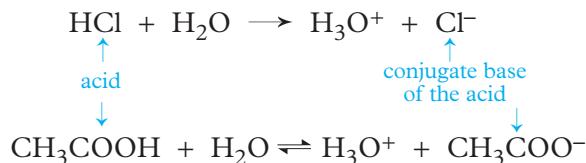


In this way, the Brönsted–Lowry concept necessarily relates acidity and basicity to the structure of both the substance *and* the solvent; production of hydrogen ions is seen to be due not solely to the properties of the acid, but rather to the properties of the acid *relative to those of the solvent*.

The Brönsted–Lowry definitions bring with them the idea of conjugates.

Conjugates

An acid gives up a proton to form what is called its **conjugate base**:



That is:

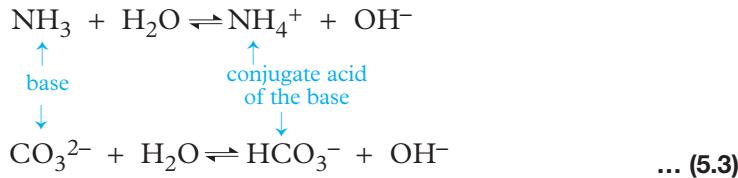


The reaction product is called a conjugate *base* because in solution it tends to gain (accept) a proton:



The acetate ion is acting here as a base. ‘Conjugate’ means ‘linked with’—linked with the acid in question, acetic acid.

Similarly, a base accepts a proton to form what is called its **conjugate acid**:



That is:



The reaction product is called a conjugate *acid* because in solution it tends to give up (donate) a proton:



The ammonium ion is acting here as an acid.

Some common acids with their conjugate bases, and some common bases with their conjugate acids, are shown in Table 5.1. By the Brönsted–Lowry

definitions, anions and cations as well as neutral molecules can be acids and bases.

TABLE 5.1 Some common acids and bases and their conjugates

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl ⁻	OH ⁻	H ₂ O
HNO ₃	NO ₃ ⁻	NH ₃	NH ₄ ⁺
H ₂ SO ₄	HSO ₄ ⁻	C ₅ H ₅ N ^a	C ₅ H ₅ NH ⁺
HSO ₄ ⁻	SO ₄ ²⁻	CN ⁻	HCN
NH ₄ ⁺	NH ₃	CO ₃ ²⁻	HCO ₃ ⁻
CH ₃ COOH	CH ₃ COO ⁻	HCO ₃ ⁻	H ₂ CO ₃
H ₂ O	OH ⁻	S ²⁻	HS ⁻
H ₃ O ⁺	H ₂ O	H ₂ O	H ₃ O ⁺

^a pyridine, a weak base

Relative strengths of acid–base conjugates

The conjugate base of a strong acid is an extremely weak base; this means that the base reacts with water to only a minute (usually negligible) extent. The strong acids, HCl and HNO₃, react completely with water (to form Cl⁻ and NO₃⁻); consequently the conjugate bases, Cl⁻ and NO₃⁻, do not react significantly with water. This is important for explaining pH of salt solutions (Section 5.5).

The conjugate base of a weak acid is a weak base, so both acid and base react with water to a significant extent (as Equation 5.2 shows).

The conjugate acid of a strong base is an extremely weak acid; this means that the acid reacts with water to only a minute (usually negligible[†]) extent.

Figure 5.1 shows the relation between the strengths of the acid and base in conjugate pairs.

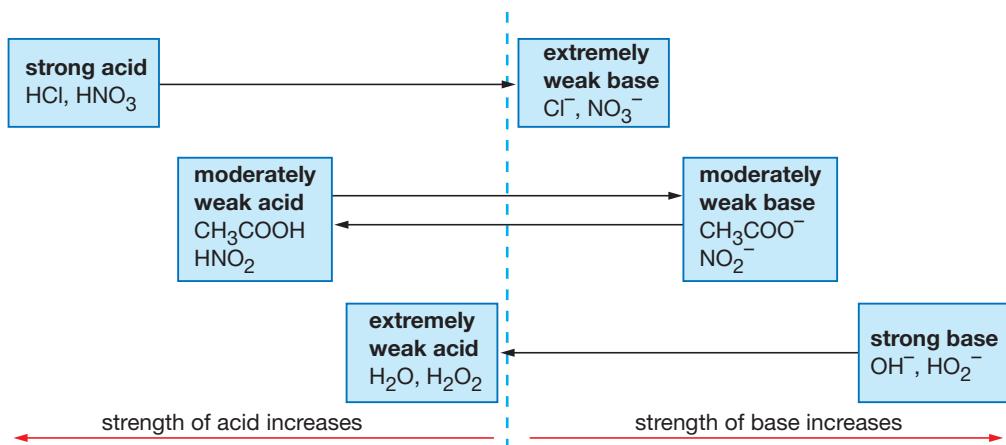


FIGURE 5.1
Relative strengths of the members of acid–base conjugate pairs

[†] However the minute extent to which the acid, water (conjugate acid of the base OH⁻) reacts with water (its self-ionisation, Section 4.16)—about one molecule in four billion—is of considerable significance for the pH of aqueous solutions (Sections 4.16 to 4.18).



Exercises

- 1 Write equations showing the acidic nature of the following substances in aqueous solution:
a HClO_2 ***c** HAsO_2^- ***e** H_3PO_3
b HOBr ***d** H_2S **f** NaHSO_4
- 2 Write equations showing the basic nature of the following substances in aqueous solution:
a methylamine, CH_3NH_2 ***d** hypochlorite ion, ClO^-
b hydrazine, N_2H_4 ***e** potassium sulfide, K_2S
c cyanide ion, CN^- ***f** sodium hydrogen sulfite, NaHSO_3
- 3 Give the conjugate bases of the acids in Exercise 1, and the conjugate acids of the bases in Exercise 2.
- 4 **a** Give the conjugate bases of the acids HCOOH , HOCN , HNO_2 , $^*\text{HOI}$, $^*\text{H}_3\text{AsO}_4$, $^*\text{H}_2\text{CrO}_4$, HSO_4^- , $^*\text{H}_2\text{PO}_3^-$ and $^*\text{HPO}_4^{2-}$.
b Give the conjugate acids of the bases aniline, $\text{C}_6\text{H}_5\text{NH}_2$; pyridine, $\text{C}_5\text{H}_5\text{N}$; hydroxylamine, NH_2OH ; $^*\text{HS}^-$; $^*\text{HCOO}^-$; H_2PO_4^- ; $^*\text{CO}_3^{2-}$; $^*\text{SO}_4^{2-}$; oxide, O^{2-} .
- 5 **a** In each of the following reactions which reactant is an acid? What is its conjugate base?
 - i $\text{NH}_4^+ + \text{HCOO}^- \rightleftharpoons \text{NH}_3 + \text{HCOOH}$
 - ii $\text{CO}_3^{2-} + \text{HCN} \rightleftharpoons \text{HCO}_3^- + \text{CN}^-$
 - *iii** $\text{H}_2\text{O}_2 + \text{HS}^- \rightleftharpoons \text{H}_2\text{S} + \text{HO}_2^-$**b** In each of the following reactions which reactant is a base? What is its conjugate acid?
 - i $\text{HNO}_2 + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NO}_2^-$
 - ii $\text{CH}_3\text{O}^- + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{OH} + \text{NH}_2^-$
 - *iii** $\text{N}_2\text{H}_4 + \text{HOCl} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OCl}^-$

5.3 IMPORTANCE OF EACH DEFINITION OF AN ACID

We have looked at four definitions of acids—those by Lavoisier, Davy, Arrhenius and Brönsted–Lowry (Sections 5.1 and 5.2). Some comment about the importance of each definition is warranted.

Lavoisier's definition was wrong. However it did stimulate a lot of research into the composition of acids and created awareness of the need to define an acid.

The Davy definition defined an acid in terms of its properties and reactions; it helped *classify* substances without trying to *interpret* properties.

The Arrhenius definition increased our understanding of acids by *interpreting* acid properties in terms of the hydrogen ions they produced, and explained weak and strong acids in terms of the extent to which the ionisation reaction proceeded. This increased our understanding considerably. Arrhenius's work was a big step forward in developing the concept of an acid. Unfortunately his definition of a base was much less successful in that it was very restrictive (a substance that produced hydroxide ions in solution);

chemists even at that time generally recognised insoluble oxides and carbonates as bases though being insoluble they could not produce hydroxide ions in solution.

The Brönsted–Lowry definition increased our understanding further by showing that acidity depends not just upon the structure of the substance itself but rather on its properties relative to those of the solvent or other reactant present in the solution. It showed that neutralisation did not need to involve ionisation to H^+ and OH^- ions but could proceed directly by proton transfer (as in $\text{NH}_3 + \text{HCl}$ in benzene solution). In addition the Brönsted–Lowry concept showed that the hydrolysis of salts (reaction with water, Section 5.5) to produce pHs significantly different from 7.0 was nothing more than simple acid or base reactions. The Brönsted–Lowry concept also provided a sound basis for the quantitative treatment of acid–base equilibria and pH calculations.

5.4 MONOPROTIC, DIPROTIC AND TRIPROTIC ACIDS

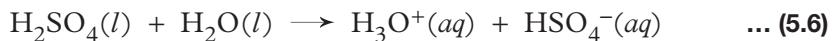
Some acids, such as hydrochloric, HCl , and nitric, HNO_3 , are able to give up only one proton (hydrogen ion) per molecule of acid. These acids are called *monoprotic*, meaning one proton.

A **monoprotic acid** is one that forms one proton (hydrogen ion) per molecule.

Other acids, such as sulfuric, H_2SO_4 , and carbonic, H_2CO_3 , are able to give up two protons (hydrogen ions) per molecule of acid:



Such acids are called **diprotic**. The ionisation of a diprotic acid occurs in a stepwise fashion:



In Brönsted–Lowry terms, HSO_4^- is the conjugate base of H_2SO_4 . However HSO_4^- is itself an acid (because it can undergo Reaction 5.7): SO_4^{2-} is the conjugate base of the acid HSO_4^- . H_2SO_4 is a strong acid (completely ionised) while HSO_4^- is a weak acid (not completely ionised).

A consequence of the stepwise ionisation of diprotic acids such as sulfuric is that such acids can form two series of salts—the normal ones such as sulfates, for example MgSO_4 and Na_2SO_4 , and another set which we call **hydrogen salts** or **acid salts**, for example sodium hydrogen sulfate, NaHSO_4 , sometimes called sodium bisulfate. Similarly, carbonic acid forms carbonates, e.g. calcium carbonate, CaCO_3 , and also forms *hydrogen carbonates*, such as sodium hydrogen carbonate, NaHCO_3 (sodium bicarbonate, or to cooks and those who overeat, bicarbonate of soda).

Phosphoric acid, H_3PO_4 , is a **triprotic acid**. It can form three series of salts: ordinary phosphates, such as sodium phosphate, Na_3PO_4 ; hydrogen phosphates, such as potassium hydrogen phosphate, K_2HPO_4 ; and dihydrogen phosphates, such as calcium dihydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (the active constituent of superphosphate fertiliser).

Common diprotic and triprotic acids and the salts they form are shown in Table 5.2.

TABLE 5.2 Diprotic and triprotic acids and the anions they form

Acid		Anions formed		Typical salt
sulfuric acid	H_2SO_4	sulfate hydrogen sulfate	SO_4^{2-} HSO_4^-	Na_2SO_4 KHSO_4
carbonic acid	H_2CO_3	carbonate hydrogen carbonate	CO_3^{2-} HCO_3^-	CaCO_3 NaHCO_3
sulfurous acid	H_2SO_3	sulfite hydrogen sulfite	SO_3^{2-} HSO_3^-	MgSO_3 KHSO_3
phosphoric acid	H_3PO_4	phosphate hydrogen phosphate dihydrogen phosphate	PO_4^{3-} HPO_4^{2-} H_2PO_4^-	Na_3PO_4 K_2HPO_4 NaH_2PO_4



Exercises

6 Write the formulae for:

- a potassium hydrogen carbonate
- b ammonium hydrogen sulfate
- *c sodium hydrogen sulfite

- *d sodium dihydrogen phosphate
- e lithium hydrogen phosphate
- *f calcium hydrogen sulfide

7 Name the following salts:

- a LiHCO_3
- b $\text{Zn}(\text{HSO}_4)_2$
- *c $\text{Cu}(\text{HCO}_3)_2$

- d $(\text{NH}_4)_2\text{HPO}_4$
- *e NH_4HS
- f KH_2PO_4

8 Write equations for the stepwise ionisation of:

- a carbonic acid
- *b sulfurous acid
- *c phosphoric acid

5.5 SALTS AS ACIDS AND BASES

In Section 4.3 a salt was defined as a compound formed when an acid was neutralised by a base. This may give the impression that solutions of salts are neutral ($\text{pH} = 7$). However as Table 5.3 shows salts may be acidic, basic or neutral.

The reason why the pH of aqueous solutions of many salts is different from 7.0 is that many anions and cations can act as acids or bases.

Salt solutions with pH greater than 7.0

These contain an anion that is a weak base. The nitrite ion, NO_2^- , is the conjugate base of nitrous acid, HNO_2 :



The nitrite ion therefore accepts a proton from water and so hydroxide ion is formed and pH is greater than 7.0:



As we saw in Section 5.2 the acetate ion is the conjugate base of acetic acid and so it reacts to some extent with water to form hydroxide ion: this makes the

TABLE 5.3 pH of 0.25 mol/L aqueous solutions of some common salts

Salt	pH
sodium chloride, NaCl	7.0 ^a
potassium nitrate, KNO ₃	7.0 ^a
sodium sulfate, Na ₂ SO ₄	7.0 ^a
sodium hydrogen sulfate, NaHSO ₄	1.3
potassium hydrogen oxalate, KHC ₂ O ₄	2.4
ammonium nitrate, NH ₄ NO ₃	4.8
potassium nitrite, KNO ₂	8.3
sodium hydrogen carbonate, NaHCO ₃	8.3
sodium acetate, CH ₃ COONa	9.1
potassium cyanide, KCN	11.3
sodium carbonate, Na ₂ CO ₃	11.8
ammonium acetate, CH ₃ COONH ₄	7.0

a Great care is needed to exclude CO₂ from these solutions to obtain these values.

solution of sodium acetate alkaline (pH > 7.0).

These two examples illustrate a general situation:

In a salt formed from a weak acid and a strong base (e.g. sodium acetate from acetic acid and sodium hydroxide), the anion is a weak base and so the salt in aqueous solution has a pH greater than 7.

Salt solutions with pH less than 7.0

These solutions contain an ion that is a weak acid. In sodium hydrogen sulfate, the HSO₄⁻ ion, as we saw in Equation 5.7, is a weak acid: it produces H₃O⁺ ions and so the pH is less than 7. The hydrogen oxalate ion, HC₂O₄⁻, is similarly a weak acid and so it also produces a pH of less than 7.

However not all acid salts produce acidic solutions as sodium hydrogen carbonate in Table 5.3 shows: we will discuss this salt in the next section.

In ammonium nitrate the ammonium ion, NH₄⁺, is the conjugate acid of the weak base ammonia (Equation 5.3), so in solution the NH₄⁺ ion produces H₃O⁺ ions (Equation 5.5) which makes the pH of the solution less than 7. It is this acidic nature of the ammonium ion that means gardeners have to add lime to their lawns occasionally if they regularly use ammonium sulfate fertiliser.

Ammonium nitrate illustrates another general situation:

In a salt formed from a weak base and strong acid (e.g. ammonium nitrate from ammonia and nitric acid), the cation is a weak acid and so the salt in aqueous solution has a pH less than 7.

A salt formed from a strong acid and a strong base

This salt has a pH close to 7.0. This is because (1) as explained in Section 5.2, the conjugate base of a strong acid (e.g. Cl⁻ from HCl) does not react with water to any significant extent and so it does not alter the pH, and (2) because by similar arguments the conjugate acid of a strong base (H₂O from OH⁻) does not react with water sufficiently to alter its pH. Hence the pH of such salts is just the pH of pure water, 7.0.

A salt formed from a weak acid and a weak base

Such a salt, (for example, ammonium acetate from ammonia and acetic acid) also has a pH close to 7.0, because both the anion and the cation react with water to small extents and so approximately cancel each other.

The pHs of solutions of these different categories of salts are summarised in Table 5.4.

Basically, what we have been considering in this section is the reaction of salts with water, which is called *hydrolysis of salts*.

Hydrolysis is a chemical reaction in which a substance reacts with water.[†]

TABLE 5.4 pH of solutions of salts formed from different types of acids and bases

	Strong base (NaOH, KOH)	Weak base (NH_3)
Strong acid (HCl, HNO_3)	pH = 7 (NaCl , KNO_3)	pH < 7 (NH_4Cl , NH_4NO_3)
Weak acid (CH_3COOH, HNO_2)	pH > 7 (CH_3COONa , KNO_2)	pH = 7 ($\text{CH}_3\text{COONH}_4$)

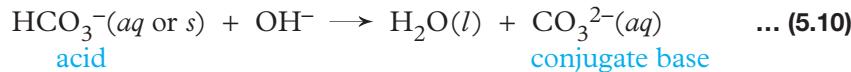
5.6 AMPHIPROTIC SUBSTANCES

A substance that can act both as a proton donor and as a proton acceptor is called an **amphiprotic** substance (*amphi* means ‘both’).

The hydrogen carbonate ion is amphiprotic, because in aqueous solution it reacts with water in two ways:



In the first equation HCO_3^- is a proton donor (acid), while in the second it is a proton acceptor (base). Both of these reactions occur simultaneously when sodium hydrogen carbonate is dissolved in water but to only small extents (hence the reversible arrows \rightleftharpoons). However if placed in alkaline (basic) solution, hydrogen carbonate acts as an acid:



If placed in acid solution hydrogen carbonate acts as a base:



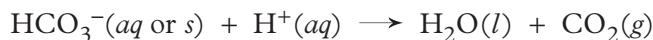
and in both cases the reactions go to completion (hence the one-way arrows \longrightarrow). We looked at the equilibrium between carbonic acid, H_2CO_3 ,

[†] The distinction between *hydrolysis* and *hydration* (Section 1.5) is this: hydration is the addition of a molecule of water to another molecule to form a new molecule as in hydration of ethylene to form ethanol. It is just one type of hydrolysis reaction. Here we have been considering hydrolysis in which one species reacts with water to form two different species as in NO_2^- reacting with water to form HNO_2 and OH^- .

and carbon dioxide gas in Sections 4.6 and 4.8. Because carbon dioxide does not have a very high solubility in water, the carbonic acid breaks up to release carbon dioxide:



As we saw previously this equilibrium lies well towards the $\text{CO}_2(g)$ side, so CO_2 comes out of solution. When we add hydrogen carbonate to acid solution, we observe rapid evolution of gas. The overall reaction is often written as:



When hydrogen carbonate is dissolved in pure water, Reactions 5.8 and 5.9 go to only a small extent. When HCO_3^- is added to acidic or basic solution, Reaction 5.10 or 5.11 (respectively) goes to completion.

The hydrogen sulfite ion, HSO_3^- , is also amphiprotic. It reacts with basic and acidic solutions in the same way as hydrogen carbonate does; in acid solution it releases sulfur dioxide which has a distinctively sharp or choking smell.

Another amphiprotic substance is water. This can be seen from Equations 5.1 and 5.2. In Equation 5.1 the solvent, water, is acting as a proton acceptor, and hence as a base; H_3O^+ is the conjugate acid of the base, H_2O . In Equation 5.2 the solvent, water, is acting as a proton donor and therefore as an acid; OH^- is the conjugate base of the acid, H_2O .

The solvent, water, can act both as an acid and as a base. If a substance (for example HCl) has a greater tendency to lose protons than water has, then that substance (HCl) is an acid in aqueous solution, and the water acts as a base. If a substance (for example ammonia) has a lesser tendency to lose protons than the solvent has, then that substance (NH_3) in aqueous solution is a base, and the water acts as an acid.

Exercises

- 9 For each of the salts below, give the formula and state whether you would expect 0.1 mol/L aqueous solutions to have a pH of about 7, less than 7 or greater than 7. Explain why, giving equations where necessary.

- a barium nitrate c sodium carbonate *f potassium bromide
b sodium formate d ammonium nitrate g sodium cyanide
(methanoate) *e sodium sulfite *h potassium sulfate

- 10 The following substances are amphiprotic:

- a HSO_3^- c H_2PO_4^-
*b HS^- *d glycine, $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$.

Write equations for the reactions of each of them with

- i water ii hydrochloric acid iii sodium hydroxide.

Take care to use the correct arrow, \rightarrow or \rightleftharpoons , in each equation.



5.7 NEUTRALISATION

In Section 4.3, neutralisation was the reaction:



For example:

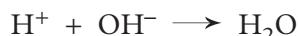


or



Neutralisation reactions are **proton transfer reactions**: in Reaction 5.12 the acid HCl transfers a proton to the base OH⁻ (to form H₂O).

In Section 4.3 we saw that the net ionic reactions for many (but not all) neutralisation reactions was:



or using the more accurate formula for the hydrogen ion,



This shows neutralisation as a proton transfer from the H₃O⁺ ion to the OH⁻ ion. There are other forms for neutralisation reactions but they still involve a proton transfer.

In the neutralisation of ammonia by nitric acid:



or in net ionic form (since HNO₃ is completely ionised):



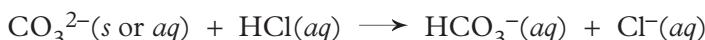
the acid transfers a proton to ammonia (to form the NH₄⁺ ion).

Similarly when sodium hydroxide solution neutralises acetic acid:



a proton is transferred from the acetic acid to the base, OH⁻ (to form H₂O).

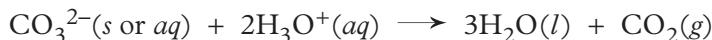
Sodium carbonate reacts with hydrochloric acid: we can consider this as a three-step process:



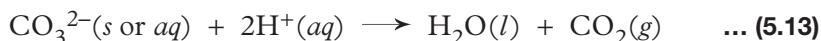
or write it as one overall reaction:



In either case, it is a reaction in which protons are transferred from HCl to the base, CO₃²⁻, and so it is neutralisation. We can write this reaction without the spectator ion, Cl⁻:



or just as



We tend to write equations in terms of H₃O⁺ when we are focusing on the proton transfer aspect of the reaction. When we are using equations for calculating quantities involved in a reaction (Sections 5.8, 5.9) we tend to write them in terms of H⁺ because that makes the equations simpler.

Heat of reaction

Neutralisation is an exothermic reaction (p. 275 CCPC), meaning that heat is liberated as it occurs and that the enthalpy change, ΔH , for the reaction is negative. The enthalpy change, ΔH , for neutralisation reactions is approximately -56 kJ/mol . It varies by a few kJ/mol depending upon whether the acid or base involved is weak or strong and upon the concentration of the solutions involved. It can be measured in the same way as in Example 3 on pp. 278–9 CCPC and summarised in Box 10.1 on p. 279 CCPC.

Exercises

11 Three common neutralisation reactions are

- a the reaction of hydrochloric acid with calcium oxide
- b the reaction of sulfuric acid with copper hydroxide
- c the reaction of nitric acid with ammonia solution.

Write equations for these reactions and identify the proton transfer that is occurring in each.

12 Sodium sulfite reacts with hydrochloric acid. Write an equation for the reaction. If the reaction mixture is heated a gas with a choking smell is formed. What is this gas? Write an equation for its formation. Would you expect to form the same gas by adding hydrochloric acid to potassium hydrogen sulfite? If yes, write an equation.

13 Nitrous acid reacts with sodium cyanide:



Would you consider this a neutralisation reaction? Explain why or why not.

14 When 25 mL of a solution at 23.2°C containing $5.00 \times 10^{-3} \text{ mol}$ sodium hydroxide was mixed with 50 mL of a solution also at 23.2°C that contained $6.00 \times 10^{-3} \text{ mol}$ hydrochloric acid in a light plastic beaker, the final temperature of the mixture was 24.1°C . Calculate the heat released and hence the enthalpy change per mole for the neutralisation reaction. Take the density and specific heat capacity of all solutions involved as 1.00 g/mL and $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ respectively, assume that the container had negligible heat capacity and that heat losses to the surroundings were negligible.

15 50 mL of a 0.28 mol/L solution of ammonia at 19.6°C was added to 100 mL of a 0.14 mol/L solution of nitric acid also at 19.6°C . The final temperature was 20.7°C . Write a net ionic equation for the reaction that occurred. Making the same assumptions and using the same values for density and heat capacity as in Exercise 14, calculate the enthalpy change for this reaction.



5.8 VOLUMETRIC ANALYSIS

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

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

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

Equivalence point

The **equivalence point** of a chemical reaction is the point at which the amounts of the two reactants are just sufficient to cause complete consumption of both reactants.

The equivalence point is sometimes called the **end point**.

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



We detect the equivalence point of a titration by using an indicator. We saw in Section 4.19 (Table 4.7) that indicators change colours over fairly narrow pH ranges. During an acid–base titration the pH changes quite suddenly at the equivalence point—as the solution in the flask changes from slightly alkaline to slightly acidic (or *vice versa*). This means that a suitable indicator in the solution in the flask will change colour quite sharply at the equivalence point.

Acid–base titrations

The basic steps for performing an acid–base titration are:

- Fill a *burette* (Figure 8.5 on p. 215 CCPC) with a solution of known concentration (for example sulfuric acid) and adjust the solution level in the burette to the zero mark[†]; the solution in the burette is called the **titrant**.
- Place a solution of the sample to be analysed (for example sodium hydroxide) in a flask under the burette.
- Add one or two drops of a suitable indicator to the flask.
- Place a white tile or card under the flask to make it easier to detect the colour change in the indicator without overshooting the equivalence point.
- Slowly run solution from the burette into the flask with continuous swirling until the indicator just changes colour; near the equivalence point add the titrant slowly, one drop at the time.
- Read the volume delivered by the burette as accurately as possible.
- Repeat the titration several times until a consistent volume of titrant is obtained (volumes differing by no more than about ± 0.1 or ± 0.2 mL); often the first titration will overshoot the equivalence point, because we do not know at what approximate volume it will occur.
- Calculate the required concentration or amount of the unknown using the basic principles of molarity calculations explained on pp. 218–20 CCPC.

A typical arrangement for performing a titration is shown in Figure 5.2(a), while (b) shows the colour change for methyl red at the equivalence point.

For volumetric analysis we need solutions of known concentration to use in titrations of the unknown solutions. This means that we need some substances of high purity that we can use as primary standards.

[†] Alternatively, accurately read *and record* the solution level in the burette, then when the equivalence point is reached, read the final level of the solution; the difference between the final and initial levels in the burette is the volume of titrant used (called the *titre*).

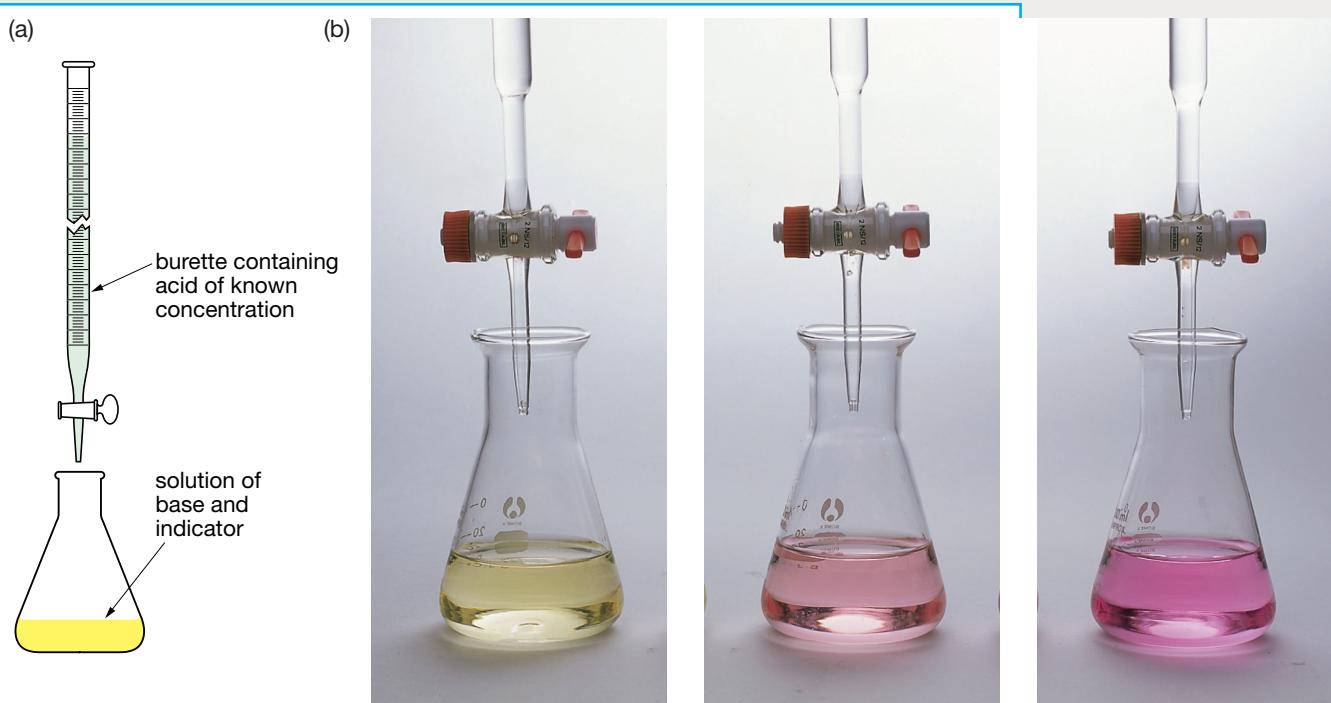


FIGURE 5.1
 (a) A typical set-up for performing a titration;
 (b) methyl red indicator just before, at, and just after the equivalence point as acid is added from the burette to alkali in the flask

5.9 PRIMARY STANDARDS AND STANDARD SOLUTIONS

We cannot make solutions of precisely known concentration of our common acids, HCl, H₂SO₄ and HNO₃, by accurate dilution of concentrated acids because the concentration of these acids changes with time. This is due to volatilisation of HCl and HNO₃ and to absorption of water by H₂SO₄ on standing. Similarly, we cannot prepare accurately known solutions of NaOH or KOH because both of them absorb moisture from the air and also react with carbon dioxide from the air (to form Na₂CO₃ and K₂CO₃). Even if we could dry out the solid, we could not be sure it was pure hydroxide.

Hence it is necessary to choose a pure stable substance with which to make up a first accurately known solution for use in titrations. Such a substance is called a primary standard.

A **primary standard** in volumetric analysis is a substance of sufficiently high purity and stability that a solution of it, of accurately known concentration, can be prepared by weighing out the desired mass, dissolving it in water, and making the volume up to an accurately known value.

The resulting solution is known as a **standard solution**—a solution of accurately known concentration. A standard solution is made up in a *volumetric flask* (p. 215 CCPC).

For acid–base titrations, sodium carbonate and sodium hydrogen carbonate are suitable primary standards. Both chemicals, after drying, have high purity and can be accurately weighed out, dissolved in water and made up to the required volume.

Such a standard solution can be used in a titration with an acid solution in order to *standardise* (measure the concentration of) the acid solution. The acid solution can then be used to determine the concentrations of other solutions.

Key equations

The key equations for calculating results from a volumetric analysis are Equations 5.1 and 8.9 from pp. 136 and 217 *CCPC*, namely:

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

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

Examples 1 and 2 will illustrate the general procedure.



Example 1

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

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

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

From Equation 5.14:

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

From Equation 5.15:

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



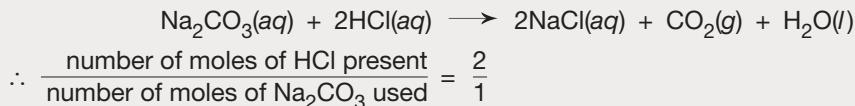
Example 2

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

From the titration, using Equation 5.15 rearranged,

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

The equation for the titration is:



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

This amount of HCl was present in 38.2 mL ($= 0.0382 \text{ L}$)

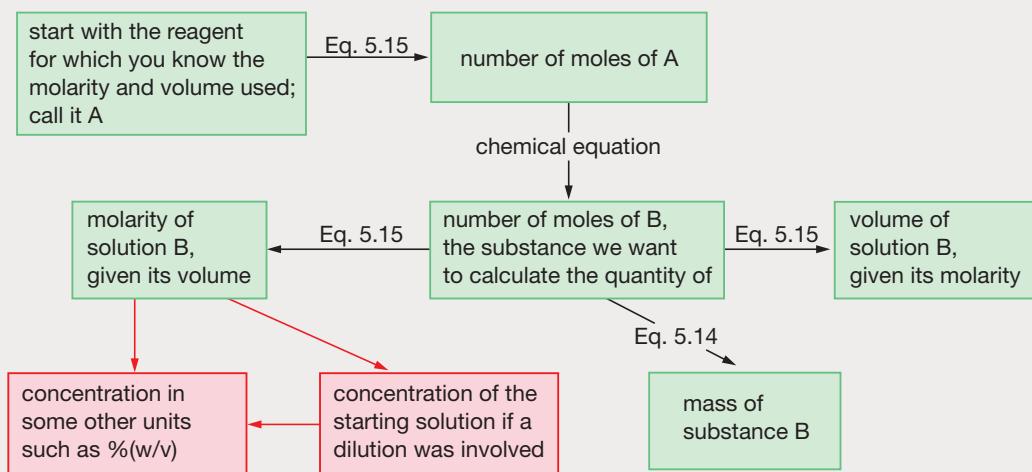
\therefore by Equation 5.15

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

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

The steps involved in a typical volumetric analysis calculation are shown in Figure 5.3

FIGURE 5.3
The steps in a volumetric analysis calculation



In volumetric analysis samples to be analysed are often quantitatively diluted so that the volume of titrant they require is within the accuracy range of the burette, say between 15 and 50 mL for a 50 mL burette. The method of calculating concentration after dilution was described on p. 215 CCPC. The following example illustrates a typical volumetric analysis using a quantitative dilution.

Example 3

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



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

The chemical equation for the titration reaction is:



From this equation:

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

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

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

This is the molarity of acetic acid in the *diluted* vinegar. To calculate the molarity of the concentrated solution (Z_1 , say), we note (as explained on p. 215 CCPC) that:

$$\text{number of moles of acetic acid in 10 mL concentrated solution} = \frac{\text{number of moles of acetic acid in 100 mL dilute solution}}{10}$$

Therefore

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

giving

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

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

$$\begin{aligned}\text{Molar mass of acetic acid, } \text{CH}_3\text{COOH} &= 2 \times 12.0 + 4 \times 1.01 + 2 \times 16.0 \\ &= 60.0 \text{ g/mol} \\ \text{so } 0.0668 \text{ mol/100 mL} &= 0.0668 \times 60.0 \\ &= 4.01 \text{ g/100 mL}\end{aligned}$$

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

In performing such calculations we must ensure that the answer is given to the correct number of *significant figures*. In Example 3 both the concentration of the sodium hydroxide solution (0.105 mol/L) and the volume of sodium carbonate solution needed (15.9 mL) had three significant figures, so the answer must have three significant figures, 0.668 mol/L and 4.01%. This would be a good time to revise the use of significant figures in the appendix on pp. 310–11 CCPC.

The vinegar and the equipment used to analyse it in Example 3



For volumetric analysis to be accurate, we must pay attention to some practical details, first to ensure that the standard solutions we make have precisely the concentrations we expect, and secondly to ensure that we reach the exact equivalence point in the titration.

5.10 PREPARING A STANDARD SOLUTION

The accuracy of any volumetric analysis depends upon the care taken in preparing the solution of the primary standard (Section 5.9) upon which the analysis is based. Hence it is essential to ensure:

- 1 that the substance being used as the primary standard is as *pure as possible*, and particularly that it is *free of moisture*: drying in an oven and cooling in a desiccator are the usual precautions in this regard

- 2** that it is weighed as accurately as possible
- 3** that the volumetric flask has been thoroughly cleaned (though it may be left wet with pure water since water will be added in making up the solution)
- 4** that care is taken to transfer *all* of the solute from the beaker used for weighing into the volumetric flask
- 5** that the solute is completely dissolved in water before making the volume up to the graduation mark
- 6** that the volume of solution is made accurately to the graduation mark on the flask (bottom of meniscus sitting exactly on the mark), preferably using a Pasteur pipette for adding the last few millilitres
- 7** that pure water, either distilled or de-ionised (demineralised), is used for preparation of all solutions and for final rinsing of all glassware
- 8** that after the solution is made up to the mark it is well shaken to ensure uniform mixing before any of it is withdrawn from the flask.

5.11 USING VOLUMETRIC GLASSWARE

Before use all volumetric glassware must be thoroughly cleaned and rinsed several times with distilled or de-ionised water. Volumetric flasks and titration flasks may be left wet with water. However *pipettes and burettes must finally be rinsed with a portion of the solution to be measured*. This final rinsing is to prevent dilution of the solution by a film of water remaining on the inside surfaces.

Using a pipette

To fill a pipette (after rinsing it with some of the solution first), the solution is drawn in, using some type of pipette filler (for hygiene and safety), until the solution is well above the graduation mark, then the solution is carefully run out until the meniscus sits exactly on the mark. To do this it is essential to hold the pipette at eye level to avoid parallax errors. It also helps if a white or plain wall can be used as background to sharpen up the appearance of the meniscus.

The solution is then let run out of the pipette into the required flask by gravity (never blown out) and finally, the pipette is held with its tip in contact with the wall of the receiving flask or beaker for the specified draining time (typically 20 s). The portion of liquid remaining in the tip of the pipette must *not* be blown out, because the pipette has been calibrated on the basis that the remaining portion of liquid stays there. In all operations, the pipette is held vertically.

Using a burette

Before filling a burette, it is rinsed with a portion of the solution to be dispensed. It is then overfilled, and the excess run out. During this procedure, care is taken to ensure that all air bubbles are removed from the section of the burette between the stopcock and the tip. To do this, it may be necessary to hold the burette at an angle to the vertical. Once any such air bubbles have been removed, the burette is clamped vertically and the liquid level lowered until the meniscus sits exactly on the zero mark. Reading most burettes is facilitated by holding a piece of white card behind the burette; this ‘sharpens up’ the appearance of the meniscus. Burettes are usually marked with 0.1 mL graduations. By estimating the fraction of a division (for example $\frac{1}{3}$, $\frac{1}{2}$ or $\frac{2}{3}$), it is possible to read a burette to ± 0.03 mL. Near the end-point of a titration, fractions of a drop can be dispensed by

allowing a portion of a drop to build up on the tip, then washing it into the titration flask with a wash bottle.

When we need to know the volume of a solution accurately, a measuring cylinder must *not* be used, because it is not accurate enough (p. 214 *CCPC*). Its accuracy is only about $\pm 5\%$ whereas for volumetric analysis we need to measure volumes to $\pm 0.5\%$ or better.

5.12 CHOICE OF INDICATOR

It is important to choose an indicator that will undergo a sharp colour change at the exact equivalence point of the titration. The pH change is slightly different for different strengths of acid and base so different indicators should be used. Table 5.5 lists suitable indicators for the common types of acid–base titration.

TABLE 5.5 Indicators for different acid–base titrations

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

a acid colour–base colour

We generally do not perform weak acid–weak base titrations (hence no entry in Table 5.5), because the pH change around the equivalence point of such titrations is not very large. Consequently we do not get a sharp colour change with any indicator; rather the change occurs over several drops, say over about 0.2 mL to 0.5 mL, and so it is not possible to determine the equivalence point accurately.

Why use different indicators?

The reason for using different indicators for different titrations (as in Table 5.5) is that we want the indicator to change colour at the equivalence point of the reaction and the pH of the equivalence point can vary from one type of titration to another as the following examples illustrate:

- When we titrate an ammonia solution with hydrochloric acid (strong acid–weak base), at the equivalence point we have a solution of ammonium chloride:



As we saw in Section 5.5 a solution of ammonium chloride has a pH < 7 (because NH_4^+ is a weak acid and so produces some H^+ ions), so we need an indicator that changes colour at pH < 7, meaning any one of the four in the first row of Table 5.5.

- When we titrate a solution of acetic acid with sodium hydroxide solution

(weak acid-strong base), at the equivalence point we have a solution of sodium acetate:



As we saw in Section 5.5, a solution of sodium acetate has a pH > 7 (because the acetate ion is a weak base that reacts with water to a small extent to produce some OH⁻ ions) and so we need an indicator that changes colour at pH > 7.

To determine which indicator to use for an acid-base titration

- Decide what salt is present at the equivalence point.
- Determine whether either ion of that salt is a weak acid or a weak base or neither.
- Hence decide whether the pH of its solution will be greater than, approximately equal to or less than 7.
- Select an indicator that changes colour in that pH region (less than, around about or greater than 7).

Exercises

- 16 5.267 g anhydrous sodium carbonate was dissolved in water in a volumetric flask and the volume made up to 250 mL. 10 mL of this solution was pipetted into a conical flask and titrated with hydrochloric acid. 21.3 mL was needed to reach the equivalence point. Calculate the molarity of the hydrochloric acid solution.

This solution was then used to determine the concentration of an unknown barium hydroxide solution. 25 mL of the barium hydroxide solution required 27.1 mL hydrochloric acid solution for exact neutralisation. Calculate the molarity of the barium hydroxide solution. In addition, calculate its concentration in grams per litre.

- 17 Phthalic acid is a weak diprotic acid for which we can write the formula as H₂(C₈H₄O₄). Potassium hydrogen phthalate, KH(C₈H₄O₄), is a good primary standard for standardising alkali solutions. It contains one acidic hydrogen per formula unit. 0.917 g potassium hydrogen phthalate was dissolved in water and titrated with an approximately 0.2 mol/L sodium hydroxide solution; 27.2 mL hydroxide solution was needed to reach the end point. Calculate the accurate molarity of the hydroxide solution.

- 18 What indicator would you use for each of the three titrations in Exercises 16 and 17? Justify your choice.

- 19 The standard sodium hydroxide solution from Exercise 17 was used to determine the concentration of acetic acid in a particular brand of vinegar. 50 mL of the vinegar (by pipette) was accurately diluted to 250 mL (volumetric flask), and then 25 mL aliquots of this diluted solution were titrated with the sodium hydroxide solution. The results of successive titrations were 21.95, 21.60, 21.55 and 21.60 mL. Calculate the molarity and % (w/v) of acetic acid in the original vinegar.

- 20 List the precautions you would take to ensure the accuracy of the analysis in Exercise 19.

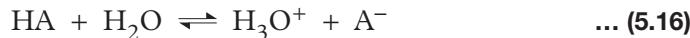
- 21 ‘Cloudy ammonia’ is often used in the home as a cleaning agent. To determine the concentration of ammonia in the solution, a chemist first accurately diluted 25 mL (by pipette) to 500 mL (volumetric flask), then titrated 25 mL (by pipette) of the diluted solution with 0.151 mol/L nitric acid solution; it required 27.2 mL. Calculate the molarity of the original ammonia solution.



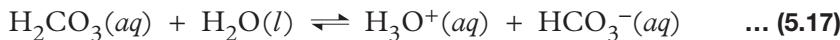
- 22** 25 mL of sulfuric acid from a car battery was accurately diluted to 500 mL. 25 mL of the diluted solution was titrated with 0.206 mol/L sodium hydroxide. It required 38.8 mL. Calculate the molarity of the original battery acid and its concentration in grams per litre. If 50 mL of this acid were spilt on the bench, how much anhydrous sodium carbonate would be needed to neutralise it?
- 23** The acidity of a particular white wine was determined by titrating 25 mL of the wine with 0.0511 mol/L sodium hydroxide solution; 8.7 mL was required. Calculate the molarity of hydrogen ions in the wine. Assume that the hydrogen ions come entirely from diprotic tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, and calculate the concentration of tartaric acid in the wine in grams per 100 mL.
- *24** Suppose you wanted to determine the percentage purity of a sample of washing soda, sodium carbonate decahydrate, that you had just purchased. Your laboratory has a solution of hydrochloric acid labelled 0.25 mol/L. It also has the usual range of pure chemicals and indicator solutions, an accurate mass balance and a full range of volumetric glassware. Explain fully how you would accurately determine the percentage purity of the washing soda. Include at least one diagram and give all experimental details. Name the indicator you would use and explain why.
- 25** Which indicator would you use for each of the following titrations? Explain why.
- formic (methanoic) acid with sodium hydroxide
 - ammonia with nitric acid
 - sulfuric acid with potassium hydroxide
 - *d** nitric acid with sodium hydrogen carbonate
 - *e** nitrous acid with sodium hydroxide
- 26 a** Oxalic acid dihydrate, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, can be used as a primary standard for standardising alkali solutions. 0.291 g diprotic oxalic acid required 18.2 mL of a potassium hydroxide solution for exact neutralisation. Calculate the molarity of the hydroxide solution.
- b** This hydroxide solution was used to determine the concentration of acetic acid in a particular type of vinegar. 10 mL aliquots (by pipette) were titrated with the hydroxide solution. The volumes of hydroxide solution in successive titrations were 24.90, 24.35, 24.45 and 24.40 mL. Calculate the molarity of acid in the vinegar. Assuming that acetic acid is the only acid present in the vinegar, calculate the percentage (w/v) of it in the vinegar.
- c** A student suggested that a more direct way of determining the concentration of acid in the vinegar would be to prepare a standard solution of sodium hydrogen carbonate (a good primary standard) and use it to titrate the vinegar directly. Why is this not a good way of accurately determining the acid concentration in the vinegar?

5.13 BUFFER SOLUTIONS

A solution containing comparable amounts of a weak acid and its conjugate base (for example carbonic acid and sodium hydrogen carbonate) is very good at maintaining an approximately constant pH even when strong acid or alkali is added. The equilibrium involved is:



where HA is the weak acid and A⁻ its conjugate base; for example



If hydrogen ion (a product) is added to this solution, then by Le Chatelier's principle (Section 4.7) the equilibrium in Equation 5.16 will move to the left:

the base A^- will combine with much of the added H_3O^+ to form HA in order to minimise the change in $[H_3O^+]$.[†] If instead hydroxide ion had been added, it would react with the H_3O^+ and cause pH to rise, but again (by Le Chatelier's principle) the equilibrium in Equation 5.16 will move to the right to try to minimise the change: HA will ionise to produce more A^- . Because of its ability to maintain an approximately constant pH, such a solution is called a *buffer solution*: it acts as a 'buffer' against change in pH.

A **buffer solution** is a solution that contains comparable amounts of a weak acid and its conjugate base and which is therefore able to maintain an approximately constant pH even when significant amounts of strong acid or strong base are added to it.

Some common buffer solutions are listed in Table 5.6 along with the pH around which they are effective.

TABLE 5.6 Some common buffer solutions and the pH around which they are effective

Buffer	pH ^a
acetic acid and sodium acetate: CH_3COOH , CH_3COONa	4.6
carbon dioxide (carbonic acid) and hydrogen carbonate: H_2CO_3 , HCO_3^-	6.4 ^b
sodium dihydrogen phosphate and hydrogen phosphate: $H_2PO_4^-$, HPO_4^{2-}	7.2
ammonium chloride and ammonia: NH_4^+ , NH_3	9.3
sodium carbonate and hydrogen carbonate: CO_3^{2-} , HCO_3^-	10.3

a of equimolar mixtures of the acid and its conjugate base.

b because of the low solubility of carbon dioxide in water, in nature this buffer works around a pH of 7.

5.14 BUFFERS IN NATURE

Because many processes in nature require carefully controlled pH, there are many natural buffer systems. The simplest is the one in Equation 5.17 which involves carbon dioxide from the air (which dissolves as carbonic acid) and hydrogen carbonate (formed from small amounts of dissolved carbonate). It occurs in freshwater lakes and rivers.

In rain water (where there is no source of HCO_3^- other than CO_2 from the air) this equilibrium produces a pH of about 5.7 to 6.0. In rivers or lakes where some HCO_3^- comes from dissolving salts out of the rocks around the rivers and lakes, this added HCO_3^- pushes Equilibrium 5.17 to the left and so raises pH to between 6.5 and 7.5. Rain water is a dilute solution of H_2CO_3 ; this is *not* a buffer solution, because the only source of HCO_3^- is the ionisation of H_2CO_3 and this provides too little to let the solution act as a buffer. To be a buffer there must be *comparable amounts* of H_2CO_3 and HCO_3^- in the solution and this means that there must be a source of HCO_3^- apart from dissolved CO_2 . Hence lakes and rivers are only buffered if there are carbonate rocks available from which HCO_3^- can be formed.

It was the absence of this buffering action in lakes in Scandinavia that resulted in the first detection of falling pH from acid rain (Section 4.11): the

[†] Remember, square brackets around a chemical formula means concentration of that species (Section 4.15).



Some test kits for home swimming pools measure 'total alkalinity' meaning buffer capacity as well as pH and chlorine (for sterilisation) content

rocks from which the lakes had been carved contained no carbonate to provide HCO_3^- to make the buffer.

This $\text{H}_2\text{CO}_3-\text{HCO}_3^-$ buffer is also used in home swimming pools. If pH is proving difficult to control in the desired range of 7.2 to 7.4, sodium hydrogen carbonate is added to increase the buffering capacity of Equation 5.17. Pool test kits often measure 'total alkalinity' of pool water meaning OH^- and HCO_3^- . This test is really measuring the buffering capacity of the water: if it is low, sodium hydrogen carbonate needs to be added.

Many of the complex processes occurring in the human body require carefully controlled pH for their proper functioning, because the enzymes involved only operate over narrow pH ranges. This same $\text{H}_2\text{CO}_3-\text{HCO}_3^-$ buffer controls the pH in many parts of the human body. However it cannot buffer against changing acidity due to changing concentrations of carbon dioxide. Therefore in blood other buffers are involved, most notably haemoglobin which is

itself a weak base (strictly it is amphiprotic), so can act as a buffer; writing Hb for haemoglobin:



Our kidneys purify blood by removing metabolic waste products, many of which are acids. Because the kidneys have to dispose of these acidic wastes without producing an excessively low pH, they too involve buffers. Many acidic wastes are excreted as dihydrogen phosphates which accounts for urine having a pH of about 6.0.

5.15 NEUTRALISATION AND SAFETY

Neutralisation reactions are widely used for safety in laboratories and factories where acids or bases are used. Because many acids and alkalis are very corrosive, it is important to neutralise any spills of these substances quickly. In addition sewage authorities put strict limits on the pH of factory and laboratory effluents discharged to sewers (so as not to upset bacterial breakdown). Neutralisation reactions are widely used to ensure that effluents from such places are neither acidic nor alkaline.

Sodium carbonate is widely used to neutralise acidic spills or effluents because:

- it is a stable solid which is easily and safely handled and stored
- it is the cheapest alkali available and
- if too much of it is used there is less danger than from excess sodium hydroxide or lime (calcium hydroxide).

For the controlled neutralisation of alkaline wastes hydrochloric or sulfuric acid is used but as a safety chemical to have readily available for neutralising spills sodium hydrogen carbonate is preferred: it is safe and easy to handle itself and there is no great problem if excess is used. In fact, because it is amphiprotic, it can be used for acid spills as well. Many laboratories have bottles of powdered

sodium hydrogen carbonate conveniently located on shelves and benches for easy access and use in case of spills of acid or alkali.

These examples illustrate the factors that need to be considered in choosing a substance to neutralise acid or alkali spills in factories or laboratories, namely:

- the speed of the reaction for neutralising the spilt material
- the need for a reagent that will not have any harmful effect if an excess of it is used (since it is hard to determine exact quantities for neutralising spills)
- the safety in handling and storing the reagent
- the cost of the reagent
- the possibility of the one reagent being able to neutralise both acid and alkali spills.

Exercises

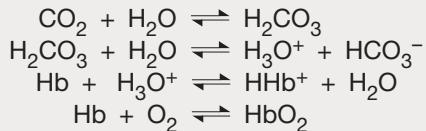
27 A mixture of sodium dihydrogen phosphate and sodium hydrogen phosphate is widely used in laboratories to buffer solutions at pHs of around 7. Explain how this combination of salts maintains approximately constant pH even when small amounts of HCl or NaOH are added to the solution.



28 Would 1 L of aqueous solution containing each of the following pairs of substances be a buffer solution or not? Explain why (or why not). Use an equation where appropriate.

- a 0.3 mol ammonia and 0.3 mol ammonium chloride
- *b 0.2 mol nitrous acid and 0.2 mol sodium nitrite
- c 0.2 mol nitric acid and 0.2 mol sodium nitrate
- *d 0.25 mol methanoic (formic) acid and 0.25 mol sodium methanoate

***29** Some equilibria involved in blood are:



where Hb is haemoglobin, HHb⁺ is its conjugate acid and HbO₂ is oxyhaemoglobin. Use Le Chatelier's principle to describe:

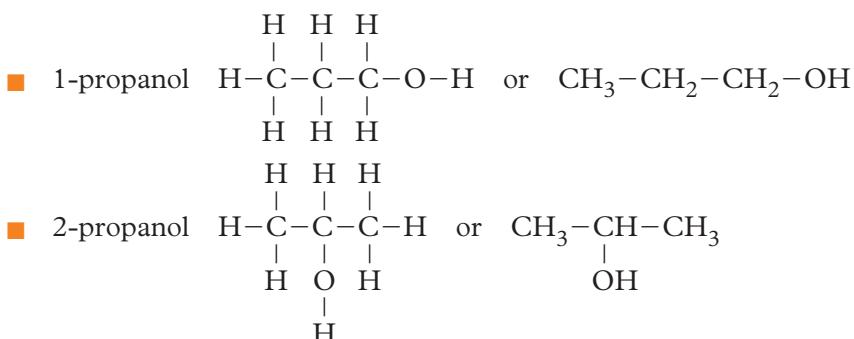
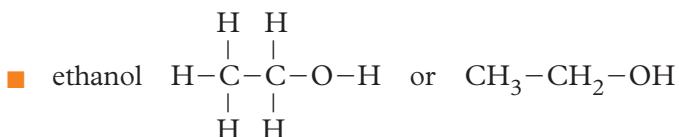
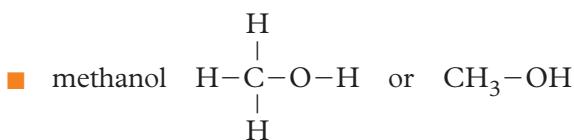
- a how each of these equilibria moves as CO₂ diffuses from tissue cells into the blood stream: in particular, explain how diffusion of CO₂ into the blood facilitates release of oxygen to tissue cells.
 - b how uptake of oxygen by haemoglobin in the lungs facilitates the release of CO₂ from the blood.
- 30** Two neighbouring factories produce large quantities of effluent that they have to dispose of safely. One effluent is acidic and the other is basic. 25.0 mL of one effluent required 29.5 mL 0.233 mol/L sulfuric acid for exact neutralisation. 25.0 mL of the other required 32.8 mL 0.274 mol/L sodium hydroxide for exact neutralisation. What volume of the first effluent should be mixed with 100 L of the second in order to produce neutral effluent?

The dominant reaction so far in this chapter has been neutralisation. For one important class of acids, the so-called *carboxylic acids*, there is another important reaction called *esterification*. To understand this we first need to look at the structure of alkanols and alkanoic acids.

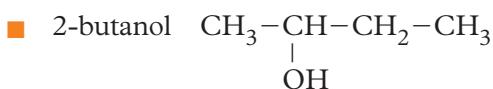
5.16 ALKANOLS AND ALKANOIC ACIDS

We saw in Section 1.5 that *alkanols* were compounds formed by replacing an H atom of an alkane with an OH group and that they are named by replacing the final *e* of the parent alkane with *-ol* and using a number prefix to denote the position of the OH group:

Some simple alkanols



and just in condensed form:



Molecular models of methanol and ethanol and of 1- and 2-propanol are shown in Figures 5.4 and 5.5.

1-propanol and 2-propanol are *isomers*, because they are different compounds having the same molecular formula, $\text{C}_3\text{H}_8\text{O}$. Similarly 1- and 2-butanol are isomers, having the molecular formula, $\text{C}_4\text{H}_{10}\text{O}$.

The alkanols form an *homologous series* having the general formula, $\text{C}_n\text{H}_{2n+2}\text{O}$ or $\text{C}_n\text{H}_{2n+1}\text{OH}$.

Alkanols are a subset of a larger class of compounds called *alcohols*.

An **alcohol** is a compound which contains an OH group attached to a C atom that only has C or H atoms attached to it, regardless of what else is in the molecule.

Both of the compounds, $\text{CH}_3-\text{CH}_2-\text{OH}$ and $\text{CCl}_3-\text{CH}_2-\text{OH}$, are alcohols, but only $\text{CH}_3-\text{CH}_2-\text{OH}$ is an alkanol. The OH group is commonly called the **alcohol group**.

Alkanoic acids

An **alkanoic acid** is a compound which has the general structure:

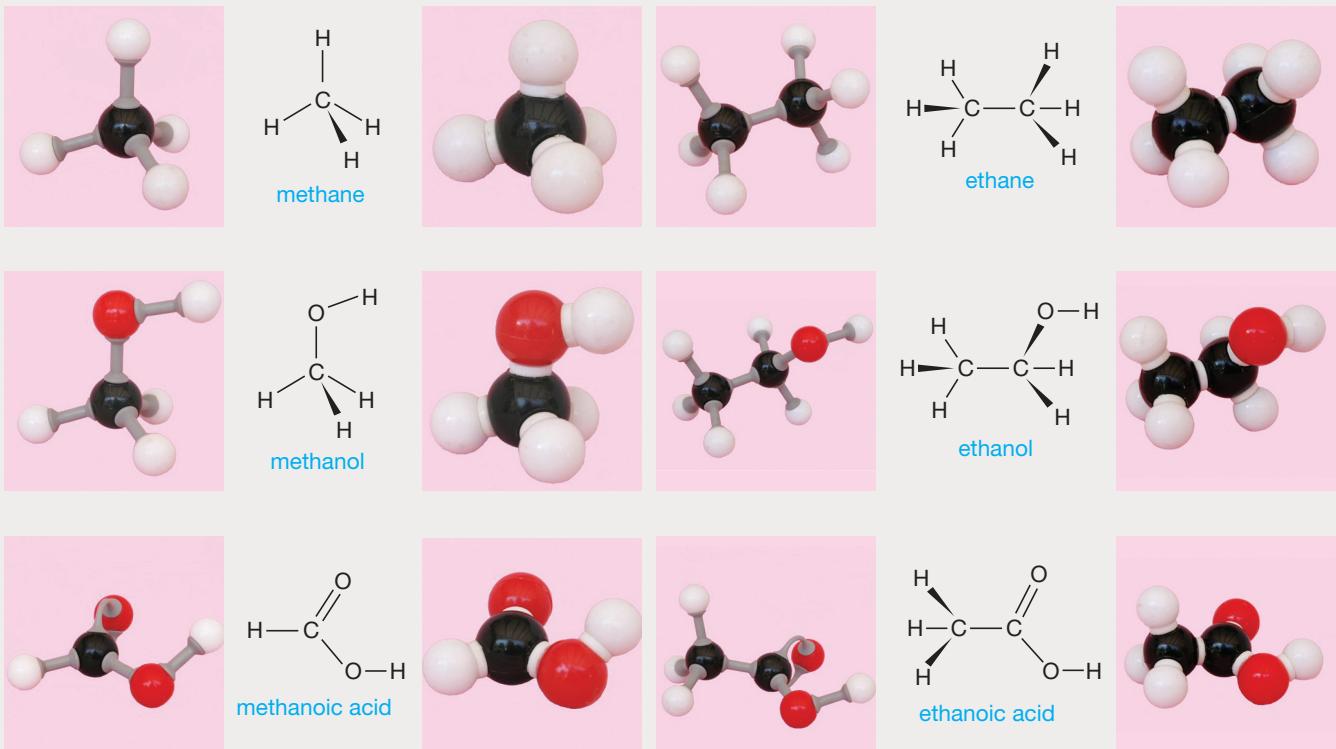
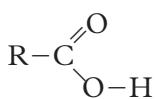
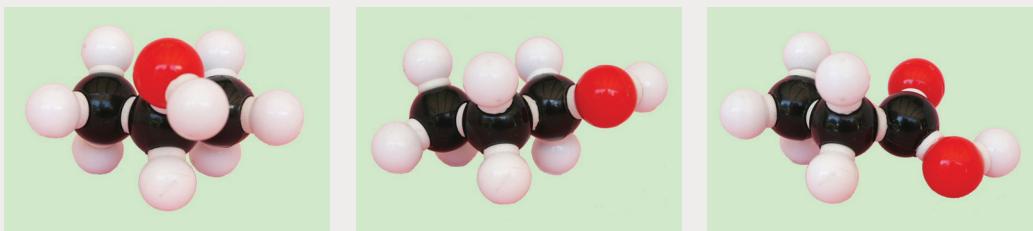
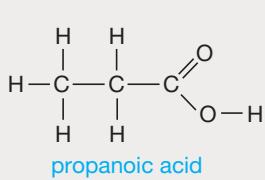
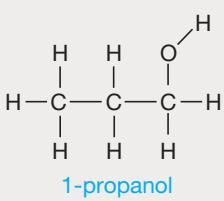
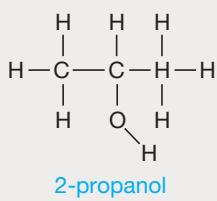
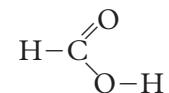


FIGURE 5.4 (above)
Ball-and-stick and
space-filling models
for the simplest
alkanes, alkanols and
alkanoic acids

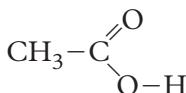


where R is an alkyl group (Section 1.4) or an H atom. The simplest alkanoic acids are:

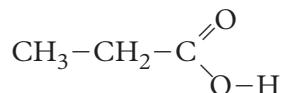
FIGURE 5.5 (left)
Ball-and-stick and space-filling models of 2- and 1-propanol and propanoic acid



methanoic acid
(formic acid)

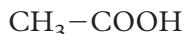


ethanoic acid
(acetic acid)



propanoic acid

For convenience we often write these structures as:



The homologous series called alkanoic acids has the general formula $\text{C}_n\text{H}_{2n}\text{O}_2$ with $n > 0$ or $\text{C}_n\text{H}_{2n+1}\text{COOH}$ with $n \geq 0$.

Models of the simplest alkanoic acids, along with the alkanes and alkanols they come from, are shown in Figures 5.4 and 5.5.

Names of alkanoic acids

These are derived by dropping the final *e* from the parent alkane and adding the suffix *-oic* and the word ‘acid’; methanoic, ethanoic and propanoic acids for the examples above. $\text{C}_5\text{H}_{10}\text{O}_2$ or $\text{C}_4\text{H}_9\text{COOH}$ is pentanoic acid, and $\text{C}_8\text{H}_{16}\text{O}_2$ or $\text{C}_7\text{H}_{15}\text{COOH}$ is octanoic acid. However, formic acid and acetic acid are the IUPAC-preferred names for methanoic and ethanoic acids†.

Because the $-\text{COOH}$ group has only one free carbon valence, it must always be at the end of a carbon chain. Hence no number is needed to signify its location.

Methanoic (formic) acid is present in ant stings, while ethanoic (acetic) acid is the key constituent of vinegar. Butanoic acid gives rancid butter its unpleasant odour.

The $-\text{COOH}$ group is called the **carboxylic acid group**. **Carboxylic acids** are compounds which contain this group, regardless of what is attached to it. CH_3-COOH and $\text{Cl}-\text{CH}_2-\text{COOH}$ are both carboxylic acids; CH_3COOH is an alkanoic acid, but $\text{Cl}-\text{CH}_2-\text{COOH}$ is not.

Alkanoic acids are weak acids and undergo the usual reactions of such acids, such as dissolving in sodium hydroxide solution to form soluble sodium salts and reacting with sodium carbonate to form bubbles of carbon dioxide.

5.17 MELTING AND BOILING POINTS OF ALKANOLS AND ALKANOIC ACIDS

Both the C–O and the O–H bonds are polar. This means that alkanols are polar molecules. The C=O bond is also polar, so with these three polar bonds alkanoic acids are even more polar. In addition to simple polarity, O–H bonds are able to form hydrogen bonds. Consequently *there are strong intermolecular forces in alkanols and in alkanoic acids*. Therefore they have much higher melting and boiling points than alkanes of similar molecular weight as shown in Table 5.7. They also have quite high solubilities in water. To show the effect of polarity and/or hydrogen bonding on physical properties we generally compare compounds with similar molecular weights, because the dispersion forces will be roughly similar in such compounds. This is because the strength of dispersion forces increases as the number of electrons in the molecule increases, and the

† See pp. 261–2 CCPC for an explanation of the use of systematic versus trivial names.

number of electrons generally increases as molecular weight increases, at least in compounds of similar structure.

TABLE 5.7 Boiling points for alkanes, alkanols and alkanoic acids of similar molecular weights

Molecular weights ^a	Alkane	Boiling point (°C)	Alkanol	Boiling point (°C)	Alkanoic acid	Boiling point (°C)
16	methane	-162				
30, 32	ethane	-89	methanol	65		
44, 46	propane	-42	ethanol	78	methanoic	100
58, 60	butane	-0.5	1-propanol	97	ethanoic	118
72, 74	pentane	36	1-butanol	117	propanoic	141
86, 88	hexane	69	1-pentanol	138	butanoic	164
100, 102	heptane	98	1-hexanol	157	pentanoic	186

a The first value is for the alkane; the second is for both the alkanol and the alkanoic acid.

Alkanols and alkanoic acids react to form compounds called *esters*.

Exercises

31 Draw structural formulae for:

- a** 2-pentanol
- c** 3-heptanol
- b** butanoic acid
- d** hexanoic acid

32 Name the following compounds

- a** $\text{CH}_3-\text{CH}_2-\underset{\text{OH}}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{CH}_3$
- c** $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3-\text{CH}_2}{\underset{|}{\text{CH}_2}}-\text{CH}-\text{OH}$
- b** $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
- d** $\text{CH}_3-(\text{CH}_2)_6-\text{COOH}$

33 a Using data in Table 5.7 and just the one set of axes, draw graphs of boiling points of

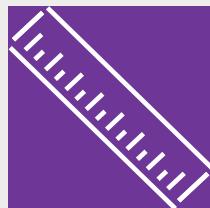
- i** alkanols
- ii** alkanoic acids

against number of carbon atoms per molecule. Draw suitable curves or lines through the points and summarise how boiling point depends upon number of carbon atoms in the molecule. Offer an explanation for any trends that you observe. In addition explain why the curves for the two sets of compounds are separated from each other.

b Use your graphs to estimate the boiling points of:

- i** 1-heptanol
- ii** hexanoic acid

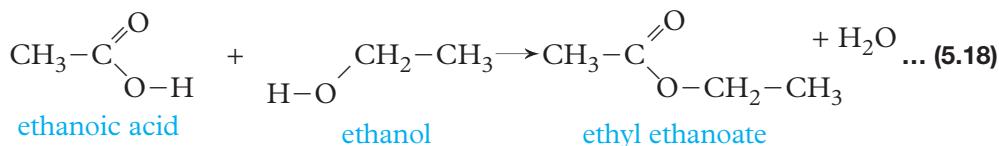
Assess the accuracy of your estimates: that is, give your estimates as $(x \pm y)^\circ\text{C}$. Keep your graph for Exercise 41 below.



5.18 ESTERS

Esters are compounds formed when alkanoic acids react with alkanols, or more generally, when carboxylic acids combine with alcohols.

When ethanoic (acetic) acid and ethanol are heated with a few drops of concentrated sulfuric acid, the ester, ethyl ethanoate (ethyl acetate) is formed:



Esters contain the structural unit



Table 5.8 presents structures and properties for some common esters. Models of the most widely used ester, ethyl acetate, are shown in Figure 5.6.

TABLE 5.8 Formulae and properties of common esters

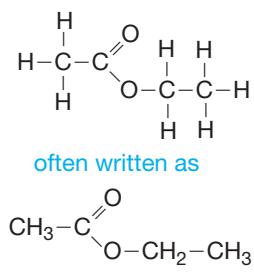
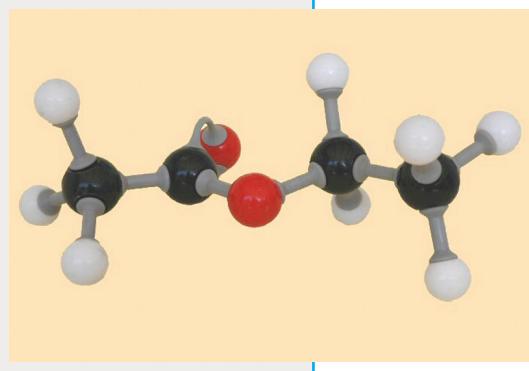
Name ^a	Formula	Molecular weight	Boiling point (°C)	Solubility in water ^b
methyl methanoate (formate)	$\text{H}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	60	32	24
methyl ethanoate (acetate)	$\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	74	57	6.7
methyl propanoate	$\text{CH}_3-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	88	80	7.3
ethyl ethanoate (acetate)	$\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_3$	88	77	7.5
propyl ethanoate (acetate)	$\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	102	102	2

a Formate and acetate are the IUPAC-preferred names, although the systematic names are methanoate and ethanoate.

b grams of solute per 100 g water

FIGURE 5.6

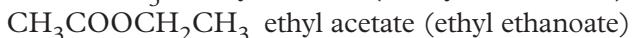
FIGURE 3.6 Ball-and-stick and space-filling models of the ester ethyl acetate (ethyl ethanoate)



Naming esters[†]

Esters from alkanols and alkanoic acid are named as *alkyl alkanoates*: the alkyl part of the name comes from the alcohol from which the ester was formed, and the alkanoate from the alkanoic acid. The first three esters of Table 15.8 are all methyl esters (because they come from methanol); the acids they were formed from are methanoic, ethanoic and propanoic acids. So their systematic names are methyl methanoate, methyl ethanoate and methyl propanoate. However because the IUPAC-preferred names for the first two acids are formic and acetic acids, the preferred names for the first two of these esters are methyl formate and methyl acetate.

For ease of printing, esters are often written as:



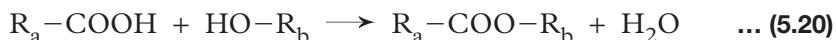
but it must be clearly understood that the $-\text{COOC}-$ means the arrangement of bonds shown in Structure 5.19.

Properties and synthesis

The C=O and C–O bonds make esters *polar substances*. However the lack of hydrogen bonding means that esters have much lower boiling points than acids or alkanols of the same molecular weight (compare Tables 5.7 and 5.8). They are also much less soluble in water.

The reaction between an alkanol and an alkanoic acid is called **esterification**.

In general terms it can be written as:

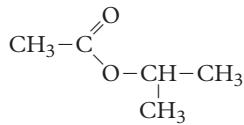


where R_a and R_b are alkyl groups. R_a and R_b may be the same group or different ones; R_a (but not R_b) may be a hydrogen atom (in which case the ester is a methanoate).

Esterification is moderately slow at room temperature and the reaction does not go to completion: it comes to equilibrium. To speed up the reaction *concentrated sulfuric acid is used as a catalyst*; it also absorbs the product water and so forces the equilibrium to the right. In addition the reaction is often carried out at temperatures near the boiling point of the alcohol. In order to prevent the alcohol being lost by vaporisation, the reaction flask is usually fitted with a water-cooled condenser as shown in Figure 5.7. This causes any alcohol vapour which rises from the hot reaction mixture to be condensed and to run back into the reaction vessel. This process is called *refluxing*.

† The naming rule given here does not address the question of which carbon atom of the alkyl group is attached to the O of the ester group. However for the NSW HSC, students are required to consider only esters with the end carbon atom of the alkyl group attached to the O, esters from so-called primary alkanols. No numbering is needed for these esters though for all other esters a number must be given to indicate which of the C atoms of the alkyl group is attached to the O of the ester group.

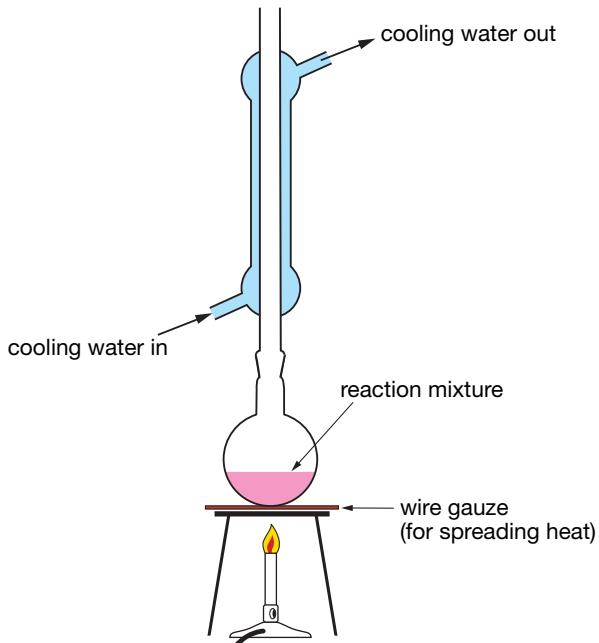
Hence 2-propyl acetate for



but just propyl acetate for the last entry in Table 5.8.

Refluxing is the process of heating a reaction mixture in a vessel with a cooling condenser attached in order to prevent loss of any volatile reactant or product.

FIGURE 5.7
Simple apparatus for refluxing



It allows the reaction to be brought about at a higher temperature than would otherwise be possible. The alternative of performing the reaction in a closed vessel could lead to a dangerous build-up of pressure and the possibility of an explosion.

5.19 OCCURRENCE AND USES OF ESTERS

Esters have pleasant, fruity odours and occur widely in nature as perfumes and flavouring agents. While the characteristic smells or flavours of many plants and fruits usually arise from a complex mixture of substances, often one ester can be identified as the major ingredient of the smell or flavour. Some such esters are listed in Table 5.9.

TABLE 5.9 Esters in some common natural flavours^a

Flavour	Main ester(s) present
apple	methyl butanoate and iso-pentyl pentanoate ^b
banana	iso-pentyl ethanoate ^b
grape	ethyl methanoate and ethyl heptanoate
orange	octyl thanoate
pear	pentyl ethanoate
raspberry	butyl ethanoate
rum	ethyl methanoate
jasmine	benzyl ethanoate

a Each natural flavour results from a complex mixture of many esters. These are just the main ones in the flavours listed.

b iso-pentyl is $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_2-$. The systematic names for these esters are 3-methyl-1-butyl pentanoate or 3-methyl-1-butyl ethanoate, though the -1- is often omitted.

What we mean by flavour is really a combination of crude taste (sweet, sour, salt, bitter) and odour; it is the odour of esters that contributes to flavours. There is now a substantial industry for developing and manufacturing synthetic flavours and perfumes. The first step is often to identify the constituents of the natural flavour and then to synthesise similar mixtures of esters which reproduce this flavour. Such artificial flavours are often cheaper than natural extracts, and provided they contain only substances that occur in the natural flavours, they represent little health hazard. Esters for such flavours are synthesised as described above using Equation 5.20.

Ethyl acetate (ethanoate) is widely used as a solvent in industry. It is also the common solvent in nail polish remover. It is manufactured on a large scale from acetic acid and ethanol (Equation 5.18), using in principle the same process as is used in the laboratory. High molecular weight (i.e. non-volatile) esters such as dialkyl phthalates are used as plasticisers in some plastics such as PVC: they make the materials soft and pliable. Again they are synthesised by using Equation 5.20.



Some everyday substances that contain esters—perfume, nail polish remover and food flavourings

Functional groups

Recall from p. 267 CCPC that a *functional group* is a *centre of reactivity* in a carbon compound. This account of alkanols, alkanoic acids and esters has introduced three functional groups:

- the *alcohol* functional group $\text{---}\overset{\text{l}}{\underset{|}{\text{C}}}\text{---O---H}$
- the *carboxylic acid* functional group $\text{---}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{---O---H}$
- the *ester* functional group $\text{---}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{---O---}\overset{\text{l}}{\underset{|}{\text{C}}}\text{---}$

Exercises

34 Name the following compounds:

- | | |
|---|---|
| a $\text{H---C}=\text{O---CH}_2\text{---CH}_3$ | c $\text{CH}_3\text{---CH}_2\text{---C}=\text{O---CH}_2\text{---CH}_2\text{---CH}_3$ |
| b $\text{CH}_3\text{---CH}_2\text{---O---C}=\text{O---CH}_3$ | d $\text{CH}_3\text{---O---C}=\text{O---CH}_2\text{---CH}_2\text{---CH}_3$ |

35 Draw structural formulae for:

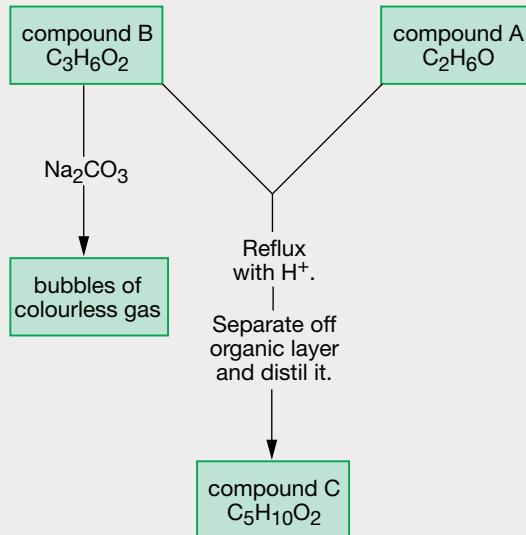
- | | | |
|----------------------------|--------------------------|-------------------------|
| a methyl propanoate | c butyl hexanoate | e ethyl formate |
| b propyl methanoate | d hexyl butanoate | f pentyl acetate |

36 Draw structural formulae for three esters of molecular formula $\text{C}_4\text{H}_8\text{O}_2$. Name them.

37 Write equations for the formation of the esters in Exercises 35 and *36. Describe with full experimental detail how you would prepare one of these esters in the laboratory.



- 38 a** Explain why methyl acetate has a much lower boiling point than ethanoic acid (57°C compared with 118°C), despite having a higher molecular weight.
- b** Explain why acetic acid has a much greater solubility in water than methyl formate.
- 39** Explain why the solubility of esters in water decreases as molecular weight increases (Table 5.9).
- 40** Consider the following reaction scheme:



Tests show that compound A is an alkanol.

- a** Deduce the structures of compounds B and C and name them.
- b** Write equations for the two reactions involved.
- c** Draw diagrams of the apparatus used to ‘reflux’ and ‘distil’ on the chart, and explain what these processes do.
- 41 *a** On the graph you drew in Exercise 33, plot boiling points of methyl esters against the number of carbon atoms in the alkanoate part of the molecule and draw a suitable curve or line through the points. Some boiling points are in Table 5.8: others are methyl butanoate, 102°C ; methyl pentanoate, 126.5°C .
- b** How does boiling point of these esters vary with number of carbon atoms in the alkanoate part of the molecule? How does the boiling point of a methyl ester compare with that of the parent alcanoic acid? Offer an explanation for this.
- 42 a** A sample of octyl ethanoate (which is insoluble in water) was contaminated with a small amount of ethanoic acid (which is soluble in water). Explain how you would use water and a separating funnel to purify the octyl ethanoate. Sketch the separating funnel.
- b** Another sample of octyl ethanoate was contaminated with a small amount of pentanoic acid, which is soluble in the octyl ethanoate but insoluble in water. Explain how you would use an aqueous solution of sodium carbonate and a separating funnel to purify this octyl ethanoate.
- 43** Compound X was prepared by the following procedure.
- 0.20 mol acetic (ethanoic) acid, 0.15 mol 1-propanol and 1 mL concentrated sulfuric acid were refluxed for 15 min. After cooling the reaction mixture was poured into 20 mL water, shaken vigorously, then allowed to settle. Two layers formed. The two layers were separated using a separating funnel and the aqueous layer was discarded. Small quantities of sodium carbonate solution were added to the organic layer until effervescence ceased. Another 10 mL water was added, the mixture shaken then allowed to settle. Again the two layers were separated and the aqueous layer discarded. The organic layer was dried by allowing it to stand over granular anhydrous calcium chloride for 15 min. The drying agent was filtered off and the remaining liquid

distilled. The first 1 mL of the distillate was discarded and the distillation was stopped when about 1 mL remained in the distillation flask.

- a What is the name of the compound X being prepared? Write an equation for the chemical reaction.
 - b Which reactant was used in excess and how was the excess removed before distillation? Why did the first extraction with water not remove all of the excess reagent? How would you determine experimentally that, after settling, the bottom layer was the aqueous one? Smell is not acceptable (why?). Why was sodium carbonate added before the second extraction with water?
 - c Draw fully labelled diagrams for:
 - i the refluxing process
 - ii the distillation
- Why were the first and last 1 mL portions discarded in the distillation?
- d Why is compound X much less soluble in water than either of the reactants?

Important new terms

You should know the meaning of the following terms.

acid (Brönsted–Lowry) (p. 147)
acid salts (p. 151)
alcohol (p. 170)
alcohol group (p. 170)
alkanoic acid (p. 170)
amphiprotic (p. 154)
base (Brönsted–Lowry) (p. 147)
Brönsted–Lowry definitions of acids and bases (p. 147)
buffer solution (p. 167)
carboxylic acid (p. 172)
carboxylic acid group (p. 172)
conjugate acid (p. 148)
conjugate base (p. 148)

diprotic acid (p. 151)
end point (p. 158)
equivalence point (p. 158)
ester (p. 173)
esterification (p. 175)
hydrogen salts (p. 151)
hydrolysis (p. 154)
monoprotic acid (p. 151)
primary standard (p. 159)
proton transfer reaction (p. 156)
refluxing (p. 176)
standard solution (p. 159)
titrant (p. 158)
titration (p. 157)
triprotic acid (p. 151)
volumetric analysis (p. 157)

Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Describe the nature of the hydrogen ion in aqueous solution.
- 3 Why is the Arrhenius definition of an acid not entirely satisfactory?
- 4 What are the conjugate bases of HCl, H₂SO₄ and CH₃COOH?
- 5 What are the conjugate acids of N₂H₄ (hydrazine), OH[−] and CO₃^{2−}?
- 6 Give the names and formulae of two diprotic acids and one triprotic acid and of the three different potassium salts that can be formed from the triprotic acid.
- 7 Name three salts that, in aqueous solution, you would expect to have a pH
 - a of approximately 7
 - b significantly less than 7
 - c significantly greater than 7.

- 8** Explain why your salts have these pHs.
- 9** Give two examples of amphiprotic substances and illustrate their amphiprotism by writing equations.
- 10** Write equations for two neutralisation reactions. Use these to explain why neutralisation is considered a proton-transfer reaction.
- 11** Name one primary standard for acid–base analysis and explain why it is suitable for this purpose.
- 12** Describe, with full experimental detail, how you would prepare a standard solution of this primary standard.
- 13** Describe, with full experimental detail, how you would use a burette and pipette to determine the concentration of an acid solution by using an alkali solution of accurately known concentration.
- 14** Explain how a buffer solution works. Give a specific example.
- 15** Describe two situations in nature where buffers are involved and explain how they function.
- 16** What is the general formula for the homologous series of alkanols?
- 17** Give the names and structural formulae of the first six alkanols.
- 18** Draw the structures and give the names of the first five alkanoic acids.
- 19** Give the full structure of the carboxylic group, –COOH.
- 20** What is the difference between the two terms
 - a** alcohol and alkanol
 - b** carboxylic acid and alkanoic acid?
- 21** Explain why alkanols and alkanoic acids have polar molecules, and give three consequences of this polarity.
- 22** Give names and structural formulae for four esters.
- 23** How are esters prepared? Give two examples, including equations.
- 24** Describe, with full practical details, how you would carry out an esterification.
- 25** What is meant by *refluxing* in chemical contexts? Sketch a simple set of apparatus for carrying out this procedure.
- 26** Sketch apparatus for carrying out a simple distillation.
- 27** Why are esters more volatile than the carboxylic acids they are derived from, despite having higher molecular weights?
- 28** Where do esters occur in nature? What are some practical uses of esters?
- 29** Draw the structures of the alcohol, carboxylic acid and ester functional groups.

EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 2

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination; for more information see p. 93.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

MARKS

- | | | |
|----|---|---|
| 1 | The solubility of carbon dioxide in water depends upon the pressure of carbon dioxide gas above the solution and upon the pH of the solution. Use these facts to demonstrate the usefulness of Le Chatelier's principle. | 5 |
| 2 | Explain why a solution of sodium acetate (ethanoate) is alkaline and a solution of ammonium nitrate is acidic, while solutions of sodium iodide and potassium nitrate are neutral. | 5 |
| 3 | Describe an experiment you have performed to prepare and test a natural indicator. List at least three everyday substances whose acidity you tested with this indicator and include the results you obtained for each. | 4 |
| 4 | Outline the human activities, using chemical equations where appropriate, that release oxides of nitrogen and sulfur to the atmosphere. Indicate whether or not these releases are leading to increases in the overall global concentrations of these gases in the atmosphere and explain why this is so. | 6 |
| 5 | Assess the usefulness of the pH scale to chemistry and the world at large. | 4 |
| 6 | Explain how a buffer works, using a specific example from a natural system. | 5 |
| 7 | Evaluate the use of a set of indicators (as opposed to an electronic pH meter) for determining the approximate pH of a solution. Mention at least one everyday example of this use. | 4 |
| 8 | Compare the melting and boiling points of alkanols, alkanoic acids and esters, and explain any similarities and differences. | 5 |
| 9 | Discuss the evidence for and against increases in atmospheric concentrations of oxides of sulfur and nitrogen. | 7 |
| 10 | Summarise the causes and effects of acid rain and explain the role of natural buffers in minimising the effects. | 6 |
| 11 | Explain with examples why acids are added to many foods. | 4 |
| 12 | Contrast, with examples, the meanings of the terms 'weak', 'strong', 'concentrated' and 'dilute' as applied to acids and bases. | 4 |
| 13 | Outline the way that the concept of an acid has developed from the time of Humphry Davy in the early 1800s to the work of Johannes Brönsted and Thomas Lowry in the 1920s. | 6 |
| 14 | Evaluate the effectiveness of placing containers of powdered sodium hydrogen carbonate around a chemical laboratory as a safety measure. | 4 |
| 15 | Explain the concept of conjugates for acids and bases and assess its usefulness. | 5 |

- 16** Describe an experiment you have performed to determine the concentration of a domestic acidic substance. Outline the measures you took to ensure that your results were accurate. **7**
- 17** A pair of students who performed the experiment described in Question 16 obtained results that were very reproducible but not accurate. What does ‘very reproducible but not accurate’ mean? Propose reasons for the students getting such results. **4**
- 18** Describe an experiment you have performed to measure the pH of a range of salt solutions. Mention the precautions you took to ensure the accuracy of your results. For three of the salts used explain why their pHs were different from 7. **7**
- 19** Contrast the two processes, refluxing and distillation. **4**
- 20** Classify each of the following oxides as acidic, basic or neutral and, for each, give an equation or reason for your classification: magnesium oxide, diphosphorus pentoxide, nitric oxide, nitrogen dioxide and copper oxide. **5**

REVISION TEST FOR MODULE 2

MODULE 2

Total marks: 50 Suggested time: 90 minutes

At a pressure of 100.0 kPa the molar volume of a gas is 22.7 L at 0°C and 24.8 L at 25°C. The ionic product constant for water, K_w at 25°C is 1.0×10^{-14} . Table 5.5 on p. 164 may be used if necessary.

Table 5.5 on p. 164 may be used if necessary.

MULTIPLE CHOICE QUESTIONS (1 mark each)

Select the alternative **a**, **b**, **c**, or **d** which best answer the question.

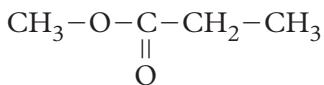
- 1** The conjugate base of the acid HCrO_4^- is:

a H_2CrO_4 **c** CrO_4^{2-}
b H_2CrO_4^- **d** CrO_4^-

2 The list which contains only acidic oxides is:

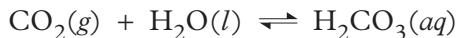
a $\text{CO}, \text{CO}_2, \text{B}_2\text{O}_3, \text{SO}_3$ **c** $\text{P}_2\text{O}_3, \text{NO}, \text{SO}_2, \text{Cl}_2\text{O}$
b $\text{Cl}_2\text{O}, \text{P}_2\text{O}_5, \text{NO}_2, \text{SO}_2$ **d** $\text{N}_2\text{O}, \text{NO}_2, \text{CO}_2, \text{SO}_3$

3 The correct name for the compound having the following structure is:



- | | | | |
|----------|------------------|----------|-------------------|
| a | methyl acetate | c | methyl ethanoate |
| b | ethyl methanoate | d | methyl propanoate |

- 4 The dissolution of carbon dioxide in water is an exothermic equilibrium reaction:



The solubility of carbon dioxide can be increased (that is, this reaction driven towards the right) by:

- 5** The boiling points for methyl propanoate, butanoic acid and 1-pentanol in that order are:

a 138°C, 80°C, 164°C	c 164°C, 138°C, 80°C
b 80°C, 138°C, 164°C	d 80°C, 164°C, 138°C

- 6 The volume of carbon dioxide measured at 0°C and 100.0 kPa pressure that can be absorbed by 0.30 mol potassium hydroxide is:

- a** 3.41 L **c** 13.6 L
b 6.81 L **d** 3.72 L

- 7 The pH of a solution of completely ionised sulfuric acid was 3.40. This means that in that solution the sulfate ion concentration in moles per litre was:

- $$\mathbf{b} \quad 2.0 \times 10^{-4}$$

- 8** When 25 mL 0.0858 mol/L sodium carbonate solution was titrated with a solution of hydrochloric acid, the volume of acid needed to reach the equivalence point was 37.8 mL. The concentration of the hydrochloric acid solution in moles per litre is:

- a** 0.0567 **c** 0.130
b 0.0284 **d** 0.113

- 9** For a titration of ammonia solution with a nitric acid solution, a suitable indicator, with a correct reason for choosing it, is:
- phenolphthalein, because it changes colour at pH > 7 and at the equivalence point of this titration the pH is greater than 7
 - litmus, because it changes colour around pH 7 and for a neutralisation reaction the equivalence point occurs at pH 7
 - methyl orange because it changes colour at pH < 7 and at the equivalence point of this titration the pH is less than 7
 - any one of the above three indicators, because for a neutralisation reaction the equivalence point occurs at pH 7
- 10** The list which contains oxides whose concentrations in the atmosphere have all been increasing significantly over the past 100 years is:
- CO₂ and N₂O
 - CO₂, SO₂ and NO₂
 - CO, SO₂ and NO
 - CO₂ and NO₂

SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

The number of marks for each part of each question is shown at the right-hand end of the question. Marks allocated are based on the HSC scale of 1 mark per 1.8 minutes.

- | | |
|--|--------------|
| | MARKS |
|--|--------------|
- 11 a** When drops of indicators were added to samples of Solutions P, Q, R, S, the colours were as shown below. Use Table 5.5 on page 164 to determine the pH of each solution. You may have to give a range within which the pH lies. 2
- | Solution | P | Q | R | S |
|-------------------|------------|------------------------|-----------|-------------------------|
| Indicator: colour | bcg: blue | pr: red | pr: red | mo: orange ^b |
| | pr: yellow | tb: green ^a | phth: red | bcg: yellow |
- bcg: bromocresol green; mo: methyl orange; phth: phenolphthalein; pr: phenol red; tb: thymol blue*
a green = yellow + blue
b orange = red + yellow
- b** The pHs of two solutions A and B are 4.0 and 5.3 respectively. In which solution is the hydrogen ion the greater? How many times greater is it in this solution than in the other one? 1
- 12** Many fresh water lakes are buffered by a mixture of carbonic acid from rain and hydrogen carbonate (leached from rocks and soils). Explain what ‘buffered’ means. Illustrate by writing equations for what happens when acid or alkali is added to such water. Include mention of Le Chatelier’s principle in your explanation. 2
- 13** Outline an experiment you have performed to prepare an ester. Include a diagram and an equation. Which reactant did you use in excess and why? 7
- 14** Naturally occurring citric acid has the molecular formula C₆H₈O₇. Like all acids it reacts with carbonate solution to form carbon dioxide gas. When 1.537 g citric acid was added to a solution containing excess sodium carbonate, 299 mL carbon dioxide (measured at 25°C and 100.0 kPa pressure) was formed.

- a** How many moles of carbon dioxide were formed? **1**
- b** Write an equation for the reaction of hydrogen ions with carbonate ions. Therefore, how many moles of hydrogen ion did the 1.537 g citric acid produce? **1**
- c** Hence determine whether citric acid is mono-, di- or triprotic. Explain your reasoning. **1**
- 15 a** Name the following compounds:
- i** $\text{CH}_3-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$
- ii** $\text{CH}_3-\text{CH}_2-\underset{\text{O}-\text{H}}{\overset{\text{O}}{\text{C}}}$
- iii** $\text{CH}_3-\underset{\text{O}-\text{CH}_3}{\overset{\text{O}}{\text{C}}}$ **2**
- b** Which, if any, of these compounds is(are) isomers? Explain why. **1**
- 16** Demonstrate that oxides of elements on the left-hand side of the Periodic Table are basic while those of elements on the right-hand side are acidic. Include chemical equations. **4**
- 17** Oxalic acid dihydrate, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, a diprotic acid, is sometimes used to standardise sodium hydroxide solutions. For one particular experiment, 0.495 g oxalic acid dihydrate was measured out and dissolved in about 50 mL of water. One drop of phenolphthalein indicator was added and the solution titrated with the sodium hydroxide solution that was required to be standardised. 38.7 mL was needed to reach the equivalence point.
- a** Give two reasons why sodium hydroxide solutions need to be standardised. **1**
- b** Give two properties or characteristics which oxalic acid dihydrate must have if it is suitable for use to standardise hydroxide solutions. **1**
- c** Describe the steps you would take to prepare the burette for dispensing the sodium hydroxide solution in order to make the titration as accurate as possible. **1**
- d** Calculate the molarity of the sodium hydroxide solution. **1**
- 18** 0.050 mol/L aqueous solutions of two acids, HP and HQ, were prepared. The solutions of HP and HQ had pHs of 3.30 and 1.30 respectively.
- a** Calculate the hydrogen ion concentrations in these solutions. **1**
- b** Classify HP and HQ as weak or strong acids, giving your reason. **1**
- c** If either of, or both, acids is(are) weak, calculate its (their) degree of ionisation. **3**
- 19** Justify the claim that for all strong and weak acids and bases neutralisation is a proton-transfer reaction. **4**
- 20** Assess the impact of human sources of oxides of sulfur and nitrogen upon the environment, using chemical equations where appropriate. **7**

MODULE 2 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 2 of the New South Wales Higher School Certificate Course.

Syllabus content

The following table lists (for Module 2) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

Location of HSC Course material in *Conquering Chemistry* for Module 2

Syllabus reference Students learn to	Sections where found in CCHSC
9.3.1 Indicators were identified with the observation that the colour of some flowers depends on soil composition	
■ classify common substances as acidic, basic or neutral	4.1, 4.13
■ 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	4.2
■ identify and describe some everyday uses of indicators including the testing of soil acidity/basicity	4.2
9.3.2 While we usually think of the air around us as neutral, the atmosphere naturally contains acidic oxides of carbon, nitrogen and sulfur. The concentrations of these acidic oxides have been increasing since the Industrial Revolution	
■ identify oxides of non-metals which act as acids and describe the conditions under which they act as acids	4.5
■ analyse the position of these non-metals in the Periodic Table and outline the relationship between position of elements in the Periodic Table and acidity/basicity of oxides	4.5
■ define Le Chatelier's principle	4.7
■ identify factors which can affect the equilibrium in a reversible reaction	4.7
■ describe the solubility of carbon dioxide in water under various conditions as an equilibrium process and explain in terms of Le Chatelier's principle	4.6, 4.8
■ identify natural and industrial sources of sulfur dioxide and oxides of nitrogen	4.9
■ describe, using equations, examples of chemical reactions which release sulfur dioxide and chemical reactions which release oxides of nitrogen	4.9
■ assess the evidence which indicates increases in atmospheric concentration of oxides of sulfur and nitrogen	4.10

Syllabus reference	Sections where found in CCHSC
Students learn to	
■ calculate volumes of gases given masses of some substances in reactions, and calculate masses of substances given gaseous volumes, in reactions involving gases at 0°C and 100 kPa or 25°C and 100 kPa	4.12
■ explain the formation and effects of acid rain	4.11
9.3.3 Acids occur in many foods, drinks and even within our stomachs	
■ define acids as proton donors and describe the ionisation of acids in water	5.2, 4.14
■ identify acids including acetic (ethanoic), citric (2-hydroxypropane-1,2,3-tricarboxylic), hydrochloric and sulfuric acid	4.13
■ describe the use of the pH scale in comparing acids and bases	4.15 to 4.18
■ describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute	4.20
■ identify pH as $-\log_{10}[\text{H}^+]$ and explain that a change in pH of 1 means a tenfold change in $[\text{H}^+]$	4.15
■ compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids and explain in terms of the degree of ionisation of their molecules	4.20
■ describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions	4.20
9.3.4 Because of the prevalence and importance of acids, they have been used and studied for hundreds of years. Over time the definitions of acid and base have been refined	
■ outline the historical development of ideas about acids including those of	5.1
– Lavoisier	
– Davy	
– Arrhenius	
■ outline the Brönsted–Lowry theory of acids and bases	5.2
■ describe the relationship between an acid and its conjugate base and a base and its conjugate acid	5.2
■ identify a range of salts that form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature	5.5
■ identify conjugate acid/base pairs	5.2
■ identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions	5.6
■ identify neutralisation as a proton transfer reaction which is exothermic	5.7
■ describe the correct technique for conducting titrations and preparation of standard solutions	5.8 to 5.12
■ qualitatively describe the effect of buffers with reference to a specific example in a natural system	5.13, 5.14

Syllabus reference Students learn to	Sections where found in CCHSC
9.3.5 Esterification is a naturally occurring process which can be performed in the laboratory	
■ describe the differences between the alkanol and alkanoic acid functional groups in carbon compounds	5.16
■ identify the IUPAC nomenclature for describing the esters produced by reactions of straight-chained alkanoic acids from C1 to C8 and straight-chained primary alkanols from C1 to C8	5.18
■ explain the difference in melting point and boiling point caused by straight-chained alkanoic acid and straight-chained primary alkanol structures	5.17
■ identify esterification as the reaction between an acid and an alkanol and describe, using equations, examples of esterification	5.18
■ describe the purpose of using acid in esterification for catalysis	5.18
■ explain the need for refluxing during esterification	5.18
■ outline some examples of the occurrence, production and uses of esters	5.19

Compulsory experiments

The table below lists the compulsory experiments (from the right-hand column of the syllabus), along with places where you can find procedures for these experiments (in *CCHSC BLM*) and the location of relevant information in *CCHSC*.

CCHSC is an abbreviation for this book *Conquering Chemistry HSC Course*.

CCHSC BLM is *Conquering Chemistry HSC Course Blackline Masters* by Debra Smith, McGraw-Hill, Sydney, 2003.

Information about compulsory experiments for Module 2

Experiment	Location in CCHSC BLM	Related material in CCHSC ^a
1 Prepare and test a natural indicator.	Module 2 Worksheet 2 (p. 53)	Section 4.2 Exam-style Question 3
2 Decarbonate soft drink and gather data to calculate the mass changes involved and calculate the volume of gas released at 25°C and 100 kPa.	Module 2 Worksheet 5 (p. 63)	Sections 4.6 to 4.8 and 4.12 Chapter 4 Exercise 24(b)
3 Use pH meters/probes and indicators to distinguish between acidic, basic and neutral chemicals.	Module 2 Worksheet 7 (p. 69)	Section 4.19 including Example 6 Chapter 4 Exercises 32, 33 Revision Test Question 11(a)
4 Measure the pH of identical concentrations of strong and weak acids.	Module 2 Worksheet 9 (p. 78)	Section 4.20 Chapter 4 Exercises 35, 36 Revision Test Question 18
5 Determine the pH of a range of salt solutions.	Module 2 Worksheet 11 (p. 85)	Section 5.5 Exam-style Question 18

Experiment	Location in CCHSC BLM	Related material in CCHSC^a
6 Carry out titrations, including the preparation of standard solutions and the calculation of results.	Module 2 Worksheet 13 (p. 94)	Sections 5.8 to 5.12 Chapter 5 Exercises 16 to 24 Revision Test Question 17
7 Determine the concentration of a domestic acidic substance.	Module 2 Worksheet 14 (p. 98)	Sections 5.8 to 5.12 Chapter 5 Exercises 19, 23, 26
8 Prepare an ester using reflux.	Module 2 Worksheet 17 (p. 111)	Section 5.18 Chapter 5 Exercise 43 Revision Test Question 13

^a Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.

Other items in the student activity (right-hand) column

The table below lists (in abbreviated form) the non-experimental items in the student activity (right-hand) column of the syllabus and indicates where in *Conquering Chemistry* relevant information is located.

Location of material for other Module 2 activities

Syllabus item	Relevant material in CCHSC
9.3.1	<ul style="list-style-type: none"> ■ Experiment 1 (see previous table) ■ identify data ... about the colour changes of ... indicators ■ solve problems ... indicators ... to classify some household substances as acidic, neutral or basic
9.3.2	<ul style="list-style-type: none"> ■ Experiment 2 (see previous table) ■ analyse information ... industrial origins of [SO₂ and NO_x]... and evaluate reasons for concern about their release into the environment
9.3.3	<ul style="list-style-type: none"> ■ Experiment 3 (see previous table) ■ Experiment 4 (see previous table) ■ gather ... information ... to write ionic equations ... ionisation of acids ■ ... model the molecular nature of acids and ... ionisation of strong and weak acids ■ gather ... information ..., to explain the use of acids as food additives ■ identify data ... examples of naturally occurring acids and bases and their chemical composition ■ process information ... to calculate the pH of strong acids ...
9.3.4	<ul style="list-style-type: none"> ■ gather ... information ... to trace developments in understanding ... acid/base reactions

Syllabus item	Relevant material in CCHSC
■ Experiment 5 (see previous table)	
■ Experiment 6 (see previous table)	
■ Experiment 7 (see previous table)	
■ analyse information ... use of neutralisation reactions as a safety measure ...	Section 5.15 Exam-style Question 14
9.3.5 ■ Experiment 8 (see previous table)	
■ process information ... uses of esters as flavours and perfumes ...	Section 5.19

Prescribed focus areas

The five prescribed focus areas of the syllabus are listed on p. 101.

As with most modules, the material of Module 2 (in this book and in the syllabus) relates strongly to focus areas 2 and 3, the nature and practice of chemistry, and applications and use. However there are several opportunities in Module 2 for involving areas 1 and 4.

For area 1, the history of chemistry, there is the development of the concept of an acid from Lavoisier to Brönsted and Lowry. On a different level there is the move away from indicators to pH meters for measuring pH as the latter have become increasingly cheaper (relatively). Or more speculatively, the future of the concept of pH now that electronic calculators have made logarithms virtually redundant (at least for calculation purposes).

For area 4, implications for society and the environment, there is considerable scope on the environmental side, particularly in discussing oxides of sulfur and nitrogen in the atmosphere and acid rain and possibly the enhanced greenhouse effect, though that issue is not specifically mentioned in the syllabus. Implications for society could become involved if discussions of acids as food additives were allowed to expand into the question of food additives generally and the questions of what is ‘natural’ and what is not, and of the desirability of the former over the latter.

Module 2 does not offer much opportunity to treat area 5, current issues, research and development.