

MODULE 3

# Chemical monitoring and management

Industrialised societies today manufacture many substances and discard large amounts of wastes into the environment. Careful monitoring and management are essential if we are to produce substances efficiently with a minimum of waste, and if we are to protect the environment from the harmful effects of those industrial wastes and of the numerous other wastes we generate in our consumer-oriented society.

In this module, then, we shall look at several aspects of chemical monitoring and management.

We shall start with a survey of what chemists do in industry. This will involve a close look at one industrial process, the synthesis of ammonia (which is made in huge quantities worldwide, largely for fertiliser production). The discussion will show that careful monitoring and management improve the efficiency of the process (in materials, energy and dollar terms). This discussion will also let us explore further the nature of chemical equilibrium and the importance of reaction rates.

Monitoring chemical processes is only part of the job: the starting materials and the products of manufacturing must be analysed to ensure that they meet quality standards (i.e. are sufficiently pure and free from harmful contaminants).



Attention will therefore turn to analysing (both qualitatively and quantitatively) for ions in various products or mixtures. This monitoring of processes and products constitutes Chapter 6.

Many of the products of chemical industry either directly or indirectly end up in the environment, causing considerable harm. Therefore we shall turn to the question of monitoring and managing pollution of the atmosphere and of water.

To understand the effects and fates of chemicals released into the air, we need knowledge of the structure and functioning of the atmosphere and of the structure and properties of the chemicals involved. So in Chapter 7 we shall survey the atmosphere generally then look at several forms of air pollution and their sources. Particular attention will focus on the so-called ozone hole, the destruction of stratospheric ozone over the Antarctic in spring: the chemistry involved and the strategy for overcoming the problem will be discussed.

In Chapter 8 we shall consider monitoring water in the environment. The main criteria for assessing water quality will be described and several forms of water pollution will be discussed. We shall explore the variety of ways in which ions get into waterways, and the chapter will finish with a discussion of methods of treating and sanitising water for town and city supplies.



## BOTH MANUFACTURING AND THE ENVIRONMENT NEED CHEMICAL MONITORING

The efficient operation of large factories requires careful monitoring which is often done in separate chemical laboratories. One common side effect of manufacturing and other human activities is air pollution such as the Sydney smog in the photograph. Close monitoring of the environment is necessary in order to control and manage our pollution problems.



# Monitoring and management in the chemical industry

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In this chapter we shall look at some of the ways that chemists monitor and manage chemicals and chemical processes in industry. But first let us survey the roles of chemists in industry.

### 6.1 WHAT CHEMISTS IN INDUSTRY DO

In industry chemists mainly monitor and manage industrial processes. The main reasons for such monitoring and managing are to ensure that:

- chemical reactions proceed efficiently in terms of speed and yield
- the products are sufficiently pure and free from dangerous contaminants
- the raw materials meet specifications (i.e. that they do not contain impurities that would upset the process or pass through to the final product)
- the workplace remains safe and healthy
- gaseous and aqueous effluents and solid wastes from the factory meet statutory requirements in terms of not exceeding allowable amounts of pollutants.

The more highly qualified chemists are also involved in research and development as it relates to the chemicals and processes used in their particular manufacturing plant.

The job of one particular chemist will further illustrate the role of chemists.

## 6.2 THE JOB OF ONE PARTICULAR CHEMIST

Luke (not his real name) is a plant chemist at a major Australian chemical manufacturing company that makes ethylene from ethane, then polymerises it to polyethylene as described in Sections 1.1 and 1.6. This company is part of the chemicals and plastics manufacturing industry. It sells some of its ethylene to another company that uses it to make ethylene oxide and ethylene glycol (Section 1.5), non-ionic surfactants (Section 10.14) and starting materials for making other plastics (polymers).

### Components of Luke's job

- Monitoring the quality of the ethylene produced by the plant to ensure that it meets the requirements for the next stage of manufacture: in particular determining the nature and amount of any impurities present
- Monitoring waste water from the plant to ensure that it meets environmental requirements (such as pH, suspended solids, sulfate, grease, hydrocarbons) before it is discharged
- Monitoring gaseous emissions to the atmosphere to ensure that they do not contain particulates (solid particles plus small droplets of liquid) or polluting chemicals above what the statutory authorities allow, and
- Collaborating with process engineers at the cracking furnace (ethane to ethylene) to adjust operating conditions in order to optimise product yields.

As a chemist in the central laboratory, Luke is not so much concerned with the hour-by-hour monitoring of products and water wastes (that is done by shift workers); rather his job is to check that the equipment operates properly, to calibrate instruments from time to time, train shift workers in the use of the instruments, carry out occasional analyses to ensure the reliability of results, solve problems that arise and generally look out for ways of improving the overall monitoring process.

The efficient operation of plants as complex as this one requires regular routine monitoring. In addition there needs to be skilled chemists available to oversee this routine work, check on its reliability, solve problems that occur and develop new procedures as circumstances or operating conditions change. Luke is one of those chemists at this plant.

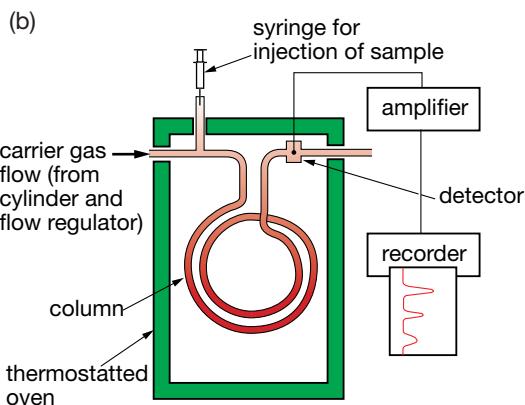
### The branch of chemistry

Luke mainly works in *analytical chemistry*—the part of chemistry concerned with determining what substances (and how much of each) are present in materials.

Many of Luke's analyses use **gas chromatography**. This is a technique in which a liquid or gaseous mixture is vaporised into a stream of helium that flows over a stationary phase which can be a solid, or a liquid coated on the surface of a solid. The stationary phase can be a finely divided solid packed in a long thin tube or column (for example, 0.5 to 2 m long, 3 to 9 mm diameter), called gas–solid chromatography, or it can be a liquid coated on the walls of a long thin glass (silica) capillary tube (10 to 100 m long, 0.1 to 0.5 mm diameter), called gas–liquid chromatography, GLC.

### The chemical principles involved

These are *adsorption* (for gas–solid chromatography) and *solubility* (for GLC).



(a) Our featured chemist setting up one of the gas chromatographs in his laboratory;  
 (b) the essential features of a gas chromatograph

If the stationary phase is a solid, then the components of the mixture injected into the flowing carrier gas adsorb on to it (stick on to its surface) to differing extents and desorb back into the gas phase at different rates, which means that they pass through the column at different rates and so are separated. A device at the end of the column detects each substance as it passes out of the column and measures it quantitatively.

If the stationary phase is a liquid, then the components of the injected mixture dissolve in it and evaporate back out of it at differing rates and so pass through the column at different speeds. The more soluble a substance is in the stationary liquid, then the slower that substance moves through the column (tube). Hence a separation is effected and the detector measures the amount of each component as it emerges from the column. Polarity of molecules is often a key factor in GLC separations: if the stationary phase is a polar liquid, then the more polar a component of the mixture to be analysed, the greater is its solubility and so the more slowly it moves through the column.

## 6.3 BRANCHES OF CHEMISTRY

Chemistry is a very broad subject and for convenience is often broken into several branches such as:

- *analytical chemistry*, the determination of what substances are present in samples (qualitative analysis) and how much of each is present (quantitative analysis)
- *physical chemistry*, the study and measurement of physical aspects of compounds and reactions, such as rates of reactions, energy aspects, structures of compounds and the nature of chemical bonding
- *organic chemistry*, the study of compounds of carbon, compounds that are usually but not exclusively associated with living matter, such as hydrocarbons, alcohols, carboxylic acids, fats, carbohydrates (sugars), amino acids and proteins
- *inorganic chemistry*, the study of compounds that are not organic; that is, compounds in which carbon is not the predominant element. Inorganic chemistry often focuses of metals, their extraction, reactions and compounds.

These have been the traditional branches of chemistry: they are based upon the intrinsic nature of chemistry—how it could most effectively be divided

for purposes of study and research. However in recent decades, as chemistry has become more involved in industrial and everyday activities of human society, further branches have become recognised based upon the uses to which chemistry is being put in the world at large. These newer branches have developed because to study many everyday problems chemists have needed to straddle the traditional boundaries. Some such branches are:

- *environmental chemistry*, concerned with determining how substances interact in the environment and with monitoring concentrations of substances, particularly pollutants, in air, water and soil
- *polymer chemistry*, a branch involved with developing new polymers with particular properties, working out how polymerisation occurs and how it can be made more efficient, and studying the properties of polymers
- *industrial chemistry*, concerned with the chemistry of industrial processes such as the manufacture of ammonia, sulfuric and nitric acids and the thousands of other compounds that are made industrially in modern society
- *food chemistry*, which looks at chemical aspects of the production, preservation and use of foods and chemicals added to food
- *pharmaceutical chemistry*, which involves the discovery, testing, synthesis and commercial development of chemicals for use as medicines
- *nuclear chemistry*, which focuses on the production and use of radioisotopes in medicine and industry as well as studying the fundamental nature of nuclear reactions
- *forensic chemistry*, concerned with the collection of evidence for use in law courts, particularly with identifying and tracing the origins of substances found at crime scenes.

This list of specialist areas of chemistry is by no means exhaustive.

These newer branches of chemistry have developed because the everyday activities they address require chemical inputs that straddle the traditional boundaries of the subject. For example environmental chemists use a lot of analytical chemistry but they also need knowledge of physical chemistry and often organic and inorganic chemistry. Forensic chemists again need analytical chemistry, but often need physical chemistry to master the complex instrumental techniques needed to trace origins of extremely small samples.

## 6.4 NEED FOR COLLABORATION

Chemistry is such a broad discipline that chemists tend to specialise in particular branches of it such as the ones listed above. Such specialisation usually starts during university training of chemists and develops further with professional experience and on-the-job training.

However many chemical problems in the real world require expertise from more than just one branch of chemistry. This is particularly true in industry where the production of a particular product can require detailed knowledge of physical chemistry (equilibrium and rate considerations), organic chemistry (how the reaction occurs and how to optimise yield), analytical chemistry (to monitor quality of raw materials and the product), industrial chemistry or chemical engineering (to be able to ‘scale up’ a laboratory experiment to industrial production quantities with inherent problems of energy inputs or outputs, mass flow problems and the selection of suitable construction materials) and environmental chemistry (to appreciate the significance of possible wastes).

and how to manage them in an environmentally responsible way). Solving such broad-ranging and complex problems requires input from many chemists with different specialties, and they cannot solve their aspect of the problem in isolation: it may have implications for other aspects being handled by other chemists. Therefore it is essential that chemists work collaboratively, regularly talk to one another and exchange their different viewpoints about problems as they arrive.

This need to collaborate means that chemists must have good communication skills—that they are able to communicate essential aspects of their particular sub-disciplines to others not expert in the same fields without using too much specialised jargon.

While collaboration between chemists is important, of equal importance is collaboration between chemists and other scientists. For example environmental problems often require input from chemists (who do analysis), microbiologists (who monitor organisms), botanists and horticulturalists (who can identify problems for flora and crops), ecologists (who oversee the interrelationships between organisms, plants and animals), geologists (who can determine the effects of constructions and earth-moving), hydrologists (who study changing water-flow patterns) and engineers (who design and supervise the construction of major works). As the work of one scientist or engineer has consequences for other areas of science or the environment, it is essential that all professionals involved work in close collaboration and talk to each other on a frequent and regular basis. And again good communication skills with the avoidance of excessive technical jargon is essential.

## 6.5 NEED FOR MONITORING

In industry it is important to monitor the conditions (such as temperature, pressure, state of catalyst) under which a chemical reaction is being conducted and the amount of product being formed in order to ensure:

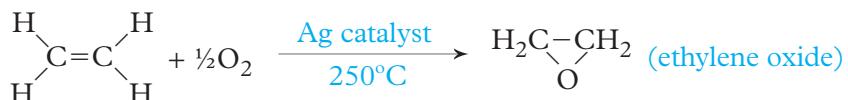
- that the maximum amount of desired product is being formed while production of unwanted by-products is minimised
- that no pollutants are being produced, either from the reaction itself or from impurities in the starting materials
- that the reaction is going to completion and not coming to an unfavourable equilibrium
- that, if the reaction is being used to generate energy, the maximum amount of energy is being produced.

We saw on pp. 286–8 *CCPC* that combustion reactions can produce solely carbon dioxide or a mixture of carbon dioxide with carbon monoxide and/or soot (carbon), depending upon the relative amount of oxygen provided. In such reactions it is important to monitor products of the reaction, so that if an undesirable product starts to form, conditions can be changed in order to stop its formation—in this case by increasing the proportion of oxygen (air) in the reaction mixture.

Another example is the reaction of ethylene with oxygen. In a plentiful supply of oxygen at a high temperature ethylene reacts to form carbon dioxide (normal combustion):



However at a lower temperature ( $250^{\circ}\text{C}$ ), with lesser amounts of oxygen and with a silver catalyst a quite different product is formed, namely ethylene oxide (Section 1.5):



Even with this catalyst and the lower temperature some ethylene reacts by Reaction 6.1. Therefore it is important to monitor reaction conditions and products to ensure that the yield of the desired product is maximised. In this reaction we would monitor the reaction temperature and pressure (to ensure that they were at the values that maximised production of ethylene oxide) and monitor the concentration of the unwanted product  $\text{CO}_2$  (to ensure its concentration was low and that the catalyst was in good condition and not becoming poisoned).

Another example of a reaction where careful monitoring of reaction conditions is needed to maximise yield is the very important industrial synthesis of ammonia. But first: why is synthesis of ammonia so important?

## 6.6 USES OF AMMONIA

Ammonia ranks second to sulfuric acid in terms of quantity produced worldwide per year. It is used to make:

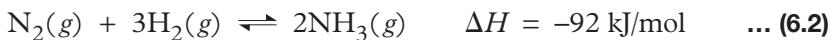
- fertilisers (sulfate of ammonia, ammonium nitrate, urea)
- fibres and plastics (rayon, acrylics, nylon)
- nitric acid, which in turn is used to make fertiliser (ammonium nitrate), dyes, fibres and plastics, and explosives such as ammonium nitrate, TNT (trinitrotoluene) and nitroglycerine (in dynamite)
- household cleaners
- detergents (non-ionic ones).

By the beginning of the twentieth century there was a growing need for an industrial method of synthesising ammonia. Increasing demands for nitrogenous fertiliser to grow food for increasing world populations were placing strains on the supply of naturally-occurring Chile saltpetre (sodium nitrate), the main ‘artificial’ fertiliser at that time. In addition the growing militancy of Germany was promoting calls for more explosives (generally made from nitric acid which in turn was mainly produced from saltpetre).

## 6.7 INDUSTRIAL SYNTHESIS OF AMMONIA

The German, Fritz Haber, in 1908 first developed a method of synthesising ammonia from its elements, though it was not until 1914 that Carl Bosch successfully converted it into an industrial process. This synthesis contributed significantly to the German war effort in World War I in that it insulated German agriculture from any harm caused by interrupted supplies of saltpetre from South America and it facilitated the production of nitric acid and hence of explosives.

The synthesis of ammonia uses the simple exothermic reaction:



This is an equilibrium reaction which at ordinary pressures and temperatures lies well to the left.

## Equilibrium considerations

Le Chatelier's principle (Section 4.7) shows us how to maximise the conversion of nitrogen and hydrogen to ammonia.

- 1 If the pressure on a reaction system is increased, the equilibrium moves in the direction which tends to reduce pressure; that is, the direction which corresponds to a decrease in the number of moles of gas, since a decrease in the number of moles of gas in a container of fixed volume leads to a decrease in pressure. This is because the pressure of a gas arises from gas particles hitting the walls of the container. The more particles in a given volume, the more collisions there are (per unit area per unit time) between gas particles and walls.

If the pressure on an equilibrium mixture of  $\text{N}_2$  and  $\text{H}_2$  is increased, the reaction moves to the right: some  $\text{N}_2$  and  $\text{H}_2$  react to form  $\text{NH}_3$ . This happens because that direction corresponds to a decrease in the number of moles of gas:



- 2 If the temperature is lowered, the equilibrium will move in the direction which tends to increase temperature (release heat). Reaction 6.2 is exothermic, so if temperature is lowered, it will move towards the right (form more ammonia).

Figure 6.1 shows how the percentage conversion of nitrogen to ammonia varies with pressure (at constant temperature) and temperature (at constant pressure). On equilibrium considerations alone the reaction should be conducted at high pressure and low temperature.

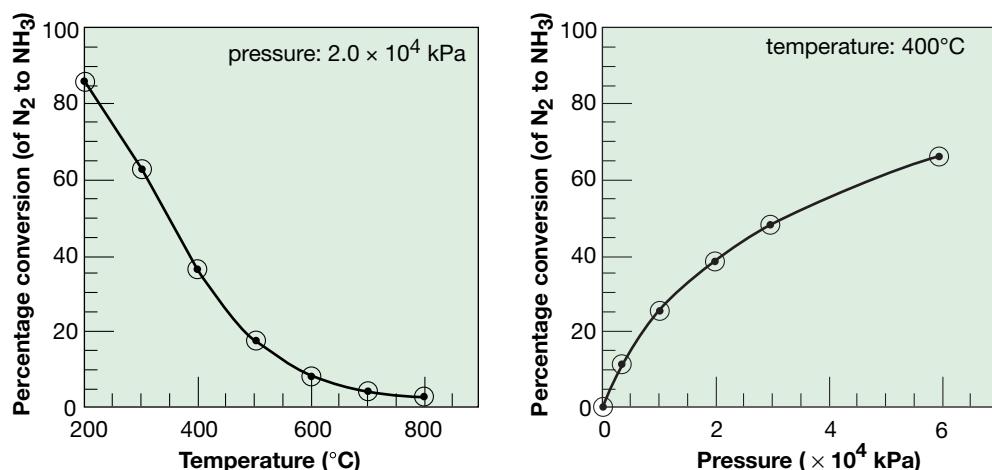


FIGURE 6.1  
The temperature and pressure dependence of the equilibrium percentage conversion of nitrogen to ammonia for a stoichiometric mixture of  $\text{H}_2$  and  $\text{N}_2$

## Rate considerations

However another consideration is *how long* it will take for the reaction to reach equilibrium: that is, we need to consider the *rate* of the reaction. As for most reactions, the rate of Reaction 6.2 decreases as temperature decreases. If we lower the temperature in order to move the equilibrium towards the right, we make the reaction very slow and so it takes a very long time to reach equilibrium. The reason for rate of reaction increasing as temperature increases (or decreasing as temperature decreases) was explained on p. 295 CCPC.

One way to increase the rate of a reaction is to find a suitable catalyst (pp. 291, 296 CCPC). Iron is a good catalyst for Reaction 6.2. While this catalyst does speed up the reaction, the rate is still too low at room temperature to be practical. Remember that while a catalyst speeds up a reaction, *it does not affect the position of equilibrium*. This is because it speeds up both the forward and reverse reactions.

Hence we have these situations: a low temperature produces a high yield (say 90% conversion of hydrogen to ammonia), but a very long time (weeks to months) is required to reach equilibrium, even with a catalyst. A high temperature causes equilibrium to be reached quickly (in a few minutes) but the equilibrium yield is extremely low (say 0.1%).

## Compromise

Compromise conditions are therefore used. A moderate temperature produces a moderate yield moderately quickly. Typical conditions for the industrial process, called the **Haber process** are:

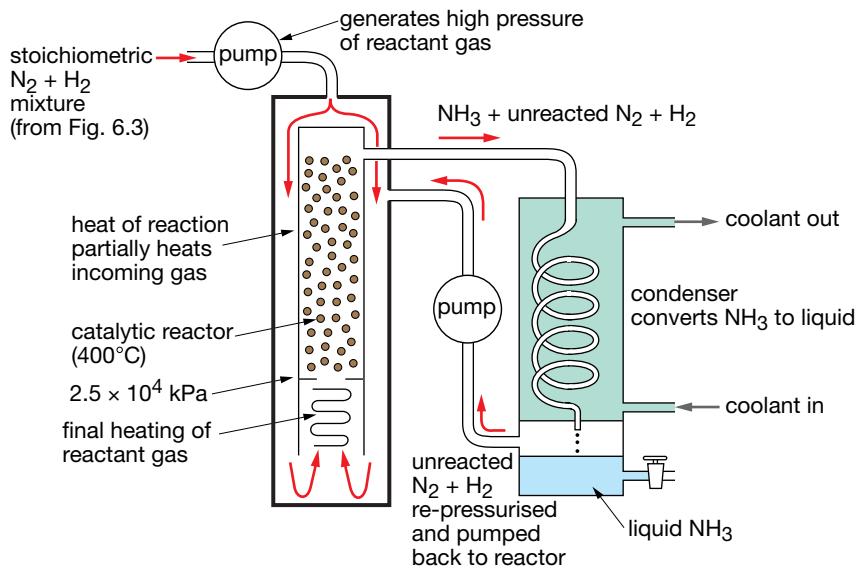
- a temperature of about 700 K (or about 400°C) and
- a total pressure of about  $2.5 \times 10^4$  kPa (250 times standard atmospheric pressure).

With a reactant mixture having H<sub>2</sub> and N<sub>2</sub> in the ratio of 3:1, these conditions give an equilibrium conversion to ammonia of about 45%. However industrial plants generally do not allow sufficient time for equilibrium to be reached and so yields of about 30% are more common. The catalyst is magnetite, Fe<sub>3</sub>O<sub>4</sub>, with its surface layer reduced to free iron.

The process is illustrated in Figure 6.2. Reactants pass through the catalytic reactor, then the mixture is cooled to condense out the ammonia formed; this can be drained off as required. Unreacted gases are fed back into the catalyst chamber along with incoming fresh reactants. None of the reactant mixture is wasted. We essentially drive the reaction to completion by condensing out the reaction product.

A stoichiometric mixture of hydrogen and nitrogen is used so that, as ammonia is formed and condensed out, left-over reactants can be recycled

**FIGURE 6.2**  
The Haber process  
for making ammonia  
(schematic)



through the process (with some fresh reactant mixture added) without any build-up of one reactant over the other.

An important factor in designing an industrial process is energy management. In the Haber process we would like to use the heat released by Reaction 6.2 to heat up, at least partially, the incoming reactants and so minimise our energy costs: this has the added advantage that it stops the catalyst overheating and so losing activity. This is the reason for the incoming reactants flowing over the outside of the catalyst chamber before entering it.

## The source of reactants

Nitrogen can be obtained from the atmosphere, so hydrogen is the ‘difficult’ or expensive reactant to obtain.



Huge quantities of ammonia are synthesised mainly for making fertiliser in production facilities such as this one operated by CSBP Limited in Kwinana, WA

In the laboratory we make hydrogen gas by reacting zinc or magnesium with hydrochloric acid. This process is too expensive for industrial use. Alternatively hydrogen can be made by the electrolysis of water (p. 71 CCPC), but except in special situations this also is very expensive. Industrially, hydrogen is generally produced by reacting methane (natural gas) or some other hydrocarbon with steam in the presence of a nickel catalyst at a temperature of about 750°C:



Carbon monoxide poisons the iron catalyst in the Haber process and so must be removed. This is done with another catalytic reaction:

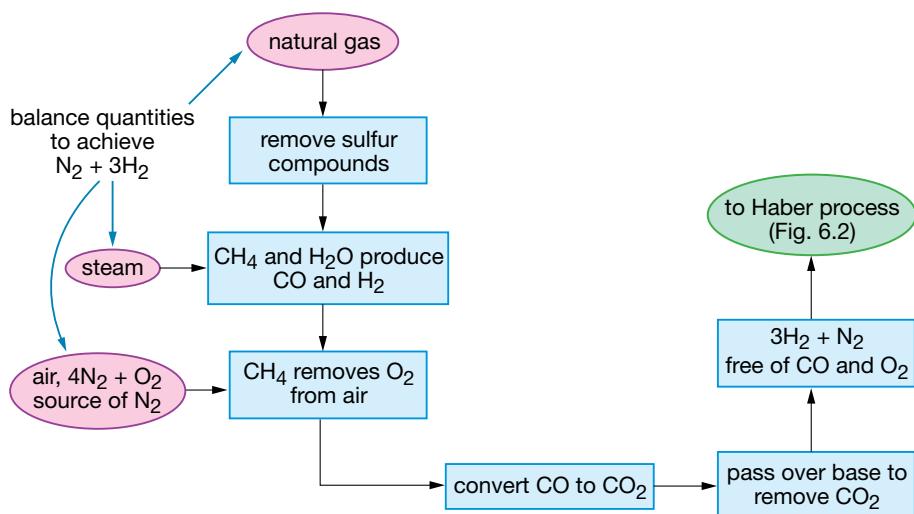


which has the added advantage of producing more hydrogen. The catalyst used is either  $\text{Fe}_3\text{O}_4$  at 500°C or Cu at 250°C.

A complication for the Haber process is that we want a mixture of hydrogen and nitrogen that does not contain any oxygen (which can react explosively with hydrogen under the conditions used). Methane is also used to remove oxygen from air (in effect just normal combustion to  $\text{CO}_2$  and steam). By adjusting the quantities of methane, steam and air used, this combination of reactions can be

made to produce a 3:1 mixture of hydrogen and nitrogen. The only unwanted gas in the mixture is carbon dioxide. This is removed by reaction with a base. If oxygen has to be excluded and if the reactant mixture has to be recycled through the reactor (Fig. 6.2), then use of a 3:1 mixture is the most efficient way of making ammonia. Figure 6.3 presents a flowchart for this preparation of the H<sub>2</sub>, N<sub>2</sub> mixture.

**FIGURE 6.3**  
A flowchart for the preparation of reactants for the Haber process



## Monitoring

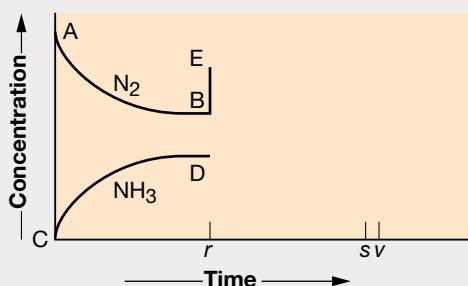
Because many different conditions must be maintained for efficient and safe operation of the Haber process, monitoring is essential. The conditions that need to be monitored include:

- *temperature and total pressure in the reaction vessel*, to keep them in the range for optimum conversion of reactants to products: in addition excessive temperature can damage the catalyst
- *ratio of H<sub>2</sub> to N<sub>2</sub> in the incoming gas stream*: we need to ensure that this ratio is kept at 3:1 to avoid a build-up of one reactant
- *concentrations of O<sub>2</sub>, CO, CO<sub>2</sub> and sulfur compounds in the incoming gas*: we must ensure that oxygen is absent to avoid risk of explosion, and that concentrations of CO, CO<sub>2</sub> and sulfur-containing species are sufficiently low to prevent poisoning of the catalyst; with a well-maintained plant the catalyst can last up to eight years
- *concentrations of argon and methane in the reaction vessel*, because any build-up of these gases will lower the efficiency of the conversion
- *purity of the product ammonia*, to ensure that no impurities contaminate the product of the process.

## Exercises

- 1 A mixture of 3 moles of hydrogen and 1 mole of nitrogen in a container of fixed volume was brought into contact with a suitable catalyst at 400°C. When equilibrium was reached 40% of the nitrogen had been converted to ammonia.
  - a Write an equation for this equilibrium reaction, then draw a graph showing the concentrations of the three substances as functions of time until well after equilibrium had been reached. Make the relative starting and equilibrium concentrations as quantitative as possible.

- b** After equilibrium was reached the mixture was rapidly cooled to remove (by liquefaction) 90% of the ammonia; the remaining gas mixture was brought back to 400°C (still in contact with the catalyst). Show on your graph how the concentrations would change from this point forward until equilibrium had been re-established. Explain why your curves have the shape and equilibrium values that you gave them.
- 2** A mixture of nitrogen and hydrogen gases was brought into contact with an iron catalyst at 700 K. The concentrations of nitrogen and ammonia followed curves AB and CD respectively on the graphs below. At time  $r$  extra nitrogen was added to the mixture: this immediately increased the concentration of nitrogen from B to E. By time  $s$  the system had returned to equilibrium. Copy both graphs into your workbook and sketch the curves that the concentrations of nitrogen and ammonia would follow between  $r$  and  $s$ .



At time  $v$  the volume available to the reaction mixture was suddenly doubled. Show on your graphs how the concentrations would change after time  $v$ . Explain why your graphs have their particular shapes.

- 3** For the gaseous reactions:

- a**  $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2$  (exothermic)
- b**  $\text{CH}_3\text{OH} \rightleftharpoons \text{CO} + 2\text{H}_2$  (endothermic)
- \*c**  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$  (exothermic)
- d**  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  (endothermic)

predict the effect upon the position of equilibrium of:

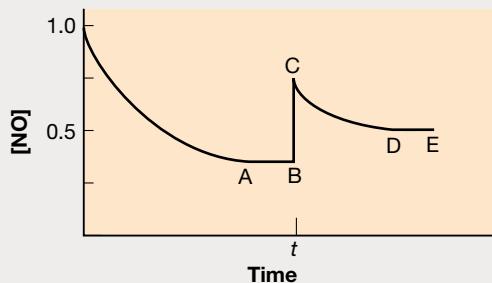
- i** increasing the pressure (i.e. compressing the reaction mixture into a smaller volume)
- ii** adding oxygen to (a) and (c)
- iii** adding hydrogen to (b) and (d)
- iv** increasing temperature
- v** increasing the volume available to the reaction mixture.

- 4** If each of the reactions in Exercise 3 were at equilibrium in a flask of fixed volume, and if helium were added so that the total pressure in the flask doubled, what change, if any, would there be in the equilibrium position?
- 5** Select conditions which would maximise the conversion of the underlined reactant to the underlined product in the following reactions at room temperature:
- a**  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
  - \*b**  $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$
  - c**  $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$
- 6** Nitric oxide reacts with chlorine to form nitrosyl chloride:



The graph below shows the concentration of NO as a function of time after mixing 1.0 mol NO with 0.5 mol  $\text{Cl}_2$  in a 1.0 L flask at a constant temperature. At time  $t$

the gaseous mixture is suddenly compressed into a volume which is half of the initial volume.



a Explain:

- i why  $[NO]^{\dagger}$  remains constant from A to B on the graph
  - ii why  $[NO]$  increased to C when the volume was decreased
  - iii why  $[NO]$  decreases from C to D
  - iv why  $[NO]$  between D and E is higher than between A and B.
- \*b Suppose that the volume available to the reaction mixture had been doubled at B. Copy the graph into your workbook and sketch on it the curve you would expect for  $[NO]$  versus time after B. Give your reasoning.
- \*c Sketch the curve you would expect if a catalyst had been used in the original experiment.

7 The reaction:



is the main way that polluting oxides of nitrogen are formed in petrol driven motor cars. This reaction proceeds to greater extents at higher temperatures. Is the reaction exothermic or endothermic? Explain.

## 6.8 MONITORING MANUFACTURED PRODUCTS

Not only is it essential to monitor production processes, but also the final products of chemical factories must be monitored, for example food, drugs and household chemicals. This is to ensure that the products match their stated specification (i.e. contain the stated percentage of active ingredients) and that they do not contain unacceptable amounts of impurities.

Some impurities or minor constituents that can be present in manufactured chemicals are ionic compounds. Therefore it is often necessary to determine, first qualitatively then quantitatively, which if any cations or anions are present in substances.

## 6.9 IDENTIFICATION OF CATIONS IN SOLUTION

There are two types of problems involving the identification of cations:

- 1 identification of the one and only cation present in a sample known to be a pure substance (such as a bottle in a chemical store which has lost its label)
- 2 identification of all the cations present in a sample known to be a mixture.

† Remember, square brackets around a formula mean ‘concentration of’.

The second is by far the more common situation: it occurs in the analysis of ore samples from mines and of effluents being discharged by factories, and in testing for impurities in manufactured chemicals. It is also the more difficult task, so let us start with the simpler one.

## Tests for identifying the one cation in a solution

In this discussion we will consider only the six cations  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In the real world chemists have to consider many more cations than this, but this limited list will demonstrate the principles involved in identification without needing to get involved with large numbers of tests.

*Cations in solution are primarily identified by precipitation reactions.* By observing whether or not precipitates form when solutions of hydrochloric acid, sulfuric acid and sodium hydroxide are added to samples of the solution to be identified we can deduce which cation is present. Hence it is necessary to be familiar with the solubility table, Table 8.1 on p. 205 CCPC. This would be a good time to revise pp. 202–7 CCPC. That table is reproduced inside the back cover of this book. Table 6.1 shows selected information from that table which is relevant to the present discussion.

**TABLE 6.1 Cations (from our list of six) that form precipitates with chloride, sulfate and hydroxide. Precipitates are white unless a colour is given**

with $\text{Cl}^-$	$(\text{Pb}^{2+})^a$
with $\text{SO}_4^{2-}$	$\text{Pb}^{2+}$ , $\text{Ba}^{2+}$ , $(\text{Ca}^{2+})^a$
with $\text{OH}^-$	$\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ (blue), $\text{Fe}^{2+}$ (green), $\text{Fe}^{3+}$ (brown), $(\text{Ca}^{2+})^a$

a provided concentration is high enough, say  $> 0.05 \text{ mol/L}$ , and the mixture is well shaken

Table 6.2 gives the common tests we use to identify each of the cations in the above list. The cations are shown in an order in which we can conveniently test for them, by using solutions of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  in that sequence.

Before performing any test we would first note the colour of the solution: colour sometimes gives us a clue to the identity of the cation. Common colours (of our selected cations) are:

- copper: pale blue
- iron(II): pale green (may be colourless if dilute)
- iron(III): yellow (nearly colourless if dilute)

While evidence based on colour is useful, it cannot be taken as positive identification of the cation.

## 6.10 PROCEDURE WHEN ONLY ONE CATION IS PRESENT

If we know that our solution contains only one cation, then we would perform the  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  tests in that order on separate samples of the solution. In outline:

- 1 Add  $\text{HCl}$ : if a precipitate forms, then the cation is  $\text{Pb}^{2+}$
- 2 Add  $\text{H}_2\text{SO}_4$ : if a precipitate forms, the cation is either  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$
- 3 Add  $\text{NaOH}$ : if a precipitate forms, the cation is one of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ .

**TABLE 6.2 Tests used to identify cations (from our set of six)**

**Cation Tests**

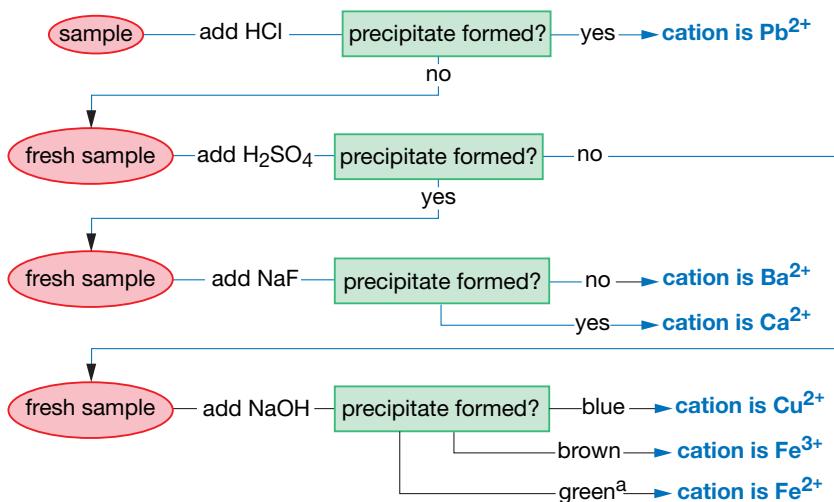
Pb <sup>2+</sup>	1 with Cl <sup>-</sup> forms a white precipitate (if solution not too dilute, say > 0.05 mol/L) 2 with I <sup>-</sup> forms a yellow precipitate
Ba <sup>2+</sup>	1 with SO <sub>4</sub> <sup>2-</sup> forms a white precipitate 2 gives a pale green flame colour <sup>a</sup> 3 no precipitate with OH <sup>-</sup> or F <sup>-</sup> (compare Ca <sup>2+</sup> )
Ca <sup>2+</sup>	1 with SO <sub>4</sub> <sup>2-</sup> forms a white precipitate (if solution not too dilute, say > 0.05 mol/L) 2 with F <sup>-</sup> forms a white precipitate 3 gives a brick-red flame colour <sup>a</sup>
Cu <sup>2+</sup>	1 with OH <sup>-</sup> forms a blue precipitate 2 this precipitate dissolves in NH <sub>3</sub> to form a deep blue solution 3 gives a blue-green flame colour <sup>a</sup>
Fe <sup>2+</sup>	1 with OH <sup>-</sup> forms a green or white precipitate which may turn brown <sup>b</sup> 2 decolorises acidified dilute potassium permanganate solution
Fe <sup>3+</sup>	1 with OH <sup>-</sup> forms a brown precipitate 2 with thiocyanate, SCN <sup>-</sup> forms a deep red solution

a See Section 6.14.

b *Fe(OH)<sub>2</sub> most commonly forms as a green crystalline precipitate, but under some conditions can be a white amorphous precipitate. Green Fe(OH)<sub>2</sub> is oxidised by dissolved oxygen to brown Fe(OH)<sub>3</sub>. Freshly prepared solutions of Fe<sup>2+</sup> will generally give a green precipitate that goes brown very slowly if at all; older solutions of Fe<sup>2+</sup> tend to form darker green precipitates that discolour to brown fairly rapidly.*

The detailed procedure is shown in Figure 6.4.

**FIGURE 6.4**  
Flowchart for identifying the one cation (of our set of six) present in a solution



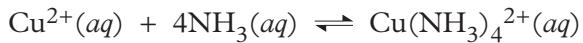
<sup>a</sup> though it may go brown on standing (oxidation to Fe(OH)<sub>3</sub>). See footnote to Table 6.2.

If a precipitate forms when HCl solution is added, the cation present is Pb<sup>2+</sup> and we need proceed no further (since the sample contained only one cation).

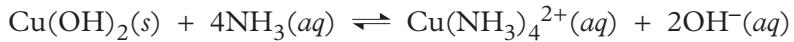
If H<sub>2</sub>SO<sub>4</sub> solution produces a precipitate, the cation is either Ba<sup>2+</sup> or Ca<sup>2+</sup>; to determine which, we use the fact that calcium fluoride is insoluble while barium fluoride is soluble. A fresh sample of the solution is used for this.

If HCl and H<sub>2</sub>SO<sub>4</sub> produce no precipitate, we test the solution with NaOH solution. A blue precipitate shows that the cation is Cu<sup>2+</sup>: in this case the original

solution probably had a pale blue colour. We can confirm that the cation is  $\text{Cu}^{2+}$  by adding ammonia to the blue precipitate: it dissolves to form a deep blue solution. Copper ion reacts with ammonia solution to form a *complex ion*:



or in this particular case:



A **complex ion** is an ion formed when one or more small molecules or ions attach themselves to a cation to form a combined ion that has properties that are quite distinct from those of the parent ions or molecules.

In the complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$  four  $\text{NH}_3$  molecules are attached to a  $\text{Cu}^{2+}$  ion; the complex ion has an intense blue colour while  $\text{Cu}^{2+}$  is pale blue and ammonia is colourless. The species  $\text{Fe}(\text{SCN})^{2+}$  mentioned below is also a complex ion, being made by a thiocyanate ion,  $\text{SCN}^-$ , attaching itself to a  $\text{Fe}^{3+}$ . This complex ion has a blood red colour whereas thiocyanate,  $\text{SCN}^-$  is colourless and  $\text{Fe}^{3+}$  is pale yellow.

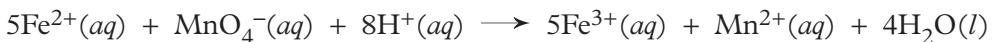
If  $\text{NaOH}$  produces a green or white precipitate, then the cation present is  $\text{Fe}^{2+}$ ; if it produces a brown precipitate, the cation present is  $\text{Fe}^{3+}$ .

## Distinguishing between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$

Because of the ease of oxidation of  $\text{Fe}(\text{OH})_2$  to  $\text{Fe}(\text{OH})_3$ , the results of the hydroxide test may not clearly show which of these two cations is present. In that case there are two further tests we can perform to resolve the difficulty. An  $\text{Fe}^{3+}$  solution forms a blood red colour when drops of colourless potassium thiocyanate KSCN solution are added to it:



When drops of purple potassium permanganate solution are added to a colourless solution containing  $\text{Fe}^{2+}$  ions, the  $\text{Fe}^{2+}$  decolorises the permanganate:



One or both of these tests can be used to determine which iron cation is present.

## Solubility problems

We saw on p. 205 CCPC that lead chloride and calcium sulfate are only sparingly soluble. This means that if the concentration of  $\text{Pb}^{2+}$  or  $\text{Ca}^{2+}$  is low, then a precipitate of  $\text{PbCl}_2$  or  $\text{CaSO}_4$  will not form.

If no precipitate is formed with  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ , then the cation present (of the six possibilities under consideration) is either  $\text{Pb}^{2+}$  or  $\text{Ca}^{2+}$ . Therefore a fresh sample of the unknown solution is tested with potassium iodide solution: if a yellow precipitate is formed, then  $\text{Pb}^{2+}$  is present.<sup>†</sup> If no precipitate forms then the solution is tested with a dilute solution of sodium fluoride: a white precipitate shows that  $\text{Ca}^{2+}$  is present.

<sup>†</sup> We do not use iodide instead of chloride in the basic procedure because iodide reacts with  $\text{Cu}^{2+}$  to form a mixture of white  $\text{CuI}$  precipitate and brown iodine solution.

The procedure just described for identifying which one of the nominated six cations is present in a solution of a pure substance is not the only one that can be used. However it has the advantage of using simple chemicals and most of the reactions involved should already be familiar to you.

## 6.11 IDENTIFYING CATIONS IN MIXTURES

When we are trying to identify the one cation present in a solution of a pure substance, we can perform our HCl,  $H_2SO_4$ , NaOH tests on fresh samples of solution, because there is no fear of interference: one cation cannot foul up the test for another cation, because there is only one cation present.

However when we come to the more usual task of identifying the several cations present in a mixture, we have to modify our procedure to prevent one cation interfering with the test for another cation. For example, if both  $Pb^{2+}$  and  $Ba^{2+}$  are present in a solution, the  $Ba^{2+}$  does not upset the test for  $Pb^{2+}$  (formation of  $PbCl_2$ ), but  $Pb^{2+}$  gives a precipitate with  $H_2SO_4$  which complicates interpretation of the test for  $Ba^{2+}$  (precipitate with  $H_2SO_4$ ).

Hence when we analyse mixtures, we separate the precipitate from the filtrate in each major test and perform the next test on the filtrate from the preceding test. In this way we eliminate interference. However, before separating off the precipitate we must ensure that all of the relevant cation has been precipitated (removed from the solution); hence we add drops of the reagent (HCl or  $H_2SO_4$ ) until no further precipitate forms.

Although filtration can be used to separate the precipitate from the filtrate, it is slow. A quicker method is to use a centrifuge.

A **centrifuge** is a machine that spins test tubes at high speed and so flings the precipitate to the bottom of the tube very quickly.

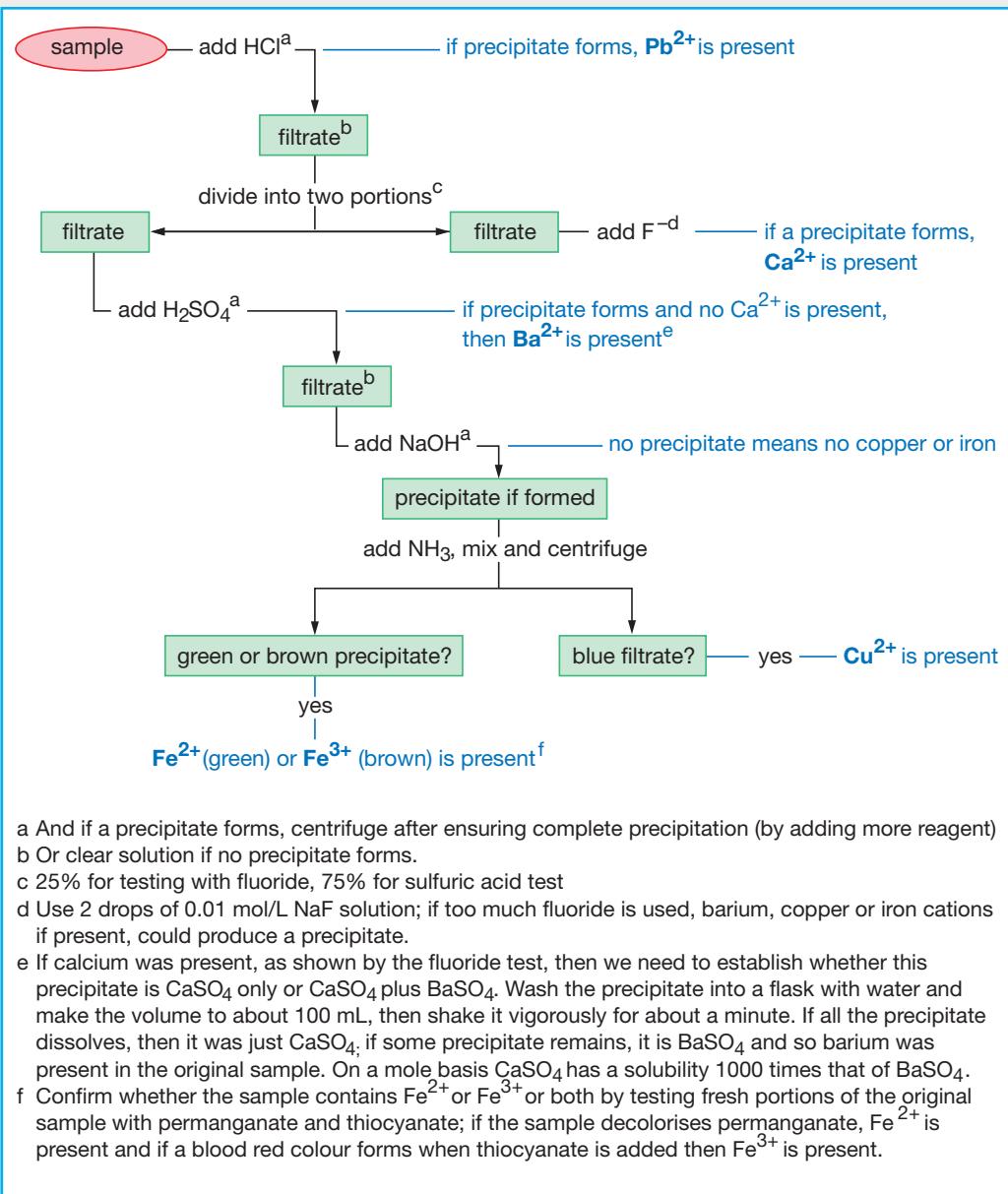
Figure 6.5 shows a typical laboratory centrifuge. After centrifuging, the filtrate is removed with an eye dropper (Pasteur pipette), and the next test performed on that solution.

Providing each of the  $H_2SO_4$  and NaOH tests is done on the filtrate from the previous test, the method of determining the cations present in a mixture is the same as for a pure substance. A flowchart is set out in Figure 6.6.

FIGURE 6.5  
(a) A typical laboratory centrifuge (b) samples of iron(III) hydroxide (left) and lead iodide (right) before and after centrifuging



FIGURE 6.6  
A scheme for identifying cations in mixtures



## Exercises

- 8 Write net ionic equations for all the reactions mentioned in Table 6.2.
- 9 Describe tests to determine whether a solution of a pure substance contained:
- a lead nitrate or barium nitrate
  - b copper sulfate or iron(II) sulfate
  - c calcium chloride or iron(III) chloride
  - \*d iron(II) sulfate or iron(III) sulfate
  - \*e barium nitrate or copper nitrate
- 10 A pair of students were given six solutions and told that each solution contained one (and only one) of the cations,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ . To determine the cation present in each solution they added solutions of hydrochloric acid, sulfuric acid and sodium hydroxide in turn to separate samples of each solution. Their results are tabulated below. Identify the cation present in each solution. If for a particular solution the tests do not identify just one cation, state the possibilities and suggest further tests to distinguish between the possibilities. If the tests performed do not allow the



identification of any cation in a particular solution, suggest further tests and explain why they are necessary.

Reagent	A	B	C	*D	*E	*F
HCl	NP <sup>a</sup>	NP	NP	ppt	NP	NP
H <sub>2</sub> SO <sub>4</sub>	ppt <sup>b</sup>	NP	NP	ppt	ppt <sup>b</sup>	NP
NaOH	NP	brown ppt	blue ppt	ppt	NP	NP

a NP = no precipitate; ppt = precipitate formed.

b When sodium fluoride solution was added to Solution A a precipitate formed; when added to Solution E, no precipitate formed.

- 11 Would sodium carbonate solution be a suitable reagent for deciding which cation (out of Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>) was present in a solution? Explain.
- 12 With the only possibilities being Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, what cations are present in a solution which:
  - a forms a white precipitate with sulfate and with fluoride, no precipitate with chloride, and a blue precipitate with hydroxide which dissolves in ammonia solution
  - b forms a white precipitate with chloride (with the filtrate from this giving no precipitate with sulfate), and a brown precipitate with hydroxide: when ammonia solution is added to this precipitate, none of the precipitate appears to dissolve and the filtrate remains colourless. The original solution does not decolorise permanganate solution.
  - c forms a brown precipitate with hydroxide but no precipitate with chloride or sulfate: separate samples of the original solution decolorise permanganate and form a red colour with thiocyanate.
- 13 A solution was thought to contain at least one of the cations, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, but it gave no precipitate with chloride, sulfate or hydroxide. Offer an explanation for this and suggest ways of proving the presence of one or more of these cations.
- 14 You may use Table 6.1 or the solubility table inside the back cover for this question. Some students were asked to identify the (one) cation present in a solution. They tested samples of the solution with sulfuric acid, sodium hydroxide and potassium carbonate solutions and obtained precipitates with sulfuric acid and with potassium carbonate but not with sodium hydroxide. Student A decided that the sample contained Pb<sup>2+</sup>, student B that it contained Ca<sup>2+</sup> and student C that it contained Ba<sup>2+</sup>. Which student or students gave an answer that is consistent with the results? Explain your reasoning.
- 15 To determine the cations present in five unknown samples labelled P, Q, R, S and T a group of students performed the following procedure on each sample:
  - i Add HCl solution; if precipitate forms, centrifuge it off.
  - ii To the solution or filtrate from (i) add H<sub>2</sub>SO<sub>4</sub> solution; if precipitate forms centrifuge it off.
  - iii If a precipitate forms in (ii), repeat (i) and test the solution or filtrate with NaF solution.
  - iv To solution or filtrate from (ii) add NaOH solution; if precipitate forms, centrifuge it off and note its colour.
  - v To precipitate from (iv), if any, add ammonia solution, centrifuge and note colour of solution and of precipitate, if any remains.
  - vi If a brown precipitate remains in (v) test a portion of the original sample with (a) permanganate solution and (b) thiocyanate solution.

Their results are summarised below. What cations are present in each solution?

Test	P	Q	R	*S	*T
i (HCl)	ppt <sup>a</sup>	NP	NP	ppt	ppt
ii (H <sub>2</sub> SO <sub>4</sub> )	NP <sup>a</sup>	ppt	NP	ppt	ppt
iii (NaF) <sup>b</sup>		NP		ppt	NP
iv (NaOH)	blue ppt	brown ppt	blackish ppt	NP	ppt
v (NH <sub>3</sub> ) <sup>c</sup>	blue soln, no ppt left	colourless soln, brown ppt <sup>d</sup>	blue soln, green- brown ppt <sup>e</sup>		blue soln, no ppt left

a NP = no precipitate; ppt = precipitate formed

b only performed if (ii) gave a precipitate

c only performed if a precipitate formed in (iv)

d Test (vi) (a) did not decolorise MnO<sub>4</sub><sup>-</sup> (b) deep red colour with SCN<sup>-</sup>.

e Test (vi) (a) decolorised MnO<sub>4</sub><sup>-</sup> (b) no colour with SCN<sup>-</sup>.

## 6.12 IDENTIFICATION OF ANIONS IN SOLUTIONS

Often we need to identify the anions present in a solution. As with cations we shall illustrate the general approach by using only four anions, namely carbonate, chloride, phosphate and sulfate.

As with cations there are two situations:

- 1 identifying the one anion present in a solution known to contain only one pure substance
- 2 identifying all the anions present in a mixture.

Again the first task is the simpler, so let us start with it.

The common tests for identifying the four chosen anions are set out in Table 6.3. The order of listing provides a convenient sequence to use for identifying an unknown anion.

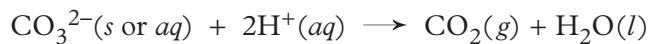
Because the metal ions used in these tests form precipitates with more than one of our anions, care is needed in interpreting results. Table 6.4 shows which combinations of four common cations and the four selected anions (plus hydroxide) produce precipitates.

Note that colour of the solution is of no help in identifying these anions, because they are all colourless: any colour in the solution is due to the cation(s) present.

Note also that a precipitate with silver nitrate does not prove the presence of chloride (footnote to Table 6.3).

### Carbonate

Because carbonates form precipitates with many cations, including those we want to use to test for sulfate, phosphate and chloride, we need to avoid using a precipitation reaction to test for carbonate. Hence we use a common acid–base reaction of carbonates. *All carbonates react with dilute acids to form carbon dioxide gas:*



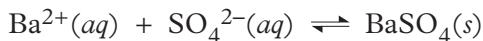
In analysing mixtures we use enough nitric acid to destroy all the carbonate so it will not interfere with tests for the other anions.

## Use of Ba<sup>2+</sup> for sulfate and phosphate

In dilute acid solution barium ions produce a precipitate with sulfate but not with phosphate. This is because HPO<sub>4</sub><sup>2-</sup> is a much weaker acid than HSO<sub>4</sub><sup>-</sup>. In dilute acid solution the reaction



proceeds to sufficient extent to produce enough SO<sub>4</sub><sup>2-</sup> to form a precipitate with Ba<sup>2+</sup>:

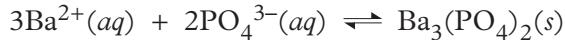


On the other hand HPO<sub>4</sub><sup>2-</sup> is so weak that in dilute acid solution the equilibrium



lies so far to the left that insufficient PO<sub>4</sub><sup>3-</sup> is formed to produce a precipitate of Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

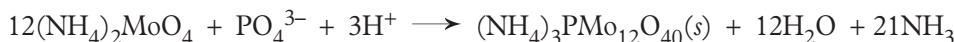
However in ammonia solution (pH about 10 or 11), [H<sub>3</sub>O<sup>+</sup>] is so low that Reaction 6.4 moves well to the right (Le Chatelier's principle) and so produces enough PO<sub>4</sub><sup>3-</sup> for barium phosphate to precipitate:



A similar situation occurs for phosphate with silver and lead ions.

## Other tests for phosphate

Two tests for phosphate not involving barium ion are listed in Table 6.3. Both of these have the advantage that they can be applied directly to the sample without interference from any of our anions. The equations for these tests are:



The polynuclear phosphomolybdate complex (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> can be thought of as (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub>.

TABLE 6.3 Tests used to identify the four selected anions

Anion	Test
carbonate	1 solution has a pH between 8 and 11 (pH paper suffices) 2 addition of dilute HNO <sub>3</sub> produces bubbles of colourless gas (CO <sub>2</sub> ) <sup>a</sup>
sulfate	1 addition of Ba(NO <sub>3</sub> ) <sub>2</sub> to an acidified sample of the solution produces a thick white precipitate 2 acidification and addition of Pb(NO <sub>3</sub> ) <sub>2</sub> produces a white precipitate
phosphate	1 addition of ammonia followed by Ba(NO <sub>3</sub> ) <sub>2</sub> produces a white precipitate 2 addition of Mg <sup>2+</sup> in an ammonia, ammonium nitrate buffer produces a white precipitate of Mg(NH <sub>4</sub> )PO <sub>4</sub> 3 acidification with HNO <sub>3</sub> followed by addition of ammonium molybdate solution (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> produces a yellow precipitate; warming the mixture for a few minutes may be necessary
chloride	1 addition of AgNO <sub>3</sub> to an acidified sample produces a white precipitate <sup>b</sup> 2 this precipitate dissolves in ammonia solution and darkens in sunlight

<sup>a</sup> Any strong acid (i.e. H<sub>3</sub>O<sup>+</sup>) would do but for analysing mixtures (next section) we do not want to introduce any Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>.

<sup>b</sup> In non-acidic solutions silver nitrate also produces precipitates with carbonate and phosphate (and with sulfate at all pHs if sulfate concentration is moderately high), so this test alone does not prove the presence of chloride: it is also necessary to prove the absence of sulfate.

**TABLE 6.4 Does each of the cations in the left-hand column form a precipitate with the anions in the top row?**

	$\text{OH}^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$ <sup>a</sup>	$\text{CO}_3^{2-}$ <sup>b</sup> in alkaline solution	$\text{PO}_4^{3-}$	
					solution pH < 2	solution pH > 6
$\text{Ba}^{2+}$	no	no	yes	yes	no	yes
$\text{Pb}^{2+}$	yes	yes <sup>c</sup>	yes	yes	no	yes
$\text{Ag}^+$	yes <sup>d</sup>	yes	yes <sup>c</sup>	yes	no	yes
$\text{Cu}^{2+}$	yes	no	no	yes	no	yes

a in acidic or alkaline solution

b cannot have carbonate in acid solution: it decomposes to  $\text{CO}_2(g)$

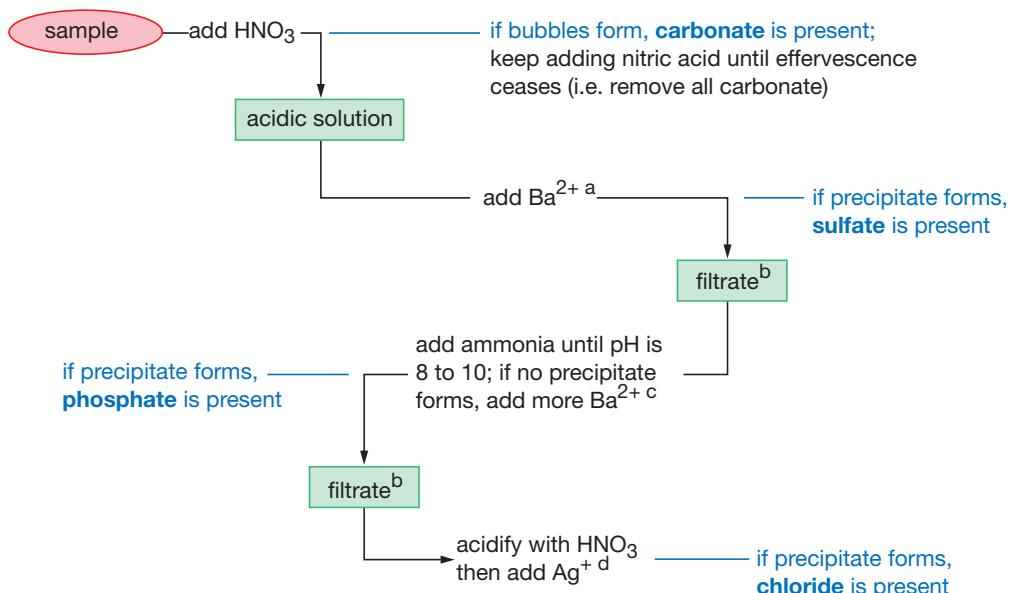
c provided concentration of  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  is not too low, say  $> 0.05 \text{ mol/L}$

d precipitate is brown  $\text{Ag}_2\text{O}$

## 6.13 IDENTIFYING ANIONS IN MIXTURES

As with identifying cations in mixtures (Section 6.11) we use the same tests as for identifying single anions, but again we need to follow a sequence that avoids one anion interfering with the test for another anion. This is done by performing tests for sulfate, phosphate and chloride on the solutions left over from the previous test.

Figure 6.7 presents a flow chart for identifying anions (from our list of four) in a solution. Other schemes are possible.



**FIGURE 6.7**  
A scheme for identifying anions in mixtures

a If a precipitate forms, add more  $\text{Ba}^{2+}$  until no further precipitation occurs, then centrifuge (or filter).

b or the solution if no precipitate formed.

c A precipitate may form when  $\text{NH}_3$  is added because there may be sufficient  $\text{Ba}^{2+}$  left from the sulfate test; if not, add more  $\text{Ba}^{2+}$  which may or may not produce a precipitate, depending on whether or not phosphate is present.

d Acidification is necessary because  $\text{Ag}^+$  will precipitate brown  $\text{Ag}_2\text{O}$  in alkaline solution.

## 6.14 FLAME TESTS

When compounds of some elements are volatilised in a flame, they give the flame a distinctive colour. Common ones are shown in Table 6.5. The flame decomposes the compound into elements and it is atoms of one of the elements that give the flame its colour. The flame colour can be used to confirm the presence of such elements in samples for analysis. The elements with distinctive flame colours (Table 6.5) are all metals, so a flame test confirms the presence of certain cations in the sample but gives no information about anions.

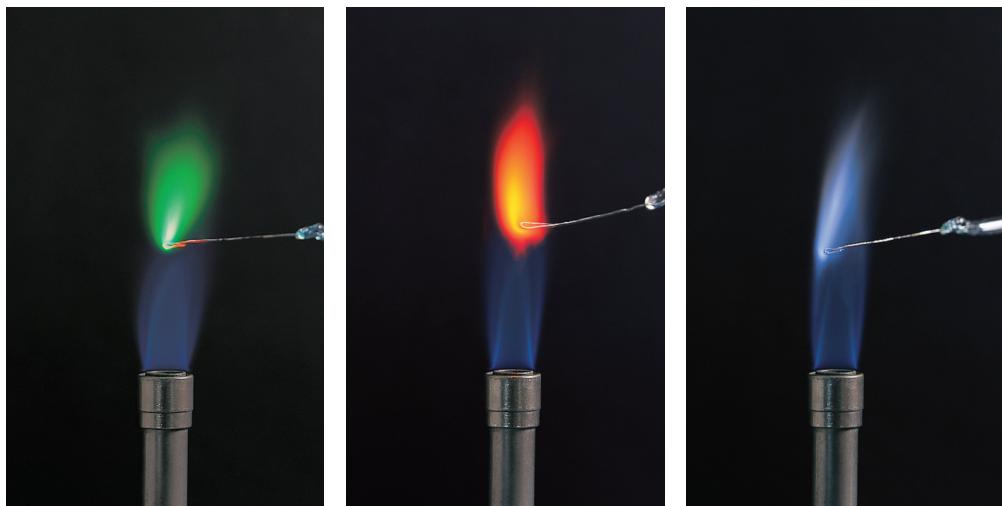
**TABLE 6.5 Flame colours for some elements**

Element <sup>a</sup>	Flame colour
lithium	carmine (dull red)
sodium	yellow
potassium	light purple (lilac)
calcium	brick-red (orange-red)
strontium	scarlet (deep red)
barium	pale green (apple-green)
copper	blue-green

a The element must be present as a compound which will vaporise at the temperature of the flame, typically 1000 to 1500°C.

To perform a **flame test**, a piece of platinum wire mounted in the end of a glass tube as holder is used. The wire is first carefully cleaned by repeatedly dipping it into concentrated hydrochloric acid and heating it to red heat in the flame. Care is taken not to heat the glass tube because it can give off sodium compounds. The reason for stringent cleaning is to eliminate sodium which has an intense flame colour that can mask other colours. Sodium is so common that it can easily contaminate samples. After cleaning, the wire is dipped into the sample to be tested and placed back into the flame. Figure 6.8 illustrates. *The flame colour is characteristic of the cation present and is independent of the anion present.*

**FIGURE 6.8**  
The flame colours produced by barium (left), strontium (centre), and potassium (right)



Flame tests are particularly useful in distinguishing between barium (pale green) and calcium (brick-red), and between sodium (yellow) and potassium (lilac). Sometimes two elements produce similar colours (for example different shades of green from copper and barium). Hence flame tests should not be used as the only method of identification.

## Exercises



- 16** **a** Write equations for all the reactions mentioned in Table 6.3.
- b** Why must sulfate be removed before testing for chloride and phosphate?
- 17** How would you distinguish between solutions of:
- sodium chloride and sodium sulfate
  - potassium chloride and potassium phosphate
  - sodium carbonate and sodium hydroxide
  - \*ammonium phosphate and ammonium sulfate
  - sodium carbonate, sodium sulfate and sodium phosphate.
- 18** What anion is present in a solution (known to contain only one anion):
- which produces a precipitate with barium chloride solution both when acidic and when alkaline?
  - which has a pH of about 11 and which produces precipitates with neutral solutions of both silver nitrate and barium nitrate?
  - which produces a precipitate with alkaline barium chloride solution but not with an acidic solution of that substance?
  - \*which produces a precipitate with silver nitrate but not with barium nitrate?
  - which has a pH of 13 but which does not produce any bubbles when hydrochloric acid is added to it?
- 19** A solution was known to contain one pure substance (apart from water). Describe tests you would perform to determine which of the ions  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  were in the solution.
- 20** Four solutions, A, B, C and D, are known to contain one pure substance each. Solutions of nitric acid, barium nitrate (both in acidic and alkaline solutions) and silver nitrate (in near neutral solution) were added to separate portions of each solution in turn. Results are given below. Which anion (out of the possibilities,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ) is present in each solution?

Test	A	B	*C	*D
$\text{HNO}_3$	NR <sup>a</sup>	bubbles of gas	NR	NR
$\text{Ba}(\text{NO}_3)_2$ in acid soln	NR	TNP	white ppt	NR
$\text{Ba}(\text{NO}_3)_2$ in $\text{NH}_3$ soln	NR	white ppt	TNP	white ppt
$\text{AgNO}_3$	white ppt <sup>a</sup>	TNP <sup>a</sup>	white ppt	TNP

*a NR = no reaction; ppt = precipitate; TNP = test not performed.*

- 21** To determine the anions present in several solutions labelled P, Q, R, S and T a group of students performed the following tests:
- Add  $\text{HNO}_3$  until effervescence, if any, ceases.
  - Add  $\text{Ba}(\text{NO}_3)_2$  solution to the solution from (i); centrifuge off any precipitate.

- iii** Add ammonia solution to the solution or filtrate from (ii); if no precipitate forms, add more  $\text{Ba}(\text{NO}_3)_2$ ; if a precipitate forms at either stage, centrifuge it off.
- iv** Acidify the solution or filtrate from (iii) with nitric acid then add silver nitrate solution.

Use the results of these tests tabulated below to determine which anions are in each solution.

Test	P	Q	R	*S	*T
i $\text{HNO}_3$	NR <sup>a</sup>	gas forms	NR	gas forms	NR
ii $\text{Ba}(\text{NO}_3)_2$ in acid	ppt <sup>a</sup>	ppt	ppt	NR	NR
iii $\text{Ba}(\text{NO}_3)_2$ in $\text{NH}_3$	NR	NR	ppt	NR	ppt
iv $\text{AgNO}_3$	ppt	NR	NR	ppt	ppt

a NR = no reaction; ppt = precipitate.

- 22** Identify the one (and only) cation present in a solution that:

- a** formed a white precipitate with sodium sulfate solution but not with sodium chloride solution and which in a flame test coloured the flame green
- b** formed a precipitate with sodium carbonate solution but not with sodium chloride, sulfate or hydroxide and which in a flame test coloured the flame orange-red
- c** was pale blue and gave a precipitate with sodium hydroxide and which in a flame test gave the flame a green colour.

Explain all the observations in each test and write equations for all reactions.

- 23 a** Two solutions, each containing one unidentified cation, each gave no precipitate with sodium hydroxide, hydrochloric acid, sulfuric acid or sodium carbonate. When flame tests were performed, one solution coloured the flame lilac while the other coloured it red. Which cation is present in each solution? Justify your answer fully.
- b** A third solution, again containing just one cation, gave the same negative tests as in (a), but the flame test for this solution was also negative. Which cation is likely to be present in this solution? Explain. What further test could you perform to verify your conclusion?

- 24** How would you distinguish between solutions of:

- a** calcium chloride and barium chloride
- b** sodium nitrate, potassium nitrate and nitric acid
- \*c** copper sulfate and potassium sulfate?

Give more than one test if possible.

- 25** Describe tests that you could perform that would establish beyond doubt that a pure solid was:

- |                            |                               |
|----------------------------|-------------------------------|
| <b>a</b> copper sulfate    | <b>*e</b> lead carbonate      |
| <b>b</b> barium chloride   | <b>*f</b> iron(II) sulfate    |
| <b>c</b> iron(III) sulfate | <b>*g</b> potassium phosphate |
| <b>d</b> calcium carbonate | <b>*h</b> potassium chloride  |

- 26** Identify the one pure substance that is present in a solution which:

- a** after acidification, gives a precipitate with  $\text{Ag}^+$  but not with  $\text{Ba}^{2+}$ , gives no precipitate with  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , but gives a green precipitate with  $\text{OH}^-$ ; when colourless potassium thiocyanate solution was added to a fresh sample of the original solution, a blood red colour was formed
- b** gives no precipitate with  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , but with  $\text{OH}^-$  produces a pale blue precipitate that dissolves in ammonia solution to form a deep blue solution; fresh samples of the original solution, after acidification, gave precipitates with  $\text{Ag}^+$  and  $\text{Ba}^{2+}$

- c when acidified, forms a precipitate with  $\text{Ag}^+$  but not with  $\text{Ba}^{2+}$ ; no precipitate with chloride or hydroxide but forms a white precipitate with sulfate
- d when acidic, gives no precipitate with silver or barium ions, but when alkaline forms a precipitate with barium ions; no precipitate with chloride, sulfate, hydroxide or carbonate, but colours a flame light purple.

If the tests do not conclusively identify the substance, state the possibilities and describe tests that would distinguish between them. Write net ionic equations for all reactions involved in these tests.

## 6.15 WHY MONITOR CATIONS AND ANIONS?

Determining qualitatively which cations and anions are present in a sample is only part of the job of monitoring. Generally we need to know *how much* of each ion is present. This is because many ions are present in the natural environment and in manufactured products and are quite harmless at low concentrations, but can become harmful at higher concentrations. Some examples are:

- *Phosphate* often occurs in natural waterways at low concentration and is essential for normal aquatic plant growth. However if its concentration becomes too high, it can set off an algal bloom. This is a rapid growth of excessive amounts of algae that can completely cover the surface of a lake or river and kill fish: then when the algae finally uses up all the phosphate, it dies and this has further detrimental effects upon the water body. By monitoring the amounts of phosphate in waterways and in consumer goods that ultimately get into waterways, scientists can guard against algal blooms.
- *Zinc and copper* are both trace elements (meaning living organisms including humans need them in very small amounts), and so small concentrations in water bodies are not just acceptable but desirable; however at higher concentrations both ions are harmful to humans and so we need to monitor their concentrations in waterways and in consumer goods to guard against poisoning.
- *Lead* is a poison: it retards intellectual development in young children, causes brain damage and can lead to neurological disorders. Until recently it was widely used in petrol and so was released to the atmosphere in vehicle exhausts and deposited out on soil near busy highways. Until a few decades ago lead was a constituent of house paints and it is often released to air, water and soil when old houses are renovated. Monitoring lead concentrations in soil near highways, in waterways and in the atmosphere in urban areas is essential to ensure that people are not exposed to harmful concentrations.
- *Iron and copper* cations are sometimes present in municipal water supplies, iron from natural sources and from a common process used to clarify water (Section 8.13), and copper from corrosion of pipes or sloppy pipe repair work. Iron causes stains on household fittings such as sinks, bath tubs and toilet bowls while high concentrations of copper ions can give water an unpleasant taste and be detrimental to health. Monitoring water for these cations (and others) is therefore important.

These and many other similar examples demonstrate the need to monitor quantitatively the amounts or concentrations of potentially harmful substances in consumer goods and in the environment. In all of the above examples (and

in many others) the element of concern is present as a cation or anion. Let us therefore look at an example of the quantitative determination of an anion.

## 6.16 AN EXAMPLE OF GRAVIMETRIC ANALYSIS

Determining *amounts or concentrations* of specific substances is called **quantitative analysis**. Determining which species are present in samples (as was done in Sections 6.9 to 6.14) is called **qualitative analysis**.

Amounts or concentrations of ionic species in samples are measured by a wide variety of techniques, such as volumetric analysis (described in Sections 5.8 to 5.12), **gravimetric analysis** (precipitating out the ion as an insoluble compound and weighing it) and a wide range of instrumental methods, particularly atomic absorption spectroscopy which will be described in Section 6.18. The following example will illustrate gravimetric analysis.



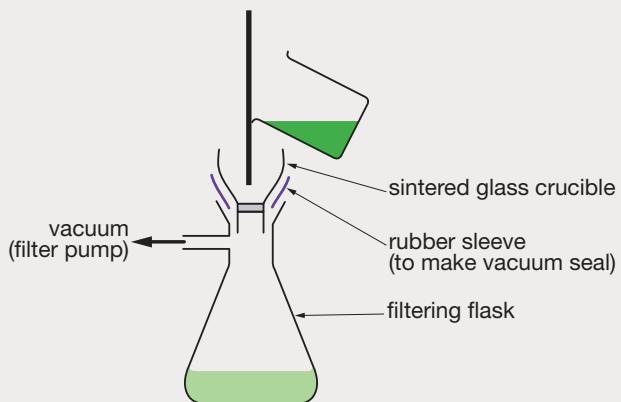
### Example 1

A chemist determined the percentage of sulfate in a lawn food (fertiliser) as follows:

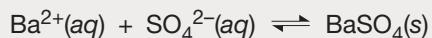
Some of the fertiliser was ground into a fine powder in a mortar and pestle then 1.03 g was placed in a beaker and dissolved in about 250 mL of 0.1 mol/L hydrochloric acid, and stirred to dissolve as much of the solid as possible. Insoluble material was filtered off. The solution was heated to near boiling, then barium chloride solution was slowly added from a burette with continuous stirring to precipitate barium sulfate until no more precipitate formed (that is, excess barium chloride was added). The mixture was digested (heated just below its boiling point) for about 30 minutes with intermittent stirring, then allowed to cool to room temperature, during which time the precipitate settled to the bottom of the beaker. The beaker and contents were then cooled in ice and filtered through a weighed sintered (porous) glass crucible as shown in Figure 6.9. After washing (first with water, then ethanol) and drying (in an oven) to constant mass, the precipitate had a mass of 1.22 g. Calculate the percentage sulfate in the fertiliser.

FIGURE 6.9

Arrangement for collecting a precipitate on a sintered glass crucible



The analysis is based on the fact that barium sulfate is very insoluble, so if we add an excess of  $\text{Ba}^{2+}$  ion to the sample it will precipitate virtually all of the sulfate as  $\text{BaSO}_4$ . The equation for the reaction is:



This equilibrium lies well to the right and by using excess  $\text{Ba}^{2+}$  we force it virtually to completion.

Mass of  $\text{BaSO}_4$  formed = 1.22 g

$$\begin{aligned}\text{mass of } \text{SO}_4^{2-} \text{ in this} &= \frac{\text{relative formula mass of } \text{SO}_4^{2-}}{\text{relative formula mass of } \text{BaSO}_4} \times 1.22 \\ &= \frac{32.1 + 4 \times 16.0}{137.3 + 32.1 + 4 \times 16.0} \times 1.22 \\ &= 0.502 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Percentage sulfate in the fertiliser} &= \frac{0.502}{1.03} \times 100 \\ &= 49\% \text{ (to an accuracy of } \pm 2\% \text{ which is all that is justified by the sensitivity of the mass measurements)}\end{aligned}$$

## Experimental difficulties

In principle, this is a simple experiment—weigh out some fertiliser, dissolve it in water, add barium chloride solution to precipitate barium sulfate, then collect, dry and weigh the precipitate. However considerable care is needed to avoid the many sources of error such as:

- 1 loss of barium sulfate due to its small but possibly significant solubility
- 2 passage of some barium sulfate through the sintered glass filter because the precipitate had formed as very small particles
- 3 leaving some of the precipitate adhering to the walls of the beaker while transferring the mixture to the sintered glass funnel
- 4 loss of some precipitate by spillage during the transfer from beaker to funnel
- 5 contamination of the precipitate with substances adsorbed from the solution during precipitation; this occurs more severely when the precipitate is formed as very small particles (greater surface area for impurities to stick to)
- 6 loss of some precipitate by dissolution while washing it if the volume of wash water is too great
- 7 incomplete drying of the precipitate so that it still contains water when it is weighed.

Errors 1, 2, 3, 4, and 6 would cause the precipitate to weigh less than it should and so would lead to a low percentage of sulfate in the fertiliser. Errors 5 and 7 would cause the precipitate to weigh more than it should and so would lead to a percentage sulfate that was too high.

The experimental procedure is devised to minimise all these errors. Minimising solubility losses (1) requires concentrated solutions but that maximises contamination by adsorption (5) so a compromise is needed. We need to use solutions that are sufficiently dilute so as to minimise contamination by adsorption but not so dilute that solubility of barium sulfate losses are significant. Using starting solutions in which the sulfate concentration is between 0.005 and 0.05 mol/L minimises both types of error.

Forming the precipitate *slowly* from *hot* solutions causes the particles to be large; this minimises contamination by adsorption (smaller surface area). Digesting the mixture causes the particles to grow larger, which makes the precipitate easier to filter and minimises losses from small particles passing through the filter;

The fertiliser being analysed in Example 1



it also reduces adsorption. Cooling the mixture in ice before filtering reduces solubility losses without changing particle size.

To minimise losses during washing, the precipitate is washed with three or four 5 mL portions of water and sucked dry between each, then finally washed with 5 mL ethanol (to aid drying). To minimise errors due to incomplete drying, the precipitate is dried, cooled, weighed, then dried again, cooled and weighed again, and this cycle is repeated until a constant mass is obtained (called *drying to constant mass*).

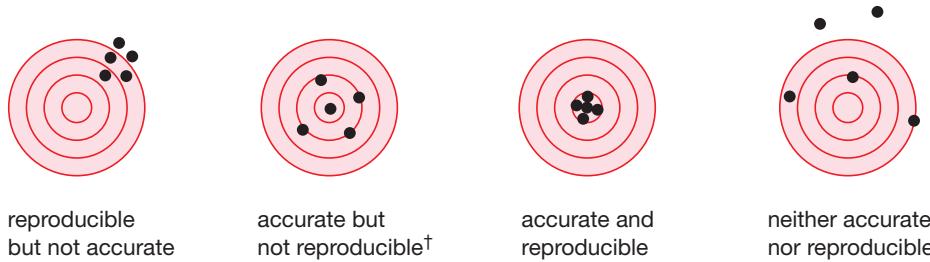
## Reproducibility and accuracy

For any experiment we perform there are two aspects we need to consider: *reproducibility* and *accuracy*.

The **reproducibility** of an experiment is the ability to get the same result when we repeat the experiment several times.

The **accuracy** of an experiment is the closeness of the result of the experiment to the true value of the quantity being measured.

An experiment may give *reproducible* results but that does not mean that they are necessarily *accurate*. However getting results that are reproducible is generally a first step to getting accurate results. The meanings of the two terms are illustrated in Figure 6.10 in which shooters fire five shots at a target, aiming to hit the bullseye (the centre circle).



<sup>†</sup>If the experiment is performed many times, the average answer is the correct value; this is not true of the far left-hand or far right-hand experiments.

*Reproducibility* depends both upon how carefully we can control all the variables that affect the results of an experiment, such as temperature, heat losses to surroundings, material losses in transfers, and upon how accurately we can make individual measurements.

*Accuracy* depends upon the design of the experiment as well as upon the sensitivity of the instruments used to make critical measurements.

We can use the sulfate analysis experiment just described to illustrate the two terms. If we had used a mass balance that could measure to only  $\pm 0.1$  g, then the mass of fertiliser taken would have been  $1.0 \pm 0.1$  g (that is,  $\pm 10\%$ ) and the mass of barium sulfate obtained have been  $1.2 \pm 0.1$  g (that is,  $\pm 8\%$ ). So in repeat experiments, even if great care was taken to use exactly the same procedure, our results would have varied by  $\pm 20\%$  or more; they would not have been very reproducible. By using a mass balance that could measure to  $\pm 0.01$  g we would have obtained results that varied by only 2 to 3%; they would have been quite reproducible. However if we did not take precautions to minimise contamination of the precipitate by adsorption or solubility or filtration losses,

FIGURE 6.10  
An illustration of reproducibility and accuracy, sometimes called *precision* and *accuracy* or in the NSW HSC syllabus *reliability* and *accuracy*

these reproducible results could still have been quite inaccurate (the left-hand diagram in Fig. 6.10).

Only by using instruments of sufficient sensitivity and adopting procedures that minimise all other sources of error can we obtain results that are both reproducible and accurate.

Many standard chemistry texts use the term **precision** for reproducibility. This is unfortunate because the meaning of the word *precision* is not as inherently obvious as that of *reproducibility*. The NSW HSC examiners in 2001, 2003 and 2004 used the term **reliability** for reproducibility, though the syllabus document itself is less clear-cut<sup>†</sup>.

<sup>†</sup> Reliability is used in several places in the NSW HSC syllabus document though its meaning is not defined, and in fact it seems to have more than one meaning there. From comments in Examiners' Reports for 2001 and 2003, the HSC examiners, at least in those years, have interpreted *reliability* to mean *reproducibility*. While it appears to have that meaning in HSC Course outcome H12 on page 17 in the phrase *accuracy and reliability*, on pages 20 and 45 in outcome 12.4(e) *reliability* would seem to have the meaning *correctness or accuracy*. It is a pity that syllabus writers and examiners, when they mean *reproducibility*, do not use that word, because its meaning is unequivocal.

## Exercises

- 27** The sulfate content of a fertiliser was measured by dissolving 1.63 g of the fertiliser in 300 mL water, then slowly adding a solution of barium chloride until no further precipitation occurred. After filtration and drying the mass of precipitate was 1.81 g. Calculate the percentage of sulfate in the fertiliser. In addition calculate the percentage sulfur in the fertiliser (assuming that sulfate is the only source of sulfur).
- 28** a A pair of students performed the experiment in Exercise 16 of Chapter 5 several times but obtained results that were not reproducible. Suggest reasons for this.  
b Another pair of students also performed the same experiment several times (though they made up the sodium carbonate solution only once) and they obtained results that were reproducible but were not accurate. Suggest reasons for this.
- 29** To determine the concentration of magnesium ion in sea water a chemist measured out 250 mL of sea water (by volumetric flask), put it in a beaker and gently heated it to evaporate off about half of the water. Excess sodium hydroxide solution was then slowly added with stirring to precipitate magnesium hydroxide. Then the mixture was allowed to settle and cool to room temperature. The precipitate was filtered off and dried: its mass was 0.703 g.  
a Calculate the percentage magnesium in the sea water.  
b Why did the chemist (i) reduce the volume before adding the sodium hydroxide solution, (ii) add the sodium hydroxide solution before cooling the sample?  
c Suggest additional things the chemist could have done to improve the accuracy of the experiment.
- 30** The phosphate content of a laundry washing powder (detergent) was determined as follows. 6.92 g of the powder was dissolved in approximately 500 mL water. A slight excess of a solution of magnesium chloride in an ammonia, ammonium chloride buffer was added to this with stirring until precipitation was complete. The precipitate



was filtered off and dried; its mass was found to be 1.83 g. The precipitate is pure magnesium ammonium phosphate hexahydrate of formula,  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . Calculate the number of moles of phosphorus in the precipitate and hence the percentage phosphorus in the original laundry powder.

The package this laundry powder came in carried a large letter P, meaning that its phosphorus content was less than 5%. Is this labelling justified?

- 31 To determine the sulfate concentration in a liquid fertiliser (aqueous solution), an analyst first diluted 50 mL of the fertiliser solution to 250 mL, pipetted out 25 mL of the dilute solution, added 200 mL water to it then precipitated the sulfate with barium nitrate solution. The precipitate was filtered, washed and dried to constant mass. In repeated experiments the mass of precipitate was 0.728 g, 0.773 g, 0.722 g and 0.732 g. As accurately as you can, calculate the percentage sulfate in the original fertiliser solution. Justify the procedure you followed.

## Sensitivity

Volumetric analysis as described in Sections 5.8 to 5.12 and the gravimetric analysis described in this section are adequate for analysing samples that contain more than about  $10^{-4}$  to  $10^{-5}$  mol (or 1 to 10 mg) of the element being detected or measured. They are not sensitive enough for much of the monitoring that is necessary today where concentrations below 1 ppm routinely need to be measured. One technique widely used for measuring concentrations of metal ions in the ppm range is *atomic absorption spectroscopy* or AAS.

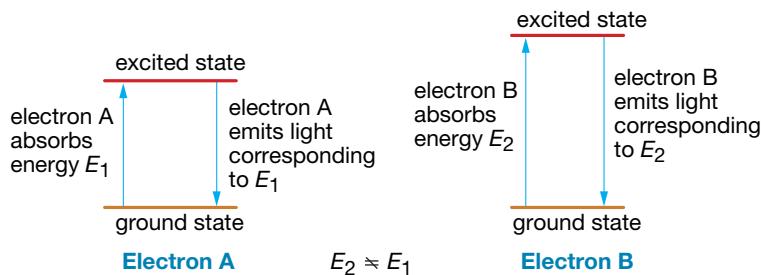
To understand how AAS works we first need to look at what is called atomic *emission spectroscopy*.

## 6.17 ATOMIC EMISSION SPECTROSCOPY<sup>†</sup>

On pp. 43–5 CCPC it was explained that electrons in atoms exist in discrete energy levels. If we heat atoms to a high temperature ( $>1500^\circ\text{C}$ ), some of the electrons get excited out of their normal energy levels into higher energy levels. However after a short time these electrons fall back from these higher energy levels to the normal levels. As they do this the excess energy is liberated as light (either visible or ultraviolet, u.v.). The energy emitted as an electron falls back to its normal state (called the **ground state**) is the same as that absorbed when it was raised to the **excited state** as shown in Figure 6.11.

If we break the emitted light into its various wavelength components (by passing it through a prism), we find that the emissions have occurred at just a few discrete wavelengths as shown in Figure 6.12. The pattern of lines

FIGURE 6.11  
How each bright line in an emission spectrum is generated; electrons A and B give rise to separate bright lines in the spectrum



The electrons absorb energy either from a high temperature flame or from an electric discharge.

<sup>†</sup> not actually required for the NSW HSC core, though it is part of the Forensic Chemistry option; it is included here to aid understanding of AAS in the next section

(wavelengths) is called an **emission spectrum** of the element (a set of bright or coloured lines on a black background). Each wavelength corresponds to the energy required to excite a particular electron in the atom from its ground state to an excited state and this is equal to the energy released when that electron falls from the excited state back to the ground state (Fig. 6.11).

Each element has its own unique emission spectrum. Several such spectra are shown in Figure 6.12. By measuring the emission spectrum of a sample and comparing it with the known spectra of elements we can identify the elements present in the sample. Measuring, studying and using such spectra is called **atomic emission spectroscopy**. It is extremely useful for qualitatively identifying elements present in samples.

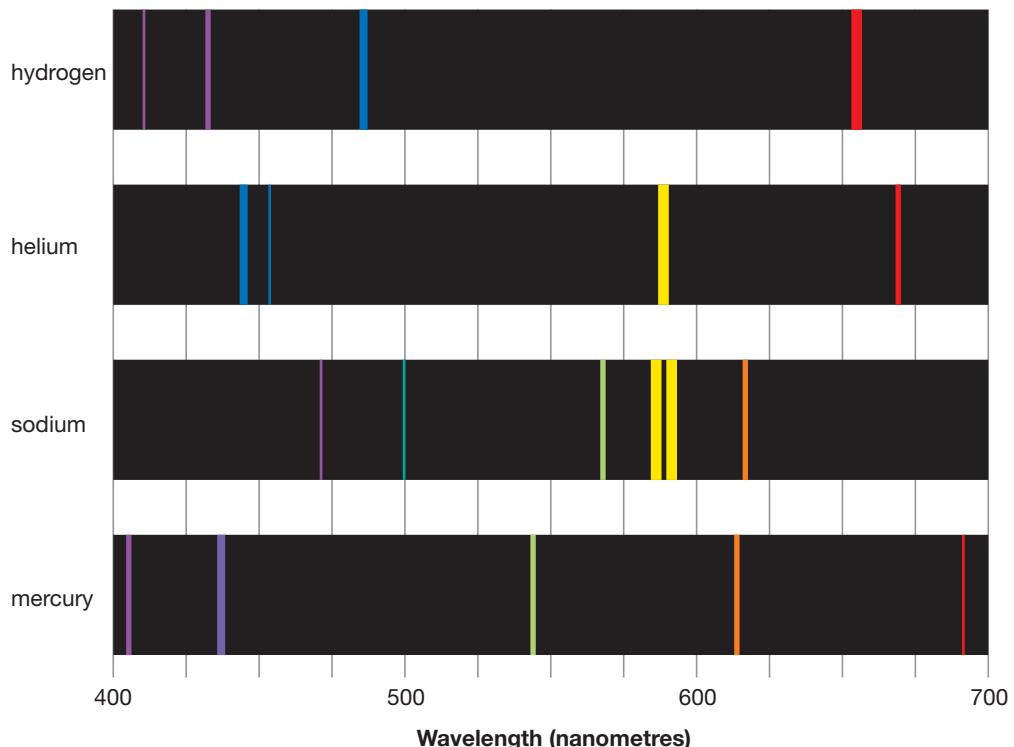


FIGURE 6.12  
Emission spectra of some common elements

By measuring the intensity of the emitted light at particular wavelengths we can also determine the amounts of particular elements present; that is, use it for quantitative analysis. However atomic *absorption* spectroscopy is often more convenient and sensitive for quantitative work.

The emission spectrum of an element tells us the wavelengths at which that element will absorb light, because an electron only absorbs light if the energy of the light corresponds to what is required to move the electron to a higher energy level (excited state). Such emission spectra are the light sources for AAS.

## 6.18 ATOMIC ABSORPTION SPECTROSCOPY

*Atomic absorption spectroscopy*, AAS, was originally developed by Alan Walsh and his team of co-workers in Australia's CSIRO in the early 1950s. Instruments were originally manufactured here, but the local manufacturer was soon bought out by an overseas company and production was later moved off-shore. Although many companies were licensed to make atomic absorption spectrometers, none have been manufactured in Australia for the past three decades. AAS is in general use throughout the world for the measurement of ppm concentrations of

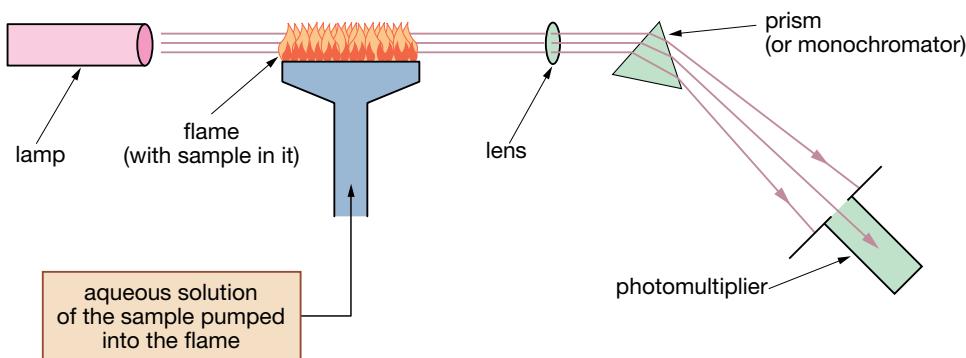
over sixty elements (mainly metals).

If ground state atoms of an element are irradiated with light of a wavelength known to be absorbed by them (i.e. of a wavelength in that element's emission spectrum), then those atoms will absorb some of that light. By measuring the fraction of the light at that wavelength that is absorbed, we can determine the concentration of the element. This is the basis of **atomic absorption spectroscopy**.

The experimental arrangement is shown in Figure 6.13. The sample to be analysed is fed into a flame which vaporises it and converts molecules and ions into atoms. The light source is a lamp that emits radiation of a wavelength which is absorbed by the element to be measured. A separate lamp is required for each element. The lamp actually produces the emission spectrum of the element to be analysed so there is an exact match of emitted and absorbed wavelengths. The light passes through the flame and into a prism or monochromator. The monochromator has a photomultiplier as detector. By rotating the prism (or grating) of the monochromator, light of different wavelengths can be focused on to the photomultiplier. By measuring the intensity of the light reaching the detector with and without the sample in the flame, the instrument calculates and displays a function called **absorbance**<sup>†</sup>.

*Absorbance is proportional to concentration*, so the measured absorbance can be used to calculate the concentration of the particular element being examined.

FIGURE 6.13  
Schematic layout of an atomic absorption spectrometer



## Why AAS is so sensitive

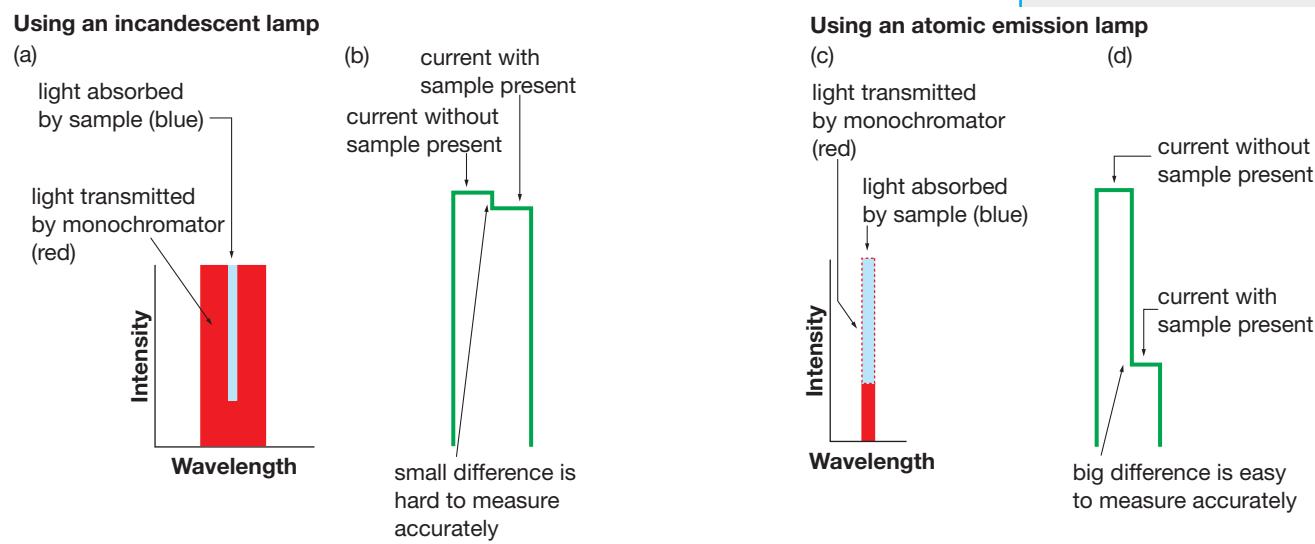
Atomic absorption spectroscopy is extremely sensitive. The reasons for this are:

- Measurements are made from absorption by the nearly 100% of the atoms that are in the ground state rather than from emission by only the 0.1% to  $10^{-5}\%$  of the atoms that are in the excited state as occurs in atomic emission spectroscopy.
- AAS uses one of the lines in the emission spectrum of the element concerned as the light source for the measurement. Figure 6.14 illustrates this.

If the light source had been an incandescent light bulb with a very high quality monochromator<sup>‡</sup> to select a very narrow band of light of the appropriate

<sup>†</sup> Absorbance is  $\log_{10} (I_0/I)$  where  $I$  and  $I_0$  are the intensities of the light reaching the detector with and without the sample being present in the flame.

<sup>‡</sup> A monochromator is an instrument that is able to select a narrow wavelength band of light (light of one colour) from a source that emits many wavelengths (colours).



wavelength range to pass through the sample, this ‘narrow’ band of light would still be very much broader than the emission (or absorption) line of the sample, so only a very small fraction of the incident light would be absorbed by the sample as in Figure 6.14(a). The intensity of light reaching the detector (and so the current produced by it) with the sample present would be only slightly less than that without the sample present (b), and because it is this difference that is related to the concentration, we would not be able to measure it very accurately.

When the light source is one line from the emission spectrum of the element to be measured, the sample absorbs a large proportion of the incident light because the emission and absorption lines are both extremely narrow and overlap exactly (c). This results in a big change in the current from the detector when the sample is present (d) and so we can measure low concentrations quite accurately.

As a result of both of these factors AAS can easily measure part per million concentrations on quite small samples. In fact detection levels of 0.01 ppm are quite common.

However because a different lamp is required for each element, the technique is not as convenient as emission spectroscopy for determining qualitatively which elements are present in a sample or for routinely measuring concentrations of several elements in the one sample.

## Uses

Atomic absorption spectroscopy is widely used to monitor:

- small concentrations of metals (and some other elements such as As and B) in the environment, particularly heavy metals such as Pb, Hg, Cd, Cr, Cu, Zn; some examples being the detection of copper and aluminium in waterways, zinc in oysters, lead fallout beside highways and mercury in fish.
- concentrations of micro-nutrients (ones needed in very small amounts) in soils
- small amounts of contaminants in foods (particularly processed foods) and medicines and other manufactured goods
- the presence of small concentrations of a variety of elements in living organisms.

**FIGURE 6.14**  
How using an atomic emission lamp increases the sensitivity of AAS

Because it is able to measure very low concentrations of a wide variety of elements, particularly metals, *atomic absorption spectroscopy is extremely effective in monitoring pollution*, particularly water and soil pollution.

A typical atomic absorption spectrometer. Notice the flame into which the sample is vaporised; the sample is being pumped into the flame from the conical flask



### Example 2

Atomic absorption spectroscopy was used to measure the concentration of iron in several natural water samples. The samples were filtered then sprayed into the flame of the instrument at a carefully regulated rate; absorbance by the iron atoms produced in the flame was measured using the appropriate lamp for iron. Results are tabulated below.

Sample	L	M	P	Q
Absorbance	0.74	0.05	0.53	0.28

To convert absorbances into concentrations a calibration curve was constructed as follows. 3.62 g hydrated iron(II) ammonium sulfate, a very pure compound of iron of formula  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , was dissolved in dilute acid solution and the volume made up to 0.500 L. Volumes of this solution were then accurately diluted to 1.000 L. These diluted solutions were analysed in the instrument in exactly the same way as was used for the samples for analysis. Results are recorded below.

Volume (in mL) of concentrated solution diluted to 1.000 L	1.00	2.00	5.00	10.00
Absorbance	0.07	0.13	0.34	0.69

Calculate the concentration (in ppm) of iron in each of the standard solutions and draw a graph of absorbance versus concentration. Use this to estimate the iron concentration in each of the unknown samples. Does this analysis measure iron(II) or iron(III) or both? Explain.

We first need to calculate the concentration of iron in the original standard solution, then the concentrations in the solutions used to calibrate the instrument, and then draw a calibration curve:

Molar mass of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  =

$$55.9 + 2 \times (14.0 + 4 \times 1.0) + 2 \times (32.1 + 4 \times 16.0) + 6 \times (16.0 + 2 \times 1.0) \\ = 392.1 \text{ g/mol}$$

$$\text{Fraction of the solid that is iron} = \frac{55.9}{392.1}$$

$$\therefore \text{mass of iron in the solution} = \frac{55.9}{392.1} \times 3.62 \\ = 0.516 \text{ g}$$

This is in 0.500 L,

$$\text{so concentration of iron in the solution} = 2 \times 0.516 \\ = 1.032 \text{ g/L}$$

If 1.00 mL of this solution is diluted to 1.00 L,

$$\text{concentration of dilute solution} = \frac{1.032}{1000} \\ = 1.032 \times 10^{-3} \text{ g/L} \\ = 1.032 \text{ ppm (taking 1.00 L as 1000 g)}$$

Concentrations corresponding to 2, 5 and 10 mL are 2.064, 5.16 and 10.32 ppm respectively.

Absorbance is plotted against concentration for these solutions in Figure 6.15. The origin is a point for the graph, because at zero concentration absorbance is zero. We note that the highest absorbance for our test solutions (0.74) is somewhat greater than for our calibration solutions (0.69) so we use a scale on the graph that extends a bit beyond the 10.32 ppm of that solution, say to 12 ppm.

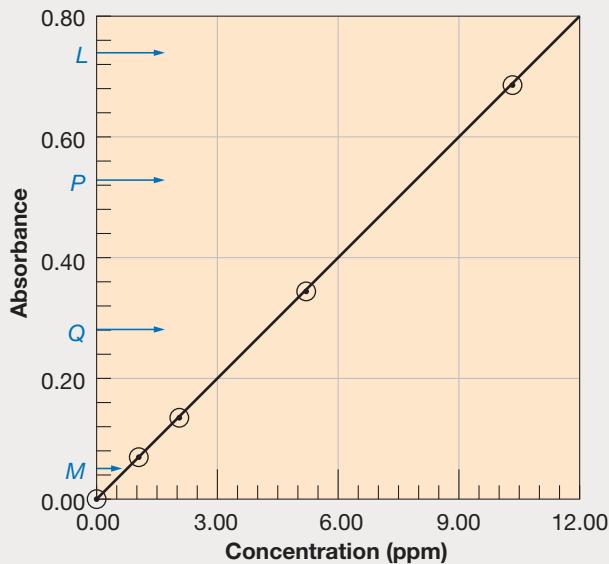


FIGURE 6.15  
Absorbance versus  
concentration for the  
calibration measurements

We can now use this graph to read off the concentrations of our natural water samples. Concentrations are: for **L**, 11.1 ppm, for **M** 0.8 ppm, for **P** 8.0 ppm and for **Q** 4.2 ppm with an accuracy (from reading the graph) of about  $\pm 0.2$  ppm.

Because the sample is decomposed into atoms in the flame, AAS measures the *total concentration of the element in the sample*; in this case it measures Fe(II) plus Fe(III).

#### Alternative calibration method

While the most accurate method of calibrating the instrument is to measure absorbances of several standard solutions and draw a calibration graph, sometimes analysts measure just one standard solution and use the fact that absorbance is proportional to

concentration. In this example, had the only calibration measurement been that a solution with 5.16 ppm iron had an absorbance of 0.34, we should have proceeded in one of two ways.

Because absorbance is proportional to concentration, we can write either

$$\frac{\text{concentration in solution L}}{\text{concentration in standard solution}} = \frac{\text{absorbance of solution L}}{\text{absorbance of standard solution}}$$

That is,

$$\frac{\text{concentration in solution L}}{5.16} = \frac{0.74}{0.34}$$

$$\text{concentration of solution L} = 11.2 \text{ ppm} \text{ (compare } 11.1 \pm 0.2 \text{ above)}$$

The other three concentrations are obtained similarly.

$$\text{or } c = kA \quad \dots (6.5)$$

where  $c$  is concentration,  $A$  is absorbance and  $k$  is the proportionality constant.

From the calibration measurement

$$k = \frac{5.16}{0.34} \\ = 15.2$$

Now applying Equation 6.5 and this value of  $k$  to the absorbance of solution L,

$$\begin{aligned} \text{concentration of solution L} &= 15.2 \times 0.74 \\ &= 11.2 \text{ ppm} \end{aligned}$$

and similarly for the other solutions.

## 6.19 AAS AND TRACE ELEMENTS

**Trace elements** are elements that are required by living organisms in very small amounts. Their concentrations in plants and/or animals are generally in the 1 to 100 ppm range. Common trace elements in humans are Zn, Co, Cu, Ni, Mo, I and Se. Small amounts of these elements are needed to help enzymes function. For plants important trace elements are Mn, Cu, B, Mo and Zn.

The need for most of these trace elements, particularly in soils, was first recognised when scientists started using AAS for measuring concentrations of species in soils and organisms. Before the introduction of AAS the commonly used analytical methods were not sensitive enough to detect the low concentrations of these elements and so their presence had gone unnoticed.

AAS not only showed that there were trace elements in living organisms and soils: it also helped demonstrate that these trace elements were essential for the well-being of the organisms and has been used to work out how these trace elements help the functioning of organisms. In these ways AAS has had a great impact upon scientific understanding of trace elements in organisms.

### Exercises

- 32 Samples were being analysed for lead by atomic absorption spectroscopy. The samples also contained significant concentrations of copper and barium. Would these ions interfere with the analysis for lead? Explain why or why not.

- 33** In order to measure the concentration of mercury in sea water near an industrial plant, a team of chemists used atomic absorption spectroscopy. They first calibrated their instrument by admitting some standard solutions to it and determining the absorbance (a measure of the fraction of incident light absorbed by the sample) for each. Then they measured the absorbance of several water samples collected from different locations near the industrial plant. For their standards they made a stock solution by dissolving 0.106 g mercury (as mercury(II) nitrate) in water and making the volume to 250 mL in a volumetric flask, then they quantitatively diluted (by pipette) 1 mL, 2 mL and 4 mL of this solution to 100 mL (volumetric flask). Absorbances for the standards and the samples are shown below.

Standards (mL)	1.00	2.00	4.00	Samples	A	B	C	D
Absorbance	0.083	0.164	0.331		0.32	0.46	0.21	0.055

Draw a calibration curve of absorbance versus concentration in parts per million (ppm) for the standards. Take 1.00 mL of aqueous solution as 1.00 g. Determine the concentration of mercury (in ppm) in each of the samples.

- 34** It was suspected that strawberry jam made from fruit grown near to a major highway was contaminated by lead (from fallout from motor car exhausts). A chemist analysed the jam for lead content as follows. Approximately 10 gram samples of jam from three separate jars were taken and mixed thoroughly with dilute nitric acid and the volume made to 50.0 mL. The mixture was then centrifuged to remove solid material. Portions of the clear solutions were then fed into an atomic absorption spectrometer. Absorbances (which are proportional to lead concentration) are shown below.

Sample	standard	A	B	C
Mass of jam taken (g)	—	10.14	9.97	10.08
Absorbance	0.28	0.30	0.19	0.24

A standard solution (for calibrating the instrument) was prepared by dissolving 0.0507 g lead nitrate in water and making the volume to 250 mL in a volumetric flask. 10 mL of this solution (by pipette) was diluted to 1 L (volumetric flask). This dilute solution was also fed into the AA spectrometer: its absorbance is shown in the table also.

Calculate the concentration of Pb in the diluted standard solution in ppm. Take 1.00 mL of solution as 1.00 g. Then use the absorbance values to calculate the concentration (in ppm) of Pb first in the sample solutions analysed then in the jam samples themselves.

AAS measurements on lead in this concentration range are generally accurate to better than 1%. Suggest reasons for the larger variation in results in this experiment.

- 35** Some householders complained to the water authority that at the beginning of each day their water had an unpleasant taste. The authorities suspected that the taste was due to copper being leached out of the water pipes overnight, so they performed the following tests. Early one morning before any water had been used by the household they collected a sample of water from an offending tap (call this sample A). Water was allowed to flow for a few minutes to partially flush out the pipes then a second sample was collected (sample B). Finally the tap was let run for a sufficiently long time to completely flush out the household pipes and sample C was collected. Water from a water main in the street about halfway between the reservoir and the house was also collected (sample D). These four samples were analysed for copper by atomic absorption spectroscopy along with a laboratory standard sample that was known to contain 2.16 ppm copper. The absorbance values were:

Sample	standard	A	B	C	D
Absorbance	0.310	0.91	0.44	0.063	0.057

Absorbance is proportional to concentration. Calculate the concentration of copper (in ppm) in each of the samples A to D. Offer an explanation for these results.

## Important new terms

You should know the meaning of the following terms:

absorbance (p. 226)  
accuracy (p. 222)  
atomic absorption spectroscopy (p. 226)  
atomic emission spectroscopy (p. 225)  
centrifuge (p. 210)  
complex ion (p. 209)  
emission spectrum (p. 225)  
excited state (p. 224)  
flame test (p. 216)

gas chromatography (p. 196)  
gravimetric analysis (p. 220)  
ground state (p. 224)  
Haber process (p. 202)  
precision (p. 223)  
qualitative analysis (p. 220)  
quantitative analysis (p. 220)  
reliability (p. 223)  
reproducibility (p. 222)  
trace elements (p. 230)

## CHAPTER 6

## Test yourself

- Explain the meaning of each of the items in the ‘Important new terms’ section above.
- Give a chemical reaction in which the products depend upon the conditions used and write equations for the formation of at least two different products from it.
- List the major uses of ammonia.
- Use Le Chatelier’s principle to explain the conditions that would be most favourable for the synthesis of ammonia (from nitrogen and hydrogen gases) on equilibrium grounds alone. Why are these conditions not used industrially? What are the conditions used and why?
- How are the reactants for the Haber process generally produced? Why must oxygen be excluded?
- Why is careful monitoring of reactant composition and reaction conditions so necessary in the Haber process?
- Describe how you would determine if the cation in a pure substance was  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . Write equations for all reactions involved.
- A solution of a pure substance produced a precipitate with sodium sulfate solution. What does this tell you about the identity of the cation in the solution?
- Why is the absence of a precipitate with chloride not conclusive proof of the absence of  $\text{Pb}^{2+}$  in a solution? How would you confirm the presence of  $\text{Pb}^{2+}$ ?
- How would you decide whether the iron ion in a solution was  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ?

- 11** Explain how you would determine which cations (of those listed in Question 7) were present in a mixture. Explain why you would use that particular sequence of tests.
- 12** Give two examples of complex ions.
- 13** Explain how a centrifuge separates precipitates from solutions and why it is preferable to ordinary filtration.
- 14** Describe tests you would perform to decide whether a solution of a pure substance contained  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$ .
- 15** Explain why the formation of a precipitate with  $\text{Ag}^+$  does not prove the presence of chloride in a solution.
- 16** Explain why phosphate ion produces a precipitate with barium ion in alkaline solution but not in acid solution whereas sulfate ion produces a precipitate in both acid and alkaline solution.
- 17** Explain how you would determine which anions (of those listed in Question 14) were present in a mixture. Explain why you would use that particular sequence of tests.
- 18** How would you perform a flame test? What precautions would you take to avoid false results?
- 19** List four elements that have characteristic flame colours and state what they are.
- 20** Give two situations in which a low concentration of a substance is desirable but a high concentration is harmful.
- 21** Describe one example of a gravimetric analysis.
- 22** What is an atomic emission spectrum? What feature of an atom gives rise to it?
- 23** Explain in words and with a diagram how atomic absorption spectroscopy works.
- 24** What is the relevance of atomic emission spectra to atomic absorption spectroscopy?
- 25** Why is atomic absorption spectroscopy, AAS, for any particular element generally free from interference from other elements?
- 26** Why is atomic absorption spectroscopy able to measure lower concentrations than most other analytical techniques?
- 27** What, if any, information does AAS provide about the compound in which an element being detected occurs? Why?
- 28** Give two everyday applications of AAS.
- 29** Explain the involvement of atomic absorption spectroscopy with trace elements.

# CHAPTER 7

# Chemistry and the atmosphere

## IN THIS CHAPTER

Composition of the atmosphere  
The layered structure of the atmosphere  
The main air pollutants and their sources  
Ozone in the atmosphere  
Photochemical smog and ozone  
Structure of ozone and coordinate covalent bonds  
Allotropes of oxygen  
Oxygen gas, ozone and oxygen atoms

Depletion of ozone in the stratosphere  
Haloalkanes, particularly CFCs  
Destruction of stratospheric ozone by CFCs  
Why over the Antarctic and why in spring?  
Combating the ozone-hole problem  
Monitoring stratospheric ozone

Human activity has released enormous amounts of material into the atmosphere and into water bodies and dumped large quantities of waste on to the land. A hundred years ago the quantities of wastes produced caused localised pollution: the air in industrial cities was unhealthy and rivers near industrial and mining sites were badly polluted, but the problems were essentially localised. Today the quantities of wastes are much larger and pollution is not just local, it has become global. Oceans remote from human activity now show signs of pollution and the whole atmosphere generally has been affected by human emissions.

Chemistry has contributed to this pollution through the manufacture of many of the products of modern society. But equally importantly chemistry has been responsible for devising ways of overcoming environmental damage. It does this in three ways:

- 1 by developing processes that create less waste and devising methods for cleaning up industrial effluents
- 2 by monitoring the environment to identify localised pollution and its sources and to detect gradual and small but significant global changes in the atmosphere and oceans, and
- 3 by working out how secondary pollutants (ones not directly released into the environment but which are made there by chemical reactions) are formed and how their formation can be minimised.

Chemists are also involved with publicising the problems and the need for remedial action.

In this chapter we shall look at the structure and chemistry of the atmosphere and at some forms of atmospheric pollution.

## 7.1 COMPOSITION OF THE ATMOSPHERE

The atmosphere is a layer of gas about 200 to 300 km thick that surrounds the Earth. Of its mass, 75% is in the lower 15 km with 99.997% being below 90 km. The composition of the atmosphere is shown in Table 7.1. We generally use percentages for the major constituents such as N<sub>2</sub> and O<sub>2</sub> and part per million for the minor ones such as CO<sub>2</sub>, He, N<sub>2</sub>O. The percentages of nitrogen, oxygen, carbon dioxide and the noble gases (in dry air) are remarkably constant at least up to an altitude of 90 km.

The percentage of water vapour, particularly in the troposphere, varies considerably, from about 0.5 to 5%. It is measured by relative humidity.<sup>†</sup> In the stratosphere its concentration is only about 5 ppm.<sup>‡</sup>

**TABLE 7.1 Composition of the dry atmosphere**

Major constituents	Percentage (v/v)		
nitrogen	78.08		
oxygen	20.95		
argon	0.93		
Minor constituents	ppm	Minor constituents	ppm
carbon dioxide	350	nitrous oxide	0.2
neon	18	carbon monoxide	0.1
helium	5	ozone	0.02
methane	1.5	NO + NO <sub>2</sub>	<0.01
krypton	1	ammonia	<0.01
hydrogen	0.5	SO <sub>2</sub> + H <sub>2</sub> S	<0.002

The ways that pollutants are dispersed through, or removed from, the atmosphere depend upon the physical structure of the atmosphere, so let us take a look at this.

## 7.2 THE LAYERED STRUCTURE OF THE ATMOSPHERE

There is an unusual vertical temperature profile through the atmosphere. It allows us to define several quite distinct zones that have been given special names.

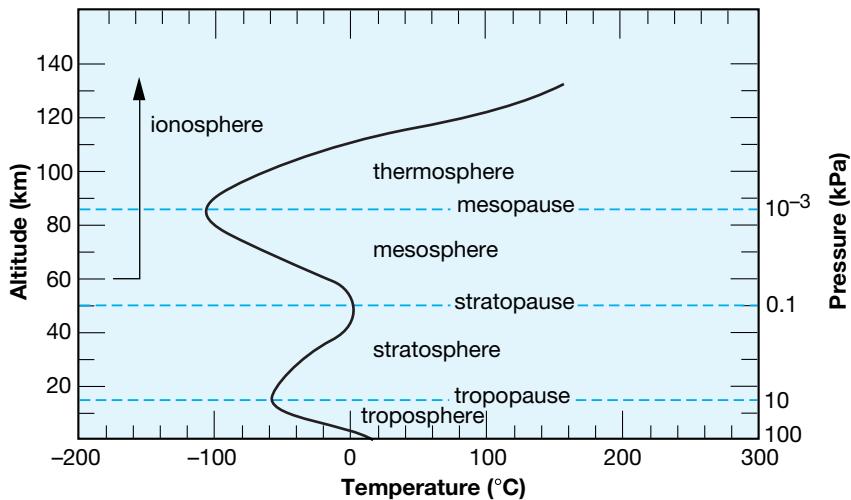
Starting from ground level, as we go up, temperature decreases—from about 15°C at the Earth's surface to a minimum of about –50°C at an altitude of around 15 km (50 000 feet). Then as altitude increases further the temperature starts to increase. Temperature increases with altitude until about 50 km when it is roughly 0°C; then it starts to decrease again. This region from 15 to 50 km

<sup>†</sup> Relative humidity is the actual pressure of water vapour expressed as a percentage of the saturated vapour pressure at the prevailing temperature.

<sup>‡</sup> ppm for gases was defined in Section 4.9.

is called the *stratosphere*. The lower portion of the atmosphere is called the *troposphere* and the region above the stratosphere is called the *mesosphere*. These regions are shown in Figure 7.1. The boundary between the troposphere and stratosphere is called the **tropopause**.

**FIGURE 7.1**  
The way temperature changes with altitude through the Earth's atmosphere



The **troposphere** is the region of the atmosphere closest to the Earth in which temperature generally decreases as altitude increases: it extends from sea level to an altitude of about 15 km.

The **stratosphere** is the region of the atmosphere in which temperature increases as altitude increases: it is from an altitude of about 15 km to 50 km.

When temperature decreases as altitude increases (as in the troposphere), we get good mixing of gases—patches of hot air near ground level rise (because hot air has a lower density) and cause cooler air at higher altitudes to fall to take place; this is convection. It is part of the weather we experience. This convective mixing of the air in the troposphere means that substances released into the air at ground level get mixed throughout the troposphere.

However when temperature rises as altitude increases (as in the stratosphere), there can be very little vertical mixing, because if we heat the air at the bottom of the stratosphere, it cannot rise as in the troposphere, because the air above it still has a lower density (it's warmer). Hence the stratosphere is a region of great stability. There is very little 'weather' in the stratosphere. Because of the temperature minimum at the tropopause, substances do not easily transfer from the troposphere to the stratosphere or *vice versa*. Hence very little of the ozone present in the stratosphere transfers to the troposphere and impurities (pollutants) in the troposphere only very slowly transfer into the stratosphere by slow diffusion not convection.

This slowness of transfer of gases across the tropopause is a key factor in the ozone hole problem (Section 7.9). First it means that the ozone that is present in the stratosphere (it is actually formed there from ordinary oxygen gas) stays there, and does not come down to ground level where it would poison us (and most other living matter). Secondly it means that pollutants released at ground level (which fairly quickly get mixed throughout the troposphere) diffuse into the stratosphere only extremely slowly. Hence it is only pollutants that survive a long time before being destroyed by sunlight which can get into the stratosphere.

Pressure steadily decreases as altitude increases: there are no minima or

maxima for pressure. At the tropopause pressure is about 10 kPa and at the stratopause 0.1 kPa (compare with 101 kPa at sea level).

The **stratopause** is the boundary between the stratosphere and the mesosphere.

### Exercises

- 1 Express the parts per million concentrations for CO<sub>2</sub>, Ne, H<sub>2</sub> and ozone in Table 7.1 as percentages.
- 2
  - a Use the molar volume of a gas (24.8 L) at 25°C and 100.0 kPa pressure to calculate the total concentration of gas in the atmosphere in moles per litre under these conditions.
  - b Calculate the number of moles of carbon dioxide per litre of dry atmosphere under these conditions of temperature and pressure.
- 3 \*
  - a Use the data below to draw a graph of atmospheric pressure *versus* altitude. In graphs we generally make the independent variable (in this case altitude) the x axis and the dependent variable the y axis. However atmospheric profiles are generally drawn with altitude as the y axis (e.g. Fig 7.1) so in your graph make altitude the y axis. Draw a smooth curve through the points.
  - b Use your graph to explain qualitatively why 75% of the mass of the atmosphere lies below 15 km and 99.997% below 90 km.



Altitude (km)	0	2.0	5.0	10.0	15.0	20.0	30.0	40.0	50.0
Pressure (kPa)	101.3	79.7	52.5	23.7	10.8	4.6	1.3	0.6	0.2

## 7.3 THE MAIN AIR POLLUTANTS AND THEIR SOURCES

The major source of atmospheric pollution is combustion, from both stationary and moving sources (power stations and vehicles). On pp. 286–8 CCPC we saw that the main pollutants from combustion were carbon monoxide and soot, sulfur dioxide, oxides of nitrogen and particulates. Other important sources of air pollutants are factories, farms and homes.

Table 7.2 lists the major air pollutants and gives their sources.

The word **particulates** (in Table 7.2 and elsewhere) is used to describe a mixture of small solid particles and small droplets of liquid.

Two of the major sources of air pollution are electricity generation and motor cars, particularly on congested city highways



**TABLE 7.2 The major air pollutants and their sources**

Pollutant	Source
carbon monoxide, CO	motor cars, cigarettes, bush, forest and farm fires, slow combustion stoves
oxides of nitrogen ( $\text{NO} + \text{NO}_2$ )	combustion (vehicles and power stations)
hydrocarbons	vehicles and factories using solvents
other volatile organic compounds (VOCs)	industry, commerce (e.g. dry cleaners) and homes (from solvents and a variety of everyday processes)
particulates (including asbestos)	combustion (transport and industry), many industrial processes (including mining), bush fires, farm and forest burn-offs, backyard incineration; asbestos in dust from insulation and pre-1986 fibrous cement board in old buildings and from their demolition
airborne lead	lead smelters (Broken Hill and Port Pirie), paint dust from renovating old houses (Section 6.15), and until recently from leaded petrol (used in pre-1986 cars)
sulfur dioxide, $\text{SO}_2$	combustion (impurities in the fuel), metals extraction (from sulfide ores), some chemical manufacturing
radioactivity	combustion (coal contains some radioactive substances), uranium mining, nuclear weapons testing, nuclear power plants (not in Australia), medical and scientific use of radioisotopes
carcinogenic compounds	benzene and toluene from unleaded petrol, vinyl chloride from plastics manufacture, dioxin from using and incinerating chlorine-containing compounds, cigarette smoke
fluoride	aluminium smelters
chlorofluorocarbons (CFCs) and other halogenated organic compounds	before 1996 from refrigeration, air conditioning, foam plastics, electronics cleaning, halon fire extinguishers
ozone	no direct sources; formed in photochemical smog (Section 7.5)

## 7.4 OZONE IN THE ATMOSPHERE

Ozone,  $\text{O}_3$ , is an *allotrope* of the element oxygen, the main allotrope being ordinary oxygen gas,  $\text{O}_2$ . Ozone is naturally present in the atmosphere. Near ground level its concentration (in clean air) is only 0.02 ppm: in the stratosphere it ranges from 2 to 8 and back to 2 ppm as altitude changes from 15 to 30 to 50 km. Ozone is poisonous to humans and most other life forms, if they breathe it in or come into contact with it. For people ozone causes breathing difficulties, aggravates respiratory problems, and produces headaches and premature fatigue. However in the stratosphere ozone protects all life forms by filtering out short-wavelength ultraviolet (u.v.) light which damages living tissue: in other words it acts as a *radiation shield*.

It is ironic that human activity is both *producing* ozone at ground level where we do *not* want it and *destroying* it in the stratosphere where we *do* want it.

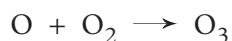
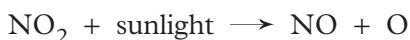
Table 7.2 lists ozone as a pollutant but there is no significant direct release of ozone to the atmosphere. It is formed in the atmosphere from other pollutants

## 7.5 PHOTOCHEMICAL SMOG AND OZONE<sup>†</sup>

**Photochemical smog** is a type of air pollution that is produced when sunlight acts upon motor car exhaust gases to form ozone and other harmful substances.

It occurs in cities which have plenty of sunlight and lots of motor cars, such as Los Angeles, Denver, Tokyo, Singapore, and to a lesser extent, Sydney and Brisbane. The most harmful component of photochemical smog is ozone, O<sub>3</sub>.

Ozone forms in the lower atmosphere when sunlight is very intense (summer) and when concentrations of nitrogen dioxide, NO<sub>2</sub>, are well above clean-air levels. This happens when there is no breeze to disperse pollutants. The sunlight splits off an oxygen atom from the NO<sub>2</sub> molecule, and this O atom combines with an oxygen molecule, O<sub>2</sub>, to form ozone:



However NO can destroy ozone:



We have already seen (pp. 290–2 CCPC) that the rate of a reaction depends upon concentration of reactants. Consequently if the concentration of NO<sub>2</sub> is low and the concentration of NO high, then the rate of the NO + O<sub>3</sub> reaction is much greater than the rate of the NO<sub>2</sub> + light reaction, and so ozone is destroyed nearly as quickly as it is formed, thus keeping its concentration below harmful levels. This is the situation when the ratio of NO<sub>2</sub> to NO in the atmosphere is less than about 0.3. However if the concentration of NO<sub>2</sub> is high and that of NO low, then ozone is formed at a much greater rate than that at which it is being destroyed, and so there is a build-up in ozone concentration, often to levels in the range of 0.1 to 0.3 ppm (0.1 ppm is harmful to health). This occurs when the ratio of NO<sub>2</sub> to NO in the air is greater than about 3:1.

As we saw in Section 4.9 motor cars are a major source of NO and NO<sub>2</sub>. The NO plus NO<sub>2</sub> mixture emerging from motor car exhausts is usually about 80% NO. If the ratio of NO<sub>2</sub> to NO stayed at about this value of 0.25, there would be no harmful build-up of ozone.

However other reactions in the air, involving other substances from the same motor car exhausts, convert

One of the NSW Department of Environment and Conservation's network of air monitoring stations around the Sydney and Wollongong metropolitan areas. This one is at Albion Park. The tall projection measures air pressure and wind speed: the smaller uprights near the roofline are intake tubes for various monitoring instruments



† not strictly required for the NSW HSC, but a discussion of ozone in the atmosphere would not be complete without it

‡ In the laboratory when a gas jar of NO is exposed to air, the reaction between NO and O<sub>2</sub> seems almost instantaneous. This is because the concentration of NO is very high. When NO concentration is less than a few ppm, however, this reaction is too slow to convert significant amounts of NO to NO<sub>2</sub> in the time available (a few hours).

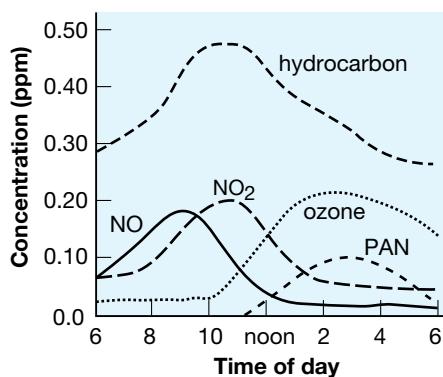
$\text{NO}$  to  $\text{NO}_2$ . This leads to a build-up of harmful concentrations of ozone. These ‘other substances’ are hydrocarbons (unburnt petrol) and their partial oxidation products.



Hundreds of such reactions involving a wide range of carbon compounds occur. These all increase the ratio of  $\text{NO}_2$  to  $\text{NO}$ .

On a smoggy day we first observe a build-up of  $\text{NO}$  and hydrocarbon (with the morning traffic peak), followed by a gradual conversion of  $\text{NO}$  to  $\text{NO}_2$  during the rest of the morning, and then a build-up of ozone in the early afternoon, particularly if there is no breeze to disperse the smog: Figure 7.2 shows this. Because reaction rate depends upon reactant concentration, high concentrations of hydrocarbons and  $\text{NO}_x$  lead to rapid rates of formation (and hence high final concentrations) of ozone.

FIGURE 7.2  
Variation in pollutant concentrations during a windless sunny day



In addition to the health problems mentioned in Section 7.4, photochemical smog can cause people’s eyes to water and to sting. The compounds responsible for this are PANs, *peroxyacetyl nitrates*. The simplest PAN is  $\text{CH}_3\text{CO}-\text{OO}-\text{NO}_2$ , *peroxyacetyl nitrate*. PANs like ozone are formed by the action of sunlight on car exhaust gases:



The chemical reactions occurring in photochemical smog also lead to the formation of relatively high concentrations of particulates, which gives rise to the haze normally associated with such smog; particulates, because of their ability to scatter light, are also the cause of the brown colour often associated with photochemical smog<sup>†</sup>.

## Minimising photochemical smog

To minimise photochemical smog formation, governments have laid down maximum permissible exhaust emissions for both hydrocarbons and oxides of nitrogen (and also for carbon monoxide which is poisonous without further reaction). Currently in Australia, the maximum allowable exhaust emissions for passenger cars (regardless of size) correspond to reductions of 90%, 90% and 70% for hydrocarbons, CO and  $\text{NO}_x$  respectively relative to uncontrolled (pre-1972) vehicles.

Since 1986, new cars in Australia have been fitted with catalytic exhausts (Fig. 10.7 on p. 297 CCPC). Current ones convert  $\text{NO}$  to  $\text{N}_2$  and hydrocarbons

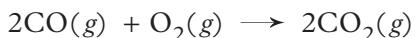
<sup>†</sup> Although  $\text{NO}_2$  is a brown gas, its concentration never gets high enough in photochemical smog for it to be the cause of the observed brown colour.

and CO to carbon dioxide. Rhodium and platinum are the catalysts. Rhodium catalyses the removal of nitric oxide before it is converted to nitrogen dioxide:



Part of the strategy to minimise pollution from motor cars is to measure exhaust emissions from selected vehicles on a dynamometer to simulate actual driving conditions to check that they are complying with statutory emission limits

Platinum metal catalyses the conversion of carbon monoxide and hydrocarbons to carbon dioxide and water. For this purpose extra air is added to the exhaust gas upstream of the catalytic converter. The reaction with carbon monoxide is:



A typical hydrocarbon reaction is



Conditions (and the relative amounts of platinum and rhodium used) need to be carefully chosen so that the  $\text{CO} + \text{NO}$  reaction proceeds more rapidly than the  $\text{CO} + \text{O}_2$  reaction. Otherwise all the CO will be converted to  $\text{CO}_2$  before it can remove all the NO. This is a situation where rates of reactions and factors affecting them are of critical importance.

## Exercises

- \*4 Prepare a table showing the main sources of air pollution (transport, electricity generation, metals processing, mining, heavy industry, homes and commercial activity, agricultural pursuits) and the main pollutants each produces.
- 5 Diesel engines use a much higher air to fuel ratio than do petrol engines. What effect do you expect this to have on the relative amounts of carbon monoxide and oxides of nitrogen produced by the two types of engine? Explain.



- \*6 It is often claimed that electrically powered vehicles that use batteries charged from the electricity mains are much less polluting than petrol engines. Explain how this claim is true in one respect but false in another.
- 7 a Why does afternoon peak hour traffic have much less effect on city ozone concentrations than the morning peak?
- b Which would be the more effective strategy for controlling photochemical smog: reducing hydrocarbon emissions or reducing emissions of  $\text{NO}_x$ ? Explain why.
- \*c What effect, if any, does daylight saving have on formation of photochemical smog? Explain carefully.
- 8 a When the ratio of  $\text{NO}_2$  to NO is so low that all the ozone formed from the  $\text{NO}_2 + \text{sunlight}$  and  $\text{O} + \text{O}_2$  reactions is destroyed by NO, what is the net result of the three reactions in this cycle? Consider energy as well as mass.
- b Do you expect the  $\text{O} + \text{O}_2$  reaction to be exo- or endothermic? Why? Can you make a prediction about the exo- or endothermicity of the  $\text{O}_3 + \text{NO}$  reaction? Explain.



#### WEBSITES

[www.epa.nsw.gov.au/envirom/princairpol.htm](http://www.epa.nsw.gov.au/envirom/princairpol.htm)

(a simple introduction to the major air pollutants; also move the cursor over *Resource Centre*, then click *For teachers and students*; under *State of Environment* click *atmosphere*) (watch the m in envirom!)

[www.deh.gov.au/soe/2001/atmosphere/introduction-9.html](http://www.deh.gov.au/soe/2001/atmosphere/introduction-9.html) and  
[... atmosphere/summary.html](http://www.deh.gov.au/soe/2001/atmosphere/summary.html)

(both addresses take you to various extracts from the 2001 State of the Environment Report and present useful information about air pollutants)

[www.epa.gov/air/urbanair/6poll.html](http://www.epa.gov/air/urbanair/6poll.html)

(a simple introduction to the six major air pollutants; also near the bottom of the page select *Ozone—good up high bad nearby* for a clear account of ozone in both the troposphere and the stratosphere)

## 7.6 STRUCTURE OF OZONE AND COORDINATE COVALENT BONDS

Molecular oxygen consists of a pair of O atoms joined by a double bond: its electron-dot structure is



Ozone consists of three O atoms joined together. We envisage this as occurring by one of the lone pairs of electrons on one of the O atoms of an  $\text{O}_2$  molecule forming a new covalent bond with the third O atom:



We call this a *coordinate covalent bond*.

A **coordinate covalent bond** is a covalent bond in which both of the shared electrons came from the one atom.

Although we envisage this bond as forming differently from an ordinary covalent bond, once formed it is identical to an ordinary covalent bond.

Figure 7.3 shows models of the oxygen and ozone molecules. Ozone has a bent shape.

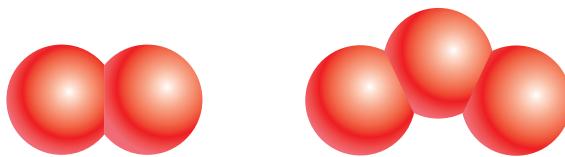


FIGURE 7.3  
Space-filling models of the O<sub>2</sub> and O<sub>3</sub> molecules

Other compounds with coordinate covalent bonds are:

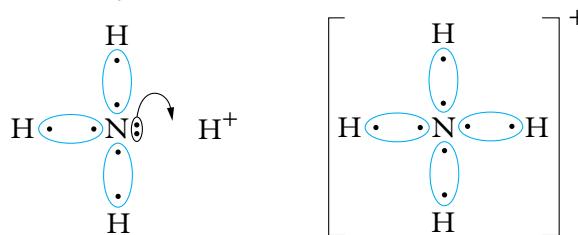
- *carbon monoxide*. Two covalent bonds are formed in the normal way:



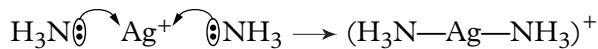
but this leaves carbon ‘unsatisfied’ in that it has only six valence electrons surrounding it instead of the desired eight. So oxygen uses one of its lone pairs to make a shared pair. Hence there is a triple bond between the O and C atoms:



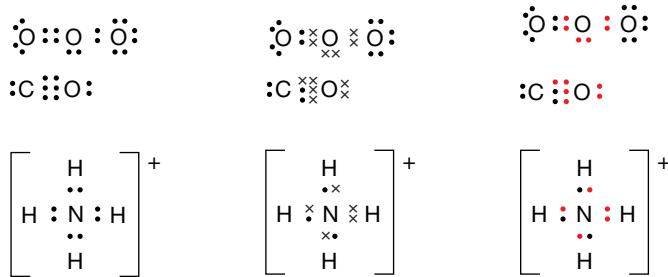
- *ammonium ion*. When ammonia combines with a hydrogen ion to form the ammonium ion, NH<sub>4</sub><sup>+</sup>, a coordinate covalent bond is formed:



- *complex ions such as Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>*. We saw in Section 6.10 that complex ions form by one or more small molecules or ions attaching themselves to a central metal ion. They do this by forming coordinate covalent bonds. For example two ammonia molecules each use their lone pair of electrons to form a coordinate covalent bond with a silver ion:



As was explained on p. 252 CCPC, there are different ways of drawing electron-dot structures. For ozone, carbon monoxide and the ammonium ion we could draw:



The right-hand ones in this set are the only ones that can be described as *Lewis* electron-dot structures (because that is the way that Lewis, who introduced this type of structure, drew them).



## Exercises

- 9 Nitrous oxide,  $\text{N}_2\text{O}$ , has the atoms arranged NNO. Draw an electron-dot structure for  $\text{N}_2\text{O}$  with a double bond between the O atom and the central N atom and a single bond between the N atoms. Why is this an unsatisfactory structure for this molecule? Show how a better structure can be obtained by introducing a coordinate covalent bond.
- 10 Nitrous acid,  $\text{HNO}_2$ , has the atoms arranged HONO. Draw an electron-dot structure for it. Nitric acid,  $\text{HNO}_3$ , has the extra O atom attached to the N atom. Draw an electron-dot structure for nitric acid.
- 11 Draw electron-dot structures for hydrogen chloride,  $\text{HCl}$ , and hydrocyanic acid,  $\text{HCN}$ . The chloride ion and cyanide ion form by loss of a proton from the respective acid. Draw electron-dot structures for these two ions. Both chloride and cyanide form a complex ion with the zinc ion,  $\text{ZnCl}_4^{2-}$  and  $\text{Zn}(\text{CN})_4^{2-}$ . Using the  $\text{Ag}(\text{NH}_3)_2^+$  ion discussed above as a guide, describe the chemical bonding in these two complex ions and draw structural formulae for them.

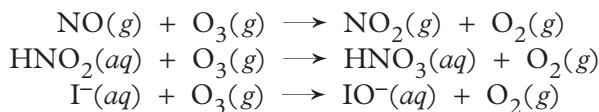
## 7.7 ALLOTROPES OF OXYGEN

Recall (from p. 249 CCPC) that *allotropes* are forms of the one element (in the same physical state) that have distinctly different physical properties (colour, density, hardness, electrical conductivity). There are two allotropes of oxygen,  $\text{O}_2$  and  $\text{O}_3$ : they have quite distinct properties as shown in Table 7.3.

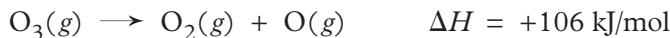
Many of the differences in properties between oxygen and ozone can be explained in terms of their different chemical structures. When molecular oxygen reacts, the double bond between O atoms in the molecule has to be broken, for example in  $\text{H}_2 + \text{O}_2$ ,  $\text{N}_2 + \text{O}_2$ ,  $\text{NO} + \text{O}_2$ ,  $\text{Mg} + \text{O}_2$ ; even in  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  and  $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$  the  $\text{O}_2$  has to be split in order to put the C or S atom in the middle. This splitting of the O=O double bond requires considerable amounts of energy:



However when ozone reacts, it generally just splits off one O atom, leaving behind a stable  $\text{O}_2$  molecule, for example in



The energy required to do this is much less than that needed to break a double bond:



Ozone is dangerous to living organisms because it attaches an O atom to many of the complex carbon molecules making up living matter and this sets off a series of reactions that lead to the breakdown of key biological compounds and so interferes with the proper functioning of the organism.

## 7.8 OXYGEN GAS, OZONE AND OXYGEN ATOMS

In discussing chemical bonding in Chapter 2 of CCPC we saw that atoms with incomplete valence shells of electrons were not stable and tended to combine

**TABLE 7.3 Properties of oxygen and ozone**

Property	Oxygen, O <sub>2</sub>	Ozone, O <sub>3</sub>
	<ul style="list-style-type: none"> <li>■ colourless gas condensing to a pale blue liquid</li> <li>■ odourless</li> <li>■ essential for all living matter (though pure O<sub>2</sub> for extended periods will kill)</li> </ul>	<ul style="list-style-type: none"> <li>■ colourless gas condensing to a distinctly blue liquid</li> <li>■ strong and distinctive odour (0.01 ppm is detectable)</li> <li>■ poisonous (with detrimental effects observable at concentrations as low as 0.1 ppm)</li> </ul>
boiling point	-183°C	-111°C
density	about the same as air	about 1.5 times that of air
solubility in water	sparingly soluble (9 ppm from air at 20°C)	considerably more soluble than O <sub>2</sub>
stability	very stable	easily decomposed to O <sub>2</sub>
reactivity	<ul style="list-style-type: none"> <li>■ reacts with most other elements to form oxides</li> <li>■ moderately strong oxidising agent</li> </ul>	<ul style="list-style-type: none"> <li>■ much more reactive than oxygen</li> <li>■ very strong oxidising agent</li> </ul>
uses	<ul style="list-style-type: none"> <li>■ widely used medically to overcome breathing problems</li> <li>■ steel-making (to oxidise carbon from pig iron)</li> <li>■ oxy-acetylene torches</li> <li>■ liquid O<sub>2</sub> used in space shuttles and rockets as oxidiser for the fuel (often liquid H<sub>2</sub>)</li> </ul>	<ul style="list-style-type: none"> <li>■ in sterilisers in food shops and kitchens (prepared <i>in situ</i> by passing air through a silent electric discharge)</li> <li>■ purification of water and as a bleaching agent in paper and textile making (it is replacing chlorine for these uses)</li> </ul>

with each other to form molecules. For example H atoms combine to form H<sub>2</sub> molecules, Cl atoms to form Cl<sub>2</sub> molecules (pp. 52–4 CCPC). Similarly O atoms, with six valence electrons, tend to combine to form O<sub>2</sub> molecules:



This means that oxygen does not normally exist as free atoms, but as diatomic molecules.

However it is possible to produce small concentrations of O atoms for short periods of time by passing an electrical or microwave discharge through low pressure oxygen gas:



But if the concentration of O atoms gets too great, they recombine to form molecules again (remember rate increases as concentration of reactants increases):



We saw in Section 7.5 that oxygen atoms are formed in very small concentrations in the lower atmosphere by the action of sunlight on nitrogen dioxide:



Where there is a relatively high pressure (concentration) of O<sub>2</sub>, as in the lower atmosphere, O atoms quickly combine with it to form ozone:



In the stratosphere (as we will discuss more fully in the next section) oxygen atoms are formed by the action of short wavelength ultraviolet radiation on O<sub>2</sub> and on O<sub>3</sub>. There O atoms react with O<sub>2</sub> to form O<sub>3</sub> and they also react with O<sub>3</sub> to re-form O<sub>2</sub>:



(because the concentration of O<sub>2</sub> in the stratosphere is not high enough to make Reaction 7.1 so fast that Reaction 7.2 becomes negligible).

The high reactivity of O atoms means that their concentration is always very low. Whenever we try to get high concentrations of O atoms, they recombine to form O<sub>2</sub>. Consequently, we cannot measure properties such as boiling and melting points for O atoms.

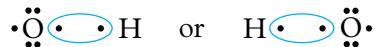
O<sub>2</sub> and O<sub>3</sub> are stable molecules, O<sub>2</sub> more so than O<sub>3</sub>. O<sub>2</sub> can be kept in a container at high pressure indefinitely without any decomposition or change; O<sub>3</sub> can be stored at moderate pressures for reasonable periods of time (days to weeks) with only small amounts of decomposition (to O<sub>2</sub>). The stability of O<sub>2</sub> and O<sub>3</sub> (relative to that of O atoms) arises because the atoms in these molecules all have completed valence shells (see the electron-dot diagrams in the previous section).

O<sub>2</sub> is moderately reactive: O<sub>3</sub> is much more reactive (Table 7.3), and O atoms are more reactive still: O atoms react with O<sub>2</sub>, O<sub>3</sub>, CO, NO, SO<sub>2</sub> (to form O<sub>3</sub>, 2O<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub>, SO<sub>3</sub> respectively). O atoms readily react with most organic compounds at room temperature (abstracting an H atom from them). By contrast ozone reacts with organic compounds only if they contain a double or triple bond, and O<sub>2</sub> reacts with organic compounds only at elevated temperatures (combustion).

## Free radicals

A neutral species that has an unpaired electron and which can be formed by splitting a molecule into two neutral fragments is called a **free radical** (or sometimes just a **radical**).

Hydrogen peroxide, H—O—O—H can be split into two OH fragments; each OH fragment contains an unpaired electron and so is called a free radical, in this case the *hydroxyl free radical*. Its electron-dot structure is:



The molecule H—O—Cl can be split into an H atom and a ClO fragment which is called the *ClO free radical*. We shall meet it again in Section 7.11.

By the definition just given an atom that can be formed by splitting a molecule into two pieces is a free radical. We can talk about the H, O, N, Cl atoms or about the H, O, N, Cl free radicals (coming from molecules such as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>). Although the O atom has six valence electrons, two of these are unpaired (based on evidence we need not go into) and so the O atom is a free radical. On the other hand atoms of metals such as Na, Li, Al are not considered to be free radicals, despite having unpaired electrons, because they cannot be formed by splitting up a molecule.

Note that the free radicals discussed here are *neutral species*: they are not ions. The chlorine free radical (or atom), Cl, has the electron-dot structure : $\ddot{\text{Cl}}$ . Compare this with the chloride ion,  $\text{Cl}^-$ : : $\ddot{\text{Cl}}$ : which is not a free radical (no unpaired electron). The Cl free radical has completely different properties from the chloride ion,  $\text{Cl}^-$ .

Free radicals are sometimes written with the unpaired electron shown as in  $\text{HO}\cdot$ ,  $\text{ClO}\cdot$ , and  $\text{Cl}\cdot$ , and sometimes without, as HO or OH (same species), ClO and Cl. The unpaired electron is almost always shown on free radicals formed from carbon compounds (such as  $\text{CH}_3\cdot$  and usually not shown on atoms (for example O).

*Because of the presence of an unpaired electron, and an incomplete valence shell, free radicals are much more reactive than stable molecules.*

## In summary

$\text{O}_2$  and  $\text{O}_3$  are stable molecules in which all the atoms have completely filled valence shells; the free O atom is a free radical in that it has an incomplete valence shell (6 electrons with two unpaired instead of 8 all paired); it is not at all stable in that pairs of O atoms readily combine to form  $\text{O}_2$  molecules. Free O atoms are much more reactive than either  $\text{O}_2$  or  $\text{O}_3$ .

## 7.9 DEPLETION OF OZONE IN THE STRATOSPHERE

One of the most worrying global environmental problems of the past twenty years has been depletion of ozone in the stratosphere—the so-called ozone hole problem. There has been a severe reduction in the amount of ozone in the stratosphere, particularly over the Antarctic in spring. This has been attributed to the presence of what are called chlorofluorocarbons (CFCs). However before we consider the chemistry of ozone destruction, let us look at what u.v. light is, the role of ozone in the stratosphere, why destruction of ozone is a problem and what CFCs really are.

### Ultraviolet radiation

**Ultraviolet radiation** (or **u.v. light**) is one of several types of radiation which go under the general name of **electromagnetic radiation**; the common types are shown in Table 7.4. All these types of radiation can transmit energy from one point to another (including across a vacuum) without any matter being transferred—that's what radiation means—and they all travel at the speed of light,  $3 \times 10^8$  metres per second. The different types of electromagnetic radiation are characterised by different *wavelengths* or *frequencies*.

The sun emits predominantly u.v. and visible radiation (with a small amount of infrared). Its wavelength range is from about 200 to 2000 nm (0.2 to 2  $\mu\text{m}$ ) with the greatest intensity being between 300 and 800 nm. Solar u.v. radiation is frequently divided into three classes:

- **u.v.-A**: 400 to 320 nm, generally considered beneficial in that it facilitates photosynthesis and helps form Vitamin D in humans; it also produces a good suntan.
- **u.v.-B**: 320 to 280 nm, considered harmful in that it causes skin cancer, eye cataracts, decreased immune response (and so more disease generally) and it damages plants; it also causes severe sunburn.

**TABLE 7.4 Types of electromagnetic radiation**

Type of radiation	Wavelength	Uses
radiowaves AM FM	200–600 m <sup>a</sup> 1–5 m <sup>a</sup>	radio broadcasts and long distance communications
microwaves	1–100 mm	telecommunications, radar, cooking
infrared	1–1000 μm <sup>b</sup>	radiant heat (lamps)
visible light	400–800 nm <sup>b</sup>	normal light
u.v. light	10–400 nm	suntan lamps, solar energy
X-rays	0.01–50 nm	medical diagnosis, structural analysis
γ-rays	10 <sup>-4</sup> –0.1 nm	cancer treatment

*a* correspond to frequencies of 1600–500 kHz (AM) and 300–60 MHz (FM)

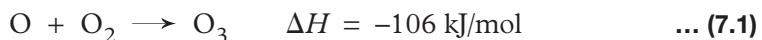
*b* μm = micrometre = 10<sup>-6</sup> m; nm = nanometre = 10<sup>-9</sup> m

- **u.v.-C:** wavelengths shorter than 280 nm, more harmful still, but there is virtually no u.v.-C in the solar radiation reaching Earth's surface.  
(u.v.-A is all right, u.v.-B is bad and u.v.-C is worse.)

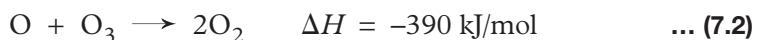
Oxygen in the stratosphere absorbs nearly all of the u.v.-C: ozone in the stratosphere absorbs most of the harmful u.v.-B and the rest of the u.v.-C, while letting through a large proportion of useful u.v.-A.

## Ozone in the stratosphere

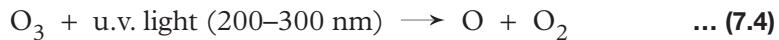
In the stratosphere short wavelength u.v. acts upon oxygen gas to form oxygen atoms which then combine with O<sub>2</sub> molecules to form ozone:



Oxygen atoms can also react with ozone:



The ozone in turn absorbs longer wavelength u.v. which decomposes the ozone back to ordinary oxygen:



There is a balance between the formation and destruction of ozone in these four reactions which leaves a ‘steady state’ concentration of ozone in the stratosphere.

These four reactions also explain why the temperature in the stratosphere is higher than at the tropopause. Reactions 7.3 and 7.4 absorb u.v. radiation and Reactions 7.1 and 7.2 release the energy as heat and so directly warm up the air.

An illustration of just how much (little) ozone there is in the stratosphere is this: if all the ozone in the stratosphere were separated out and spread as a uniform layer of pure ozone gas at standard atmospheric pressure over the whole of the Earth's surface it would be just 3 mm thick!

Decreasing the amount of ozone in the stratosphere means that more short wavelength u.v. radiation (u.v.-B) reaches the Earth's surface.

## Why ozone depletion is a problem

Depletion of ozone in the stratosphere is a problem because it results in more u.v. radiation reaching Earth's surface. This causes:

- increased incidence of sunburn and skin cancer, particularly in fair-skinned people and those who spend a lot of time in the sun
- increased risk of eye cataracts
- increased risk of disease and illness, generally because of a lowering of people's immune response
- reduced plant growth (for some species) due to u.v. interference with their mechanisms for photosynthesis, with rice being particularly vulnerable in this regard, while there is also concern that phytoplankton may suffer damage to its DNA
- increased damage (such as increased brittleness and surface powder formation) to many synthetic materials, particularly polymers (plastics) such as PVC.



The Cape Grim (Tasmania) Baseline Air Pollution Station is one of a series in remote locations worldwide that collects data on air quality away from localised pollution. The aim is to monitor long-term changes in concentrations of trace constituents of the atmosphere that are important in climate change and ozone depletion. The Cape Grim Baseline Air Pollution Station is operated by the Australian Bureau of Meteorology as part of a joint science program with CSIRO Atmospheric Research.

## 7.10 HALOALKANES, PARTICULARLY CFCs

There are many carbon compounds that contain halogen atoms (F, Cl, Br, I). The simplest are the *haloalkanes*.

**Haloalkanes** are compounds in which one or more H atom(s) of an alkane has been replaced by a halogen atom.

Figure 7.4 shows structures of some haloalkanes.

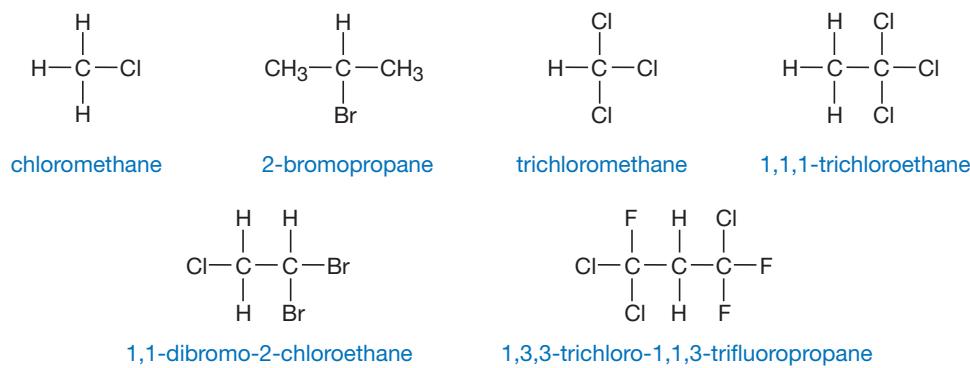


FIGURE 7.4  
Some simple haloalkanes

## Naming straight-chain haloalkanes

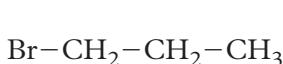
Straight-chain haloalkanes are named using the following rules (with examples in Figure 7.4):

- 1 Bromo-, chloro-, fluoro- and iodo- are used as prefixes to the alkane name; for example chloromethane.
- 2 The position of the halogen (halo) atom is denoted by a number (as was done for double bonds in alkenes (p. 265 CCPC) and for position of the alcohol group in alkanols (Section 5.16). If more than one of a particular type of halo atom is present, di-, tri-, tetra- are used and a location number is given for each such atom, for example 2-bromopropane, 1,1,1-trichloroethane, but just trichloromethane.
- 3 Number from the end of the molecule that leads to the smaller sum of all the substituent numbers; for example 1,1-dibromo-2-chloroethane, not 2,2-dibromo-1-chloroethane ( $1 + 1 = 4$ ;  $2 + 2 + 1 = 5$ ).
- 4 If more than one type of halo atom is present, they are listed alphabetically with any di-, tri-, tetra- being ignored in deciding this order; for example 1,1-dibromo-2-chloroethane, not 2-chloro-1,1-dibromoethane.
- 5 If Rules 1 to 4 lead to more than one possible name, then the correct name is the one that gives the lowest numbers to the most electronegative halogen, the order of electronegativity being F > Cl > Br > I: for example 1,3,3-trichloro-1,1,3-trifluoropropene not 1,1,3-trichloro-1,3,3-trifluoropropene.

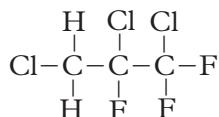
In the IUPAC system for naming compounds there must be only one correct name for a compound.

## Isomers

As explained on pp. 264–5 CCPC, *isomers* are compounds that have the same molecular formula but different structural formulae. On those pages we discussed isomers for alkenes and in Section 5.16 of this book we had isomers for alkanols. We can also have isomers for haloalkanes. The compounds below are isomers of 2-bromopropane ( $C_3H_7Br$ ) and of 1,3,3-trichloro-1,1,3-trifluoropropene.



1-bromopropane



1,2,3-trichloro-1,1,2-trifluoropropene

## Chlorofluorocarbons (CFCs)

**Chlorofluorocarbons** (CFCs) are compounds containing chlorine, fluorine and carbon only, that is, they contain no hydrogen.

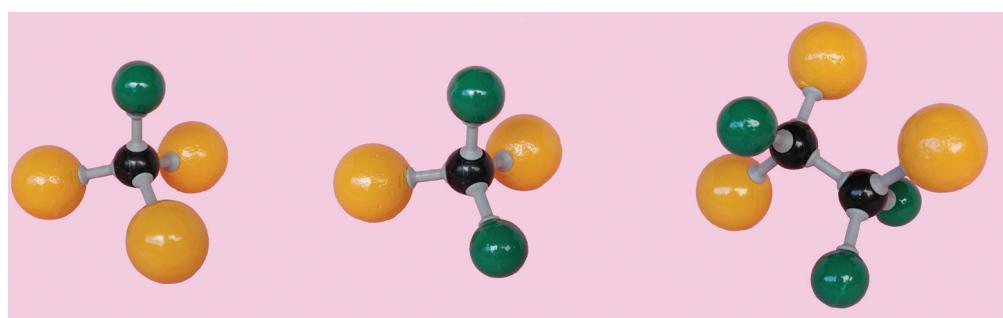
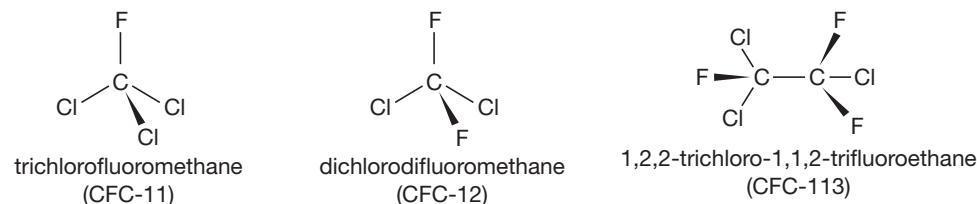
Common CFCs are shown in Table 7.5. CFCs were widely marketed under the trade name of freons—particularly freon-11 and freon-12. Figure 7.5 presents models of some CFCs.

**TABLE 7.5 Common chlorofluorocarbons (CFCs) currently in the troposphere<sup>a</sup>**

Structure	Systematic name	Common name	Major use (before 1996)
$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{F} \\   \\ \text{Cl} \end{array}$	trichlorofluoromethane	CFC-11	working fluid in refrigeration and air conditioning; making foam plastics (insulation); propellant in aerosol spray cans
$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{F} \\   \\ \text{F} \end{array}$	dichlorodifluoromethane	CFC-12	
$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ \text{Cl}-\text{C}-\text{C}-\text{Cl} \\   \quad   \\ \text{Cl} \quad \text{F} \end{array}$	1,2,2-trichloro-1,1,2-trifluoroethane	CFC-113	

*a Production and use of these compounds is now banned by international agreement*

**FIGURE 7.5**  
Ball-and-stick and space-filling models of some chlorofluorocarbons, CFCs (yellow is S, green is F)



## Why are there CFCs in the atmosphere?

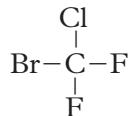
CFCs were introduced, under the trade name ‘freons’, in the 1930s as replacements for ammonia in *refrigeration*; the boiling points and their dependence on pressure made them ideal working fluids. In addition CFCs are odourless, non-flammable, non-toxic and very inert, which made them eminently more attractive than the ammonia they replaced. After World War II

they also became widely used in *aerosol spray cans* and later as *foaming agents* in the manufacture of foam plastics such as polystyrene. With the miniaturisation of electronics from the 1960s onwards they came into common use for *cleaning circuit boards*. In these latter three uses the CFCs were released directly into the atmosphere; even in refrigeration and later in air conditioners the CFCs were released into the atmosphere, but only after the ten to twenty year lifetimes of such appliances. This release into the atmosphere was considered of no concern because CFCs were inert and non-toxic.

However it was just this inertness combined with their insolubility in water (rain) that caused them to become a problem. Because they were not destroyed by sunlight or oxygen (as most organic compounds are), they spread out uniformly around the world, their concentrations in the troposphere gradually built up and slowly they diffused into the stratosphere where they began to cause a problem (see the next section).

## Halons

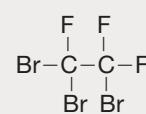
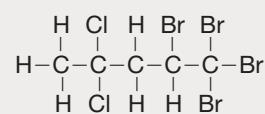
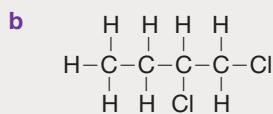
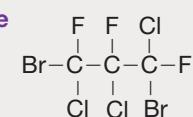
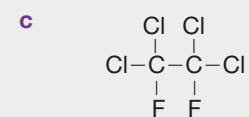
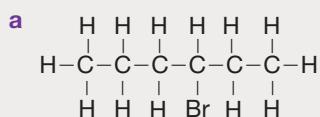
**Halons** are compounds of carbon, bromine and other halogens. They are dense, non-flammable liquids that are particularly good at extinguishing fires. The commonest one is bromochlorodifluoromethane,  $\text{CBrClF}_2$ :



This substance was used in so-called BCF fire extinguishers (BCF = bromine, chlorine, fluorine), the small yellow ones that were commonly used in cars and boats until they were banned in 1994. Another halon that had been in widespread use in automatic fire extinguishing systems is bromotrifluoromethane,  $\text{CBrF}_3$ .

## Exercises

**12** Name the following compounds:



**13** Draw structural formulae for:

- a** 1,1,1-tribromopropane
- b** 1,1,3,3-tetrabromobutane
- c** 1-chloro-3-fluoro-2-iodoheptane
- d** 1,1,2,2-tetrafluoro-1,1-dichloroethane
- \*e** 1,1,3,3-tetrabromo-1-chloro-1,2,3-trifluoropropane
- \*f** 1,1,1,4,4,4-hexachloro-2,2,3,3-tetrafluorobutane

**14** Give the molecular formulae of the compounds in Exercises 12 and 13.

**15** Give the structure and name of one isomer of each of the compounds in Exercise 13.

**16** Some haloalkanes in everyday use are:

- a chloroform,  $\text{CHCl}_3$  (solvent, anaesthetic)
- b methylene chloride,  $\text{CH}_2\text{Cl}_2$  (paint stripper)
- c halothane,  $\text{CF}_3\text{CHClBr}$  (anaesthetic).

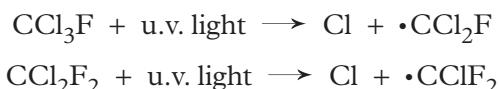
Give the systematic names of these compounds.

**17** How many isomers can there be of CFC-113 (Table 7.5)? Draw structures to justify your answer.

## 7.11 DESTRUCTION OF STRATOSPHERIC OZONE BY CFCs

CFCs are not destroyed at low altitudes by sunlight and oxygen as are most compounds released to the atmosphere. In addition they are insoluble in water so they do not get washed out of the atmosphere by rain (another major natural process for cleaning the atmosphere). Hence CFCs remain in the troposphere for very long periods of time—for several decades. This means that they are able to diffuse slowly into the stratosphere.

In the stratosphere they come into contact with short wavelength u.v. radiation (before the ozone has filtered it out) and this short wavelength u.v. breaks a chlorine atom off the CFC molecule:



### The basic destruction process

The chlorine atom formed then abstracts an oxygen atom from an ozone molecule, forming a ClO free radical (Section 7.8):



ClO, like all free radicals, is very reactive.

Because of the continual formation and destruction of ozone in the stratosphere, there are free oxygen atoms present as well as  $\text{O}_2$  and  $\text{O}_3$  molecules (Section 7.9). ClO reacts with a free oxygen atom to form a molecule of oxygen,  $\text{O}_2$  and this regenerates the chlorine atom:



The net result, the sum of Equations 7.5 and 7.6 is, that an ozone molecule and an oxygen atom have been converted into two oxygen molecules and our reactive chlorine atom has not been used up. This chlorine atom is able then to attack another ozone molecule and repeat the process all over again. And so it goes on: one chlorine atom can destroy thousands of ozone molecules. We call this a **chain reaction**, a reaction in which the reactive species—in this case the chlorine atom—is regenerated and so can go on repeating the reaction more or less indefinitely. Hence one CFC molecule can do a tremendous amount of damage. Only a very small amount of CFC needs to reach the stratosphere for a very significant amount of ozone destruction to occur.

If the above two chemical reactions were the only ones occurring then just one chlorine atom (or just one CFC molecule) could destroy all of the ozone in the stratosphere. Actually there is evidence to show that on average each chlorine

atom destroys a few thousand ozone molecules before the chain reaction is broken. There are other reactions going on in the stratosphere and some of these remove the *chain carriers* (as the reactive Cl atom and ClO radical are called).

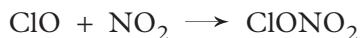
## Other reactions of Cl and ClO

One particularly important reaction is between a chlorine atom and a methane molecule. Small quantities of methane are present in the stratosphere as a result of slow diffusion up from the troposphere. This reaction forms hydrogen chloride:



This reaction effectively removes a chlorine atom and so brings the chain reaction to a halt. Another chlorine atom will need to be generated (from a CFC molecule) for destruction of ozone to continue. The hydrogen chloride formed in this reaction has no effect upon ozone and so reactive chlorine atoms are converted into unreactive HCl molecules. The  $\text{CH}_3\cdot$  radical undergoes further reactions but they have no effect upon ozone.

Another important reaction for stopping the ozone-destroying chain involves the ClO species:



Small amounts of nitrogen dioxide are present in the stratosphere.  $\text{ClONO}_2$  is chlorine nitrate (compare with nitric acid,  $\text{HONO}_2$ ); it is formed when a ClO radical hits an  $\text{NO}_2$  molecule. The occurrence of this reaction essentially removes ClO from the above chain reaction and so this is another way of bringing the destruction of ozone to an halt. Chlorine atoms cannot be regenerated from chlorine nitrate.

The importance of the chain-reaction nature of this process needs to be strongly emphasised. It is because one CFC molecule can destroy thousands, perhaps tens of thousands, of ozone molecules that the very small concentrations of CFCs that actually diffuse into the stratosphere can cause significant damage.

The process that has just been described for destruction of ozone could (and does) occur throughout the whole of the stratosphere and throughout all of the year. However dramatic depletion of stratospheric ozone has been observed only over the Antarctic and then only in spring.

## 7.12 WHY OVER THE ANTARCTIC AND WHY IN SPRING?

The story so far is that CFC molecules diffuse into the stratosphere where u.v. light splits off chlorine atoms. These chlorine atoms destroy ozone molecules but eventually get converted into hydrogen chloride and chlorine nitrate which are unreactive and quite harmless to ozone. And this happens globally.

Serious ozone depletion is localised and seasonal (over the Antarctic in spring) because winter in the Antarctic is a period of continuous darkness *and* the stratosphere there is extremely cold (due to certain wind patterns called a polar vortex which stop Antarctic air mixing with warmer lower-latitude air).

Under these extremely cold conditions certain solid particles form that are able to catalyse a reaction between hydrogen chloride and chlorine nitrate.



This conversion of hydrogen chloride and chlorine nitrate to molecular chlorine has no effect upon ozone concentrations during winter. However when the sun comes up in early spring, the situation changes dramatically. Sunlight is able to split a chlorine molecule into two separate chlorine atoms:



and each of these can destroy ozone in exactly the same way as chlorine atoms formed from CFCs. In spring, then, there is an extra source of chlorine atoms and so increased destruction of ozone. The concentration of ozone over the Antarctic is greatly reduced and so the ‘ozone hole’ is formed. The hole is at its deepest (ozone depletion at its greatest) in late October to early November. Figure 7.6 shows schematically this mechanism for ozone destruction.

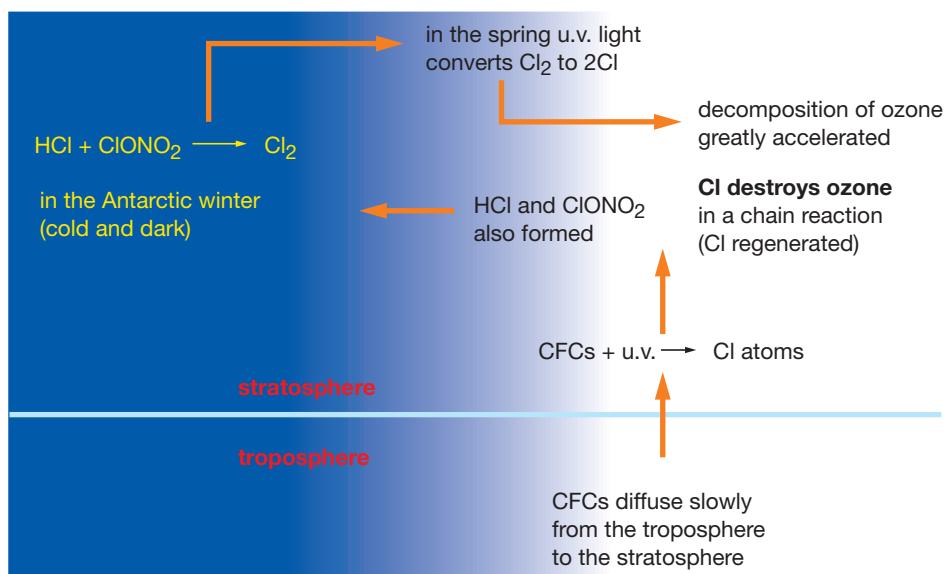


FIGURE 7.6  
The mechanism for destruction of ozone, both globally all year and over the Antarctic

Figure 7.7 shows the variation of ozone concentration with altitude on two different days, one in late winter (a normal profile) and one in spring clearly showing the ozone hole; on the latter day about 80% of stratospheric ozone had been destroyed over that location which would have been fairly typical of the Antarctic generally.

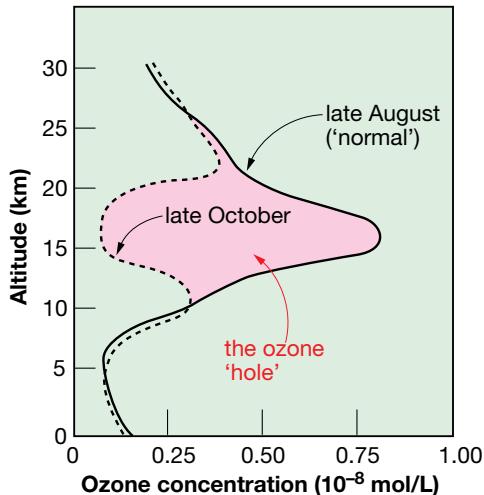


FIGURE 7.7  
Changes in the ozone profile through the stratosphere between winter (normal) and spring (severely depleted). This graph is typical of those observed from 1985 onwards. The pink shading represents the amount of ozone depletion—about 80% in this case

Only a finite amount of molecular chlorine is formed during the polar winter. By early summer this has been virtually all used up, so the rate of destruction

of ozone returns to the ‘normal’ CFC level. In addition the polar vortex breaks up in early summer and so there is mixing of Antarctic air with lower-latitude air. This brings the ozone concentration back to its normal level. The break up of the polar vortex has occasionally brought ozone depleted stratospheric air over Tasmania and parts of Victoria in early summer. Generally the ozone hole disappears by about Christmas or mid-January.

## Other ozone destroying compounds

Some other halogen-containing compounds are also sources of ozone-destroying atoms in the stratosphere. In particular:

- *Halons* (p. 262); these compounds contain C–Br bonds which can be broken by u.v. light in the same way as C–Cl bonds are, and Br atoms can decompose ozone in the same way as Cl atoms do
- *Carbon tetrachloride* (tetrachloromethane) and *1,1,1-trichloroethane* (methyl chloroform), widely used as industrial solvents; as with CFCs the C–Cl bonds cause the problem
- *Methyl bromide* (bromomethane), widely used as a fumigant for seeds and soil; the C–Br bonds cause ozone destruction (as with halons).

## In summary

On a global year-round basis, CFCs have caused a 3 to 8% decrease in the amount of ozone in the stratosphere: however, (of much greater concern) in recent years they have caused a 50 to 90% decrease over the Antarctic during spring.

## Exercises

- 18 a** Draw an electron-dot diagram for the HOCl molecule and hence for the ClO free radical (formed from HOCl by removal of an H atom).
- b** Nitric oxide and nitrogen dioxide are sometimes considered to be radicals rather than molecules. Explain why this is so. Drawing electron-dot diagrams may help.
- c** Use the electron-dot diagrams you drew in (a) and (b) to explain why you would expect ClO to react with NO<sub>2</sub>.
- 19 a** Explain why Cl and ClO can be considered catalysts for the reaction between O and O<sub>3</sub>.
- b** In the late 1960s and early 1970s there was concern that NO and NO<sub>2</sub> from exhausts of supersonic aeroplanes (which fly in the lower stratosphere) would catalyse the decomposition of ozone (in the same way as Cl and ClO do). Write equations to show this.



## WEBSITES

For the ozone hole:

<http://www.atm.ch.cam.ac.uk/tour>

(a simple but thorough account of the history, chemistry and monitoring of the ozone hole; just click on the first tutorial and follow through to the others sequentially)

<http://jwocky.gsfc.nasa.gov>

(click on the globe under ozone to see the latest global map of ozone concentrations; or click on *Ozone hole monitoring page* to see how the current year’s data compares with previous years or click on *direct access* to get maps of particular days over many years)

## 7.13 COMBATING THE OZONE-HOLE PROBLEM

The only way to stop ozone destruction by CFCs is to stop releasing them to the atmosphere, because once they are released it is impossible to remove them, and they do not decompose or get washed out by rain.

### International agreements

Since 1987 there have been several international agreements in which nations have undertaken to phase out the use of CFCs and other ozone-destroying compounds. The original agreement was called the Montreal Protocol. The most recent agreement (1992) was to:

- stop using halons by the end of 1994
- cease the manufacture and use of CFCs and 1,1,1-trichloroethane by 1996
- phase out HCFCs (see below) by early in the 21st century
- allow less developed countries some period of grace and provide some financial assistance to help them phase out CFCs.

### Alternatives to CFCs

Most of the more developed countries have been able to meet these goals because alternative compounds have been made to replace CFCs.

The first replacements were **HCFCs, hydrochlorofluorocarbons**: these compounds contain C–H bonds which are susceptible to attack by reactive radicals and atoms in the troposphere and so are decomposed there to a significant extent: this means that only a small proportion of them reach the stratosphere. Consequently their ozone-destroying capacity is much less than that of the CFCs. Nevertheless it is still significant. HCFCs were seen as temporary substitutes for CFCs until better compounds could be made and tested.

HFCs are now widely used as replacements for CFCs. **HFCs** are **hydrofluorocarbons** (compounds containing hydrogen, fluorine and carbon, but no chlorine). They contain C–H bonds so undergo some decomposition in the troposphere, and contain no C–Cl bonds so do not form Cl atoms in the stratosphere: their ozone-destroying capacity is zero. The most widely used HFC is HFC-134a (generally marketed in Australia as R134a–R for refrigerant): its systematic name is 1,1,1,2-tetrafluoroethane. It is now widely used in refrigeration and air conditioning. It is more expensive than the CFCs it replaces and somewhat less efficient, but these are small prices to pay for protecting stratospheric ozone.

### How long until improvement is seen?

The good news is that if we remove CFCs from the atmosphere, stratospheric ozone will recover: the damage is reversible. The bad news is that even if all nations observe the current restrictions it will take from 50 to 100 years for complete recovery to occur. This is because there is now so much CFC in the troposphere that it will take a long time for it all to diffuse into the stratosphere and do its damage (and so be destroyed).

However as we reduce emissions to the troposphere, the concentrations of CFCs there will fall and so diffusion into the stratosphere and ozone destruction

will decrease. Computer models suggest that ozone destruction over the Antarctic should be peaking about now (2005–2010) and then the problem should start to become less severe.

## Progress to date

Progress in reducing emissions of CFCs worldwide appears to be quite significant, since the introduction of the Montreal protocol and its later revisions (at least in terms of published inventories of quantities released). Most countries are meeting (or attempting to meet) the required targets. This has been largely due to the availability of acceptable alternative compounds such as the HFCs. However there has not as yet been much reduction in measured atmospheric concentrations of CFCs and the ozone hole has not yet been getting any ‘shallower’, though perhaps it is progress to report that it has not been getting worse!

At least there has been significant progress in solving the ozone hole problem, which is more than can be said for that other serious global atmospheric problem, the enhanced greenhouse effect (global warming).



## Exercises

- 20** The 134 in the code name R134a means two C atoms, two H atoms and 4 F atoms: the a means one particular isomer (named above). Draw structures of all possible isomers that could be called R134.
- 21** The code for labelling CFCs and related compounds is a three-digit number: the units digit is the number of F atoms in the molecule, the tens digit is the number of H atoms plus 1 and the hundreds digit is the number of C atoms minus one (and is omitted if zero) with any extra atoms if needed being Cls. A letter a, b, c... is added to signify a particular isomer if relevant.

Some intermediate and long-term replacements for CFCs are:

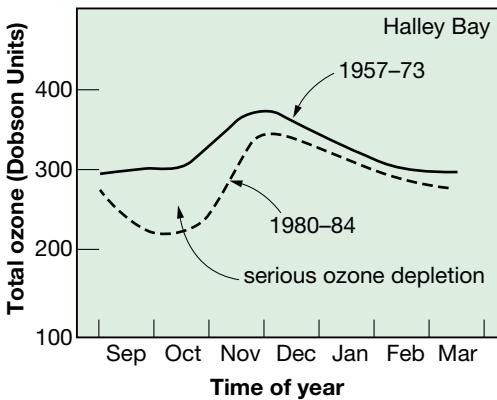
- a** HCFC-123      **\*b** HCFC-141      **c** HFC-32      **\*d** HFC-125

Draw structures and name all isomers that could be represented by these code names.

## 7.14 MONITORING STRATOSPHERIC OZONE

Stratospheric ozone is monitored from ground-based instruments, from instruments in satellites and from instruments in balloons.

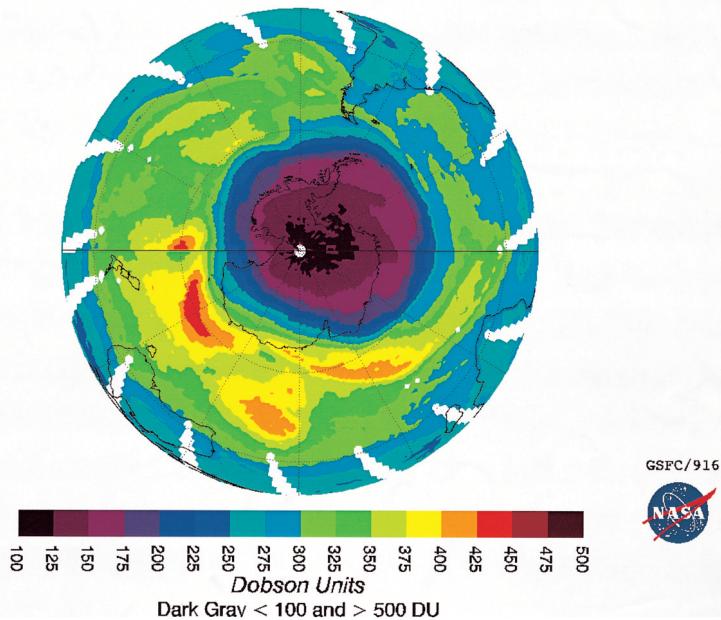
The ground based instruments are u.v. spectrophotometers pointing vertically upwards through the atmosphere. They measure the intensity of light received (from the sky, i.e. sun) at a wavelength at which ozone absorbs and then at wavelengths either side of this at which ozone does not absorb. A comparison of these intensities gives a measure of the total ozone in the atmosphere per unit area of Earth surface at that location (i.e. the average concentration multiplied by the thickness of the atmosphere). The ozone hole was first observed by such measurements (Fig. 7.8). Such spectrophotometers are located in many places around the world and provide valuable total ozone measurements as a function of geographic location.



Total ozone per unit area above a location is generally measured in **Dobson Units**, DU. 1 DU is the amount of ozone that corresponds to a 0.01 mm thickness of pure ozone at atmospheric pressure. The normal amount of ozone is 300 DU (= 3 mm; Section 7.9).

The total ozone mapping spectrophotometers (TOMS) that have been on board several US satellites over the past 20 years work similarly, but because the satellites have been in orbit, these instruments have been able to scan through the atmosphere and measure the ozone concentration as a function of altitude and of geographic position. Such measurements can produce profiles such as the one in Figure 7.7. They can also produce contour maps of total ozone over different areas of the Earth's surface as in Figure 7.9.

**EP/TOMS Version 8 Total Ozone for Oct 5, 2004**



Huge helium-filled balloons have been used to carry instruments including u.v. spectrophotometers up into the stratosphere to measure concentrations of various substances including ozone as a function of altitude. Some of the early profiles of the type in Figure 7.7 were obtained in this way (though they can also be obtained from the satellite measurements described above).

**FIGURE 7.8**  
Total ozone per unit area measurements at Halley Bay in Antarctica as a function of time of year: average values for the years 1957 to 1973 compared with 1980 to 1984 averages. This is a simplified drawing of the original data that first detected the ozone hole. It shows that in spring the total ozone has been depleted by about 30%. Worse depletions were observed in subsequent years

**FIGURE 7.9**  
A total ozone contour map from a NASA satellite

## Important new terms

You should know the meaning of the following terms:

chain reaction (p. 253)  
chlorofluorocarbons (CFCs) (p. 250)  
coordinate covalent bond (p. 242)  
Dobson Unit, DU (p. 259)  
electromagnetic radiation (p. 247)  
free radical (p. 246)  
haloalkanes (p. 249)  
halons (p. 252)  
HCFCs and HFCs (p. 257)

hydrochlorofluorocarbons, HCFCs (p. 257)  
hydrofluorocarbons, HFCs (p. 257)  
particulates (p. 237)  
photochemical smog (p. 239)  
radical (p. 246)  
stratopause (p. 237)  
stratosphere (p. 236)  
tropopause (p. 236)  
troposphere (p. 236)  
ultraviolet radiation (p. 247)  
u.v.-A, u.v.-B and u.v.-C (p. 247–8)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 List the five most abundant components of the atmosphere in their order of abundance. List another eight constituents of the atmosphere and give an order of magnitude for their concentrations (i.e. 10, 1, 0.1, 0.01 ppm).
- 3 Sketch a temperature profile through the atmosphere and identify the various regions.
- 4 Explain why pollutants from the lower atmosphere generally do not get into the stratosphere and why ozone in the stratosphere does not get down to sea level.
- 5 List the main atmospheric pollutants and give their major sources.
- 6 What is photochemical smog? How does it form? What conditions are needed for its formation?
- 7 How do most industrialised countries minimise the formation of photochemical smog?
- 8 Explain the operation of catalytic exhausts for motor cars: include at least two equations.
- 9 Draw electron-dot structures for the oxygen and ozone molecules.
- 10 Draw structures of two other species that involve coordinate covalent bonds.
- 11 Explain what is meant by saying that oxygen gas and ozone are allotropes of oxygen.
- 12 Give three properties of oxygen gas and ozone that are distinctly different for the two substances.
- 13 Why do we consider the oxygen atom a free radical? Why is it not possible to form high concentrations of O atoms?
- 14 List some contrasting properties of O atoms and O<sub>2</sub> and O<sub>3</sub> gases.
- 15 Draw structures and name three haloalkanes.
- 16 Draw structures and name a pair of isomeric haloalkanes.

- 17** What are CFCs? Give names and draw structures for three common ones. Until recently what were these compounds used for?
- 18** Explain, with equations, how ozone is formed in the stratosphere.
- 19** Explain, with equations, how CFCs destroy ozone in the stratosphere. Include explanation of how small amounts of CFC can destroy large amounts of ozone.
- 20** Explain why ozone destruction occurs most extensively over the Antarctic in spring. Include relevant equations.
- 21** How is the ozone-hole problem being overcome? When is some alleviation of the problem expected and when, if ever, will it be fully ‘cured’? Comment on the effectiveness of current strategies.
- 22** Where do HCFCs and HFCs fit into the ozone problem?
- 23** Describe ways in which stratospheric ozone is being monitored.

# CHAPTER 8

# Monitoring water quality

## IN THIS CHAPTER

Water quality	Water hardness
Temperature and pH	Tests for common anions
Turbidity	Cations in environmental water
Total dissolved solids (TDS)	Factors affecting concentrations of ions
Salinity	Algal blooms and eutrophication
Dissolved oxygen and biochemical oxygen demand (BOD)	Water treatment for domestic consumption
Micro-organisms	Membrane filters

Human activities often discharge wastes into water bodies such as oceans and rivers. To ensure that these wastes do not significantly lower the quality of the water that we use, we need to monitor effluents and the water bodies themselves. But first, what do we mean by ‘good quality’ water?

## 8.1 WATER QUALITY

The meaning of the phrase *good quality water* depends upon the purpose for which the water is being used. Humans have four major uses of water:

- 1 water for human consumption (drinking and preparing food)
- 2 water for other human domestic uses (washing, laundry, toilets, cleaning, gardens)
- 3 water for agriculture (irrigation and watering stock) and industry (often as a coolant)
- 4 water for recreation (swimming, fishing and boating) and for aesthetic appeal (attractive land- and seascapes).

Water that is considered of good quality for agriculture may not be considered good quality for drinking; water bodies that are aesthetically pleasing and suitable for boating and fishing may be considered of poor quality for agriculture. Different standards apply to the different uses.

In addition there is the question of what constitutes good quality water in a general environmental sense—the properties that water should have to maintain the health of rivers and streams, the aquatic life they support and the land they flow through.

## Good quality drinking water

- is completely colourless and clear
- is odourless
- has a pleasant taste
- has a relatively low salt content
- contains no pathogens (disease causing agents)
- contains no poisonous chemicals.

For other domestic uses such as bathing and laundering, water should be 'soft', not 'hard'.

**Hard water** is water that does not lather with soap and which leaves a grey scum around baths and basins; if water is not 'hard', we call it **soft water**.

Hardness will be discussed in Section 8.8.

## Good quality environmental water

For the wellbeing of the environment generally, water should:

- contain adequate concentrations of dissolved oxygen (needed by most aquatic organisms)
- not contain high levels of oxygen-consuming substances
- be relatively free of suspended solids (which by excluding light interfere with photosynthesis), and
- contain only low concentrations of phosphate and nitrate, because higher concentrations of these nutrients promote algal blooms.

**Algal blooms** are excessive growths of algae which cover streams and dams with a green sludge and make the water unusable for people, stock or irrigation.

Algal blooms will be discussed in Section 8.12.

A wide variety of scientific tests and measurements can be performed to assess water quality.

## Criteria for assessing water quality

In scientific terms the criteria used to assess water quality are:

- 1 turbidity (or lack of clarity, which is indicative of the amount of suspended solids present)
- 2 total dissolved solids (generally salts)
- 3 pH
- 4 temperature
- 5 dissolved oxygen
- 6 amount of biochemical oxygen demand
- 7 concentrations of nitrate and phosphate
- 8 hardness
- 9 presence of pathogens (bacteria, viruses and parasites)
- 10 concentrations of heavy metals such as iron, lead, mercury, chromium, copper, zinc
- 11 presence of toxic organic compounds such as pesticides and herbicides.

Values for some of these criteria for 'environmentally clean' and polluted fresh water are shown in Table 8.1. The meaning of some of the terms in this table will be explained as you progress through the chapter.

**TABLE 8.1 Some properties of 'environmentally clean' and polluted fresh water**

Property	Typical 'clean water' values	Polluted water <sup>a</sup>
Turbidity (NTU) <sup>b</sup>	<3	>20
TDS <sup>b</sup> (mg/L)	<100	>1000 (for fresh water)
pH	6.5–8.5	<6 or >9.0
DO <sup>b</sup> (mg/L)	7–9	<4
BOD <sup>b</sup> (mg/L)	<5	>10
total phosphate (mg/L)	<0.03	>0.05 for lakes and dams >0.1 for rivers and streams
nitrate (mg/L)	<0.1	>0.50
faecal coliforms (CFU/100 mL) <sup>b</sup>	<5	>200

<sup>a</sup> Any one of these values would make the water polluted.

<sup>b</sup> NTU = nephelometric turbidity units: less than 1 is very clear water, 30 is quite turbid; TDS = total dissolved solids; DO = dissolved oxygen; BOD = biochemical oxygen demand; CFU = colony forming units.

Sea water differs from fresh water in that total dissolved solids are much higher (35 000 ppm compared with fewer than 500 ppm for fresh water) and pH is a little higher—often slightly greater than 7 whereas fresh water is commonly just less than 7. The other properties are similar for both fresh and sea water.

## Tests used

A variety of methods can be used to test for each of the eleven criteria of water quality listed above. The emphasis in this chapter will be on tests that either:

- can be performed in a school laboratory, or
- are commonly used by local agencies to monitor the quality of drinking water or of environmental water (fresh and marine).

Several of the tests are those used by Streamwatch, an organisation set up by several water and conservation authorities in NSW to help students monitor their local waterways.



### WEBSITE

For an introduction to the Streamwatch program:

<http://streamwatch.org.au>

(the home page leads you to assorted information about the program. Select *Electronic library*, then *Streamwatch Manual* for details about various tests, often with more detail than in CCHSC)

## Sampling

Care needs to be taken when collecting water samples for testing to ensure:

- that the sample is truly representative of the water body to be tested, and

- that collecting the sample does not change the value of the parameter to be measured.

Taking a sample too close to the water's edge may give a non-representative reading; for example the temperature may be higher than the water body as a whole (because shallow water heats up more easily) or it may contain more suspended solids or micro-organisms than the bulk of the water. Not being gentle enough in collecting a sample may stir up sediments so that the sample contains more suspended matter (and hence has a greater turbidity) than the water body as a whole.

Water samples for analysis are generally collected by using a jar attached to the end of a long handle such as the telescopic handle of a swimming pool brush or leaf scoop. To ensure an accurate sample, the sampling bottle is generally filled once then emptied then filled again.

Students performing water-quality tests as part of the Streamwatch program

## 8.2 TEMPERATURE AND pH

Temperature is measured to ensure that it is not outside the acceptable range for the life forms that normally live in it in that locality. Basically this is checking that there are no significant discharges of hot or cold water into the stream (thermal pollution, p. 227 CCPC).

The pH of water samples is measured by indicator solutions, papers or a pH meter as explained in Section 4.19.



LEFT A portable pH meter for use in the field. Although the delicate sensing glass membrane (in the inset) is well protected, care is still needed not to break it



A pH outside the normal range of 6.5 to 8.5 indicates that some form of pollutant has been discharged into the water body. Possibilities are industrial waste, fertiliser run-off or, for low pH, acid drainage from a mine site: sulfide ores on exposure to moist air often form sulfuric acid.

## 8.3 TURBIDITY

**Turbidity** in water means cloudiness or lack of transparency.

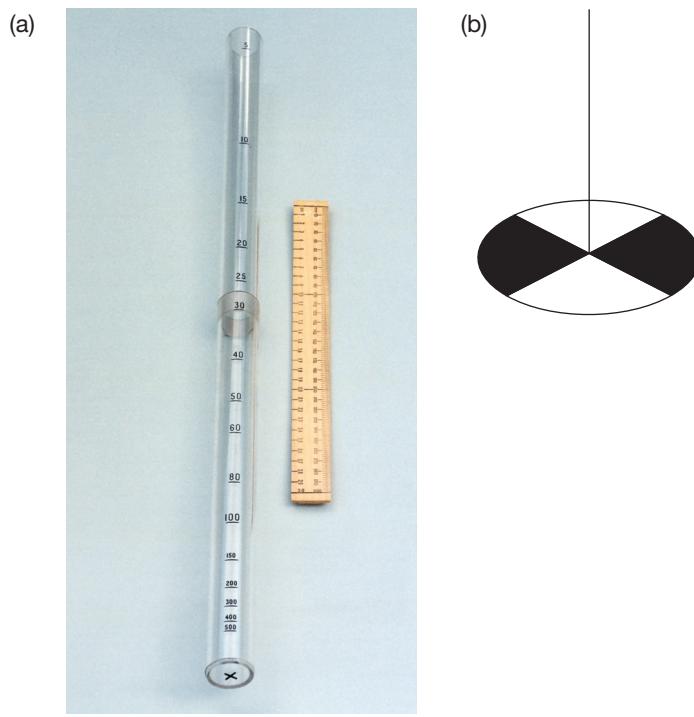
It is caused by suspended solids. Sometimes suspended particles are sufficiently large that they settle out on standing, but very small particles can remain suspended indefinitely. Such small particles cannot easily be filtered out either, because they are small enough to pass through the pores of most filter papers. It is these small particles that cause turbidity. Turbidity not only gives water an undesirable appearance but also can give it an undesirable taste.

Turbidity can be assessed by measuring the depth of water needed to render invisible a mark (such as a black cross) on the flat bottom of a specially made tube that looks like a very long measuring cylinder. The water to be assessed is slowly added to the cylinder until the mark just becomes invisible. If the tube or cylinder has been engraved with marks at different heights (depths) showing the turbidity values, turbidity can be read off directly. Alternatively the depth of water can be measured and a calibration graph used to obtain the turbidity. Figure 8.1(a) shows the turbidity tube supplied to schools by Streamwatch.

Another piece of equipment used to measure relative turbidity is a **secchi disc**. This is a circular disc divided into four quadrants with alternate ones painted black and silver as in Figure 8.1(b); a string is attached to the centre. The disc is lowered into the water until the quadrants just become invisible; the length of the string gives a relative measure of the turbidity of the water: the shorter the length of string, the higher is the turbidity. This device is a convenient method of making comparative estimates of turbidity from one location to another or at different times at the same location.

FIGURE 8.1

(a) A typical tube used to measure turbidity (from the Streamwatch test kit); for comparison the ruler is 30 cm long (b) a secchi disc for measuring relative turbidity



Turbidity is measured in *nephelometric turbidity units*, NTU. This is a fairly arbitrary scale. The absolute values have little meaning, but they are useful for comparative purposes.

Turbidity gives a measure of the amount of suspended solids present. While filtering off suspended solids and determining their mass may work on fairly dirty water in the environment (flooded rivers and polluted lagoons), it is not practical on drinking water because it contains too small a mass of particles that are usually too small to be filtered off.

## Causes of turbidity

High concentrations of suspended solids and hence high turbidities arise naturally from heavy rain and floods. Run-off across grasslands or through forests picks up suspended matter which is carried into waterways, while rapid flows in streams stir up sediments from the bottom or edges of the waterway and make all the water turbid. These natural processes are greatly accelerated by human activities. Land-clearing (cutting down forests) and farming (ploughing fields and often having bare loose earth exposed to heavy rain) both lead to increased amounts of suspended matter being carried into waterways. Cutting down trees and scrub along water courses and farming right to river banks are the most damaging practices in this regard.

## 8.4 TOTAL DISSOLVED SOLIDS (TDS)

As the name implies,

**Total dissolved solids (TDS)**, is the mass of solids dissolved in unit volume of water.

It is generally reported as mg/L or as ppm (both terms are virtually equivalent). Streams and rivers that flow through undisturbed bushland typically have TDS of less than 100 ppm. If they receive significant in-flows from underground aquifers or if they flow through farming and grazing areas, TDS often rises to 200 to 300 ppm. Drinking water for humans should have a TDS of less than 500 ppm. A TDS of greater than 1000 ppm signifies a seriously degraded waterway and such water has only limited value for irrigation, though it is still suitable for stock and poultry. Sea water has a TDS of about 35 000 ppm (3.5%).

### TDS by evaporation

The amount of total dissolved solids can be measured first by filtering off suspended solids then by evaporating a sample of water to dryness and weighing the solids left. In practice this requires considerable care if it is to be done accurately, particularly for drinking water because of the small amount of solid present. Evaporating 1.00 L of water containing 100 ppm TDS produces only 0.1 g solid, and some of this could easily be lost by turbulent bubbling and spitting during evaporation.

### TDS by conductivity measurements

Nearly all of the solid dissolved in natural water is ionic, that is, made up of salts. Therefore environmentalists frequently use *electrical conductivity* of water to measure TDS. This is much quicker and can be done in the field.

Electrical conductivity is the current that flows when a voltage of 1.000 volt is applied across opposite faces of a unit cube. In water contexts the cube is generally taken as a 1.00 cm cube (compare the 1 m cube on p. 103 CCPC). Conductivity is measured in siemens  $\text{cm}^{-1}$ ,  $\text{S cm}^{-1}$  or in millisiemens  $\text{cm}^{-1}$ ,  $\text{mS cm}^{-1}$ . A portable conductivity meter is shown in Figure 8.2.

FIGURE 8.2  
Portable conductivity meter used to measure total dissolved solids (TDS). In this meter, from the Streamwatch kit, the electrodes are a pair of stainless steel rods (inset)



By comparing conductivities of water samples with the masses of solids obtained by evaporating them to dryness, scientists have established that the relation between total dissolved salts and conductivity is:

$$\text{TDS (in ppm)} = 0.65 \times (\text{conductivity in } \text{mS cm}^{-1}) \quad \dots (8.1)$$

Although conductivity gives a measure of total dissolved *salts*, this is generally a fair approximation to total dissolved *solids* and is widely used as a measure of TDS.

## 8.5 SALINITY

**Salinity** is a term that is often used instead of total dissolved solids, though salinity can have a broader meaning in that we can talk about the salinity of land as well as of water. We often read reports about the increasing salinity of farmland in the Murray River irrigation areas or in the wheat lands of south-west Western Australia. And there is often talk about the salinity of the Murray and Darling Rivers, particularly in times of drought.

When used in connection with rivers, salinity means total dissolved *salts*, which approximates closely to total dissolved solids. The word ‘salinity’ arises from the fact that the most abundant of the dissolved solids is sodium chloride, common salt, though there are significant amounts of other salts as well.

When talking about the salinity of soils or farm land, we mean specifically the concentration of common salt (because most other salts are harmless and in fact necessary).

## Causes of salinity

A small amount of salinity (TDS) in waterways is quite natural. Rain contains 10 to 50 ppm sodium chloride, because of sea spray being caught up into rain clouds, and water as it flows across undisturbed land dissolves small amounts of various salts. However human activities have greatly increased the salinity of many rivers.

*Land clearing and deforestation* have increased both the amount of water running off land into rivers (instead of being absorbed by the trees) and the amount of solids dissolved in the water. *Farming* increases TDS because rain run-off easily dissolves salts from ploughed soil. However the greatest cause of increased salinity in rivers is *irrigation*. Water is pumped out of rivers and onto farm land; the excess water percolates through the soil, dissolving significant amounts of salt from the soil, then returns to the river, and so the salinity of the river increases, and this happens to the water several times on its way from source to mouth. This problem becomes particularly severe when a large proportion of the water in the river, say 50 to 80%, is taken out for irrigation. And the problem is further aggravated if some farming areas draw irrigation water with relatively high TDS from underground aquifers and let the excess percolate into a river. All these problems are occurring along the Murray River with the result that salinity increases from about 100 ppm at Albury (well upstream) to 500 ppm near Morgan (from near where Adelaide draws its water) in good times and up to 1000 ppm during droughts.

Increasing salinity of farmland soils causes decreased crop yields and in fact can render farmland useless. Salinity results from rising water tables that bring salt from well underground into the root zone of crops. One cause of this is land clearing and deforestation, which replaces trees that absorb large amounts of rainwater with grasses and crops that use much less water, and so more seeps into the underground aquifers and causes the water table to rise. This is called *dry land salinity* and occurs in the Western Australian wheat belt and parts of the Murray–Darling basin, and is likely to occur in recently cleared pastures in the north of Queensland.

Irrigation is the other major cause of soil salinity, called *irrigation salinity*. Because plants take up water but not the salts the irrigation water contains, irrigators apply more water than the plants need so that the excess water can carry all the salt out of the topsoil. This excess either flows back into the river, increasing its salinity (a problem for the river), or seeps into underground aquifers and causes the watertable to rise. This brings extra salt into the root zone of plants. Irrigation salinity causes decreases in crop yields and is a growing problem in many of the irrigation areas in the Murray–Darling basin.

## Solutions

To limit dry land salinity we need to restrict land clearing and to replant trees, particularly salt-tolerant ones, in affected areas. To control irrigation salinity we need to reduce the volume of water taken from rivers for irrigation (so more is left to flush out the rivers), manage irrigation more carefully and divert salty run-offs into evaporation pans instead of letting them return to the river. Unfortunately these solutions are much more difficult to put into practice than they sound!

Because of the seriousness of salinity to Australia's agriculture, careful monitoring of total dissolved solids, particularly salts by conductivity, is essential.



#### WEBSITE

For further information on salinity:

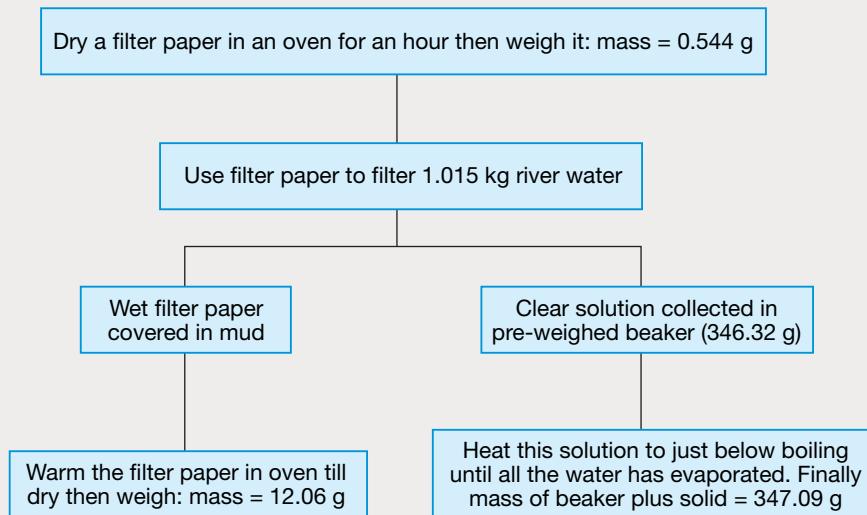
<http://www.acfonline.org.au>

(select *Salinity* in the Topics list on the left, select *Facts and figures* on the right, then click on the various fact sheets)



### Exercises

- 1 Concentrations in mg/L are approximately the same as ppm. Why are they not identical?
- 2
  - a A sample of water contained 5.0 ppm magnesium and 2.0 ppm lead ions. Express these concentrations in moles of ions per litre.
  - b Another sample of water contained  $1.05 \times 10^{-4}$  mol/L sulfate and  $3.1 \times 10^{-4}$  mol/L dissolved oxygen. Express these concentrations in ppm.
- 3 An environmental chemist did the analysis shown below on a sample of muddy river water.



Calculate the percentages of suspended solids and of dissolved solids in the sample of river water.

## 8.6 DISSOLVED OXYGEN AND BIOCHEMICAL OXYGEN DEMAND (BOD)

We saw previously (Table 7.3) that oxygen has a very low solubility in water (9 ppm at 20°C). However the small amount that does dissolve is of vital importance to fish and other aquatic life forms. Fish extract the oxygen they need by passing water through their gills. If the water is depleted in dissolved oxygen, fish die. Only a few marine species such as whales, dolphins and turtles obtain their oxygen by breathing air.

In an aquatic system, animal life (zooplankton, fish, crustaceans, worms) uses up dissolved oxygen while other life forms such as rooted plants (on shorelines or in shallows) and phytoplankton (microscopic floating plants) form it during photosynthesis. In addition surface water absorbs oxygen directly from the air. Hence there is a steady state concentration of oxygen of about 10 ppm.

One measure of the quality of water bodies is the concentration of dissolved oxygen. If this falls below about 5 ppm, many aquatic species will die or fail to reproduce with the result that the water body will develop unpleasant smells, experience increases in populations of undesirable species, develop an unsightly appearance and become unfit for human consumption.

## Causes of low levels of dissolved oxygen

The main cause of decreased concentrations of dissolved oxygen in natural water is the discharge into it of untreated or poorly treated sewage and other organic wastes. ‘Other organic wastes’ include wastes from food-processing plants such as meat works and fruit preserving factories, and from poultry farms and cattle feedlots (places where high numbers of cattle are hand fed on small areas of land; open grazing is not a problem).

These organic wastes are decomposed in the water by *aerobic bacteria*, which convert them into carbon dioxide, water, nitrate, sulfate and phosphate. Aerobic bacteria are ones that use oxygen to digest their food (that is, to decompose organic matter). *Anaerobic bacteria* live without needing oxygen: they convert organic matter into methane, ammonia and amines and hydrogen sulfide and make the water very unpleasant (from a human viewpoint).

We say that these organic wastes have a high oxygen demand or, more technically, a high *biochemical oxygen demand*.

The **biochemical oxygen demand** or **BOD** of a water body is a measure of the concentration of dissolved oxygen that is needed for the complete breakdown of the organic matter in the water by aerobic bacteria.

If a water sample has a BOD of 4 ppm, that means that the decomposition of the organic matter in the sample would reduce the dissolved oxygen



The sewage treatment works at Rouse Hill, north-west of Sydney. One of the main functions of sewage treatment is to reduce biochemical oxygen demand. This is being done in the three large cylindrical tanks

concentration from 10 to 6 ppm—not too serious a problem. However if a sample had a BOD of 100 ppm (quite typical of raw sewage), that would mean that 1 L of this water would use up all the oxygen from 10 L of clean water, which would leave the water seriously degraded. BOD is important in deciding how much dilution of effluent from sewage works is needed so as not to lower the dissolved oxygen level of the receiving water body to harmful levels.

Typical BOD levels are:

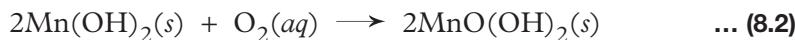
- unpolluted natural waterways, < 5 ppm
- reasonably well treated sewage, 20 to 30 ppm
- raw sewage, 150 to 300 ppm
- stormwater run-off from urban areas, 100 to 500 ppm.

## Measuring dissolved oxygen

Two methods are commonly used—one involves a chemical titration that can be done in a school laboratory while the other uses a special electrochemical sensor (using electrolysis).

### Titration method

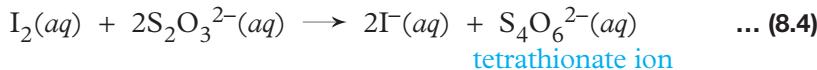
Dissolved oxygen oxidises  $\text{Mn}^{2+}$  to Mn(IV) in alkaline solution:



If this mixture is then acidified with iodide in the solution, the Mn(IV) oxidises iodide to iodine:



Iodine can then be titrated with sodium thiosulfate solution,  $\text{Na}_2\text{S}_2\text{O}_3$ , using starch as indicator (starch forms an intensely blue colour with iodine which disappears at the equivalence point):

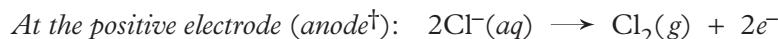
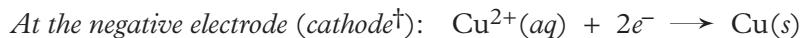


To perform the test, sample bottles of known volume, typically 250 mL, are completely filled (all air excluded) at the test site. Back at the laboratory sufficient water is removed to allow addition of small aliquots (2 to 5 mL) of a manganese sulfate solution and a solution containing both iodide and hydroxide. The bottle is firmly stoppered and agitated then allowed to stand for several minutes to let Reaction 8.2 go to completion. A few mL of concentrated sulfuric acid is then added: this redissolves the solids and causes the  $\text{MnO}(\text{OH})_2$  to oxidise the iodide (Equation 8.3). The iodine is then titrated with a 0.01 to 0.03 mol/L standard solution of sodium thiosulfate (Reaction 8.4).

### Electrolysis method (oxygen sensor)

**Electrolysis** is a process in which a chemical reaction that does not occur naturally is brought about by passing an electric current through a molten mixture or through an aqueous solution.

We saw on p. 71 CCPC that electrolysis could be used to break molten lead bromide into liquid lead and gaseous bromine. Similarly an aqueous solution of copper chloride can be electrolysed to produce solid copper and gaseous chlorine:



If there is no cation that can easily be reduced (as in electrolysing a solution of potassium chloride), then the reaction that occurs at the cathode is often:



The *electrolytic oxygen sensor* uses the fact that, at constant voltage and with constant electrode surface area and constant separation between electrodes, the rate of electrolysis of a substance is proportional to its concentration. A diagram of the sensor is shown in Figure 8.3.

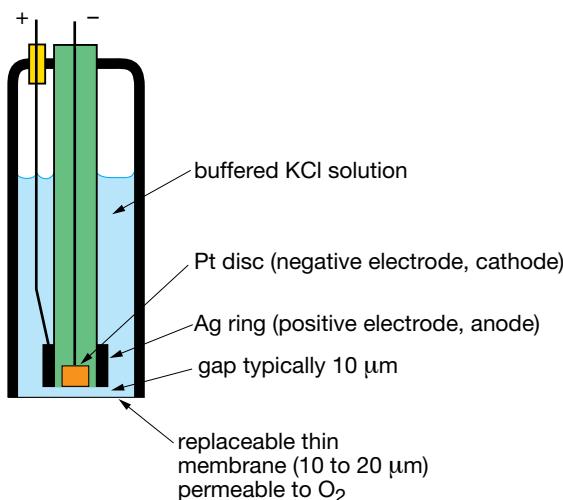


FIGURE 8.3  
An electrolytic sensor for measuring dissolved oxygen

A platinum disc cathode (negative electrode) is embedded in the end of an insulating rod. A silver ring as anode (positive electrode) is attached to the outside. A thin layer of a buffered KCl solution separates this from a polymer membrane that is permeable to oxygen gas. Oxygen diffuses from the test solution through the membrane, through the liquid film and to the cathode where it is electrolysed (reduced)—Equation 8.5 above.

The reaction at the anode (positive electrode) is:



This electrolysis causes a current to flow; this current is measured and converted to an oxygen concentration. The solution in the sensor in the absence of oxygen contains nothing that can be electrolysed at the voltage used and so current only flows when oxygen diffuses into it.

This device is simple and convenient to use and is battery operated. The membrane is easily replaceable if it becomes contaminated or clogged, so the device is widely used in environmental monitoring.

## Measuring biochemical oxygen demand (BOD)

The method used for measuring biochemical oxygen demand depends on the nature of the water to be tested. For municipal water supplies where BOD is

† Remember from Section 2.7 the definition of anode (where oxidation occurs) and cathode (where reduction occurs). This means that the anode, which was the negative electrode in a galvanic cell, becomes the positive one in electrolysis.

expected to be low (because of protection of the catchment from contaminated run-offs), it is measured by adding nutrient to the sample and incubating it at 20°C in a sealed air-free container in the dark for 5 days then measuring the residual dissolved oxygen. The difference between the dissolved oxygen readings before and after incubation is the BOD.

Samples with high BOD such as untreated or partially treated sewage would quickly use up all the dissolved oxygen, so they are analysed by adding oxygen to keep the sample saturated and measuring the amount of oxygen used. For these samples a suitable micro-organism as well as nutrient is added before incubation.



## Exercises

- 4 \*a** Use the data below to draw a graph of dissolved oxygen concentration *versus* temperature. Include zero on the temperature scale. Draw a smooth curve through your points.

Temperature (°C)	5.0	10.0	15.0	20.0	25.0	30.0
Dissolved oxygen concentration (mg/L)	12.6	11.1	9.9	9.0	8.2	7.5

- b** What is the dissolved oxygen concentration at **i** 22°C **ii** 7.0°C **iii** 1.0°C? Are any of your answers here less accurate than the others? Explain why or why not.  
**c** At what temperature is the oxygen concentration **i** 13.5 mg/L **ii** 7.8 mg/L?  
**d** Express your answer to (b)(i) in moles per litre.
- 5** What is often more important than actual oxygen concentration in assessing water quality is percentage saturation. Percentage saturation is the actual concentration of dissolved oxygen expressed as a percentage of the solubility of oxygen at the prevailing temperature. Using your graph from Exercise 4, calculate the percentage saturation in water samples in which the concentrations of dissolved oxygen and temperatures are as follows:
- a** 7.2 ppm at 25.0°C                    **c** 5.4 ppm at 22.0°C  
**b** 7.2 ppm at 8.0°C                    **d** 8.8 ppm at 13.0°C
- 6 a** The treated waste from a food-processing plant had a BOD of 45 ppm. If this waste was added to a river (with a normal dissolved oxygen level of 9.0 ppm) in such a way that it was diluted by a factor of 20, what would be the concentration of dissolved oxygen a sufficient distance downstream of the discharge point for all the waste to have been decomposed (say about 3 km)? What would be the effect of this discharge on the river? What would you expect the state of the river to be a few kilometres further downstream?  
**b** If the untreated waste (with a BOD of 220 ppm) had been discharged into this river with the same factor of 20 dilution, what would the dissolved oxygen level have been 3 km downstream from the discharge point? Explain. What effect would this have had on the river?  
**c** Contrast the state of the river a few kilometres further downstream in the two scenarios in (a) and (b).
- 7 a** In planning its sewage treatment plant a town decided that it would be able to discharge its treated waste into a river with a 50 to 1 dilution ratio. If it did not wish to lower the dissolved oxygen concentration by more than 2.5 ppm, to what level must it reduce the BOD in its treated waste?  
**b** Another town was able to discharge its treated sewage into the ocean and achieve a dilution of over 200 to 1. To what level does it need to reduce the BOD

of its sewage in order not to lower the dissolved oxygen concentration by more than 2.5 ppm?

- 8 A sample of water from a river was collected in a bottle known to contain 312 mL when completely filled and tightly stoppered. There were no air bubbles in the sample. Back in the laboratory 10.0 mL was removed by pipette, and 5 mL (by cylinder) of manganese(II) sulfate solution and enough of an alkaline potassium iodide solution to completely fill the bottle again were added. The bottle was tightly stoppered and inverted several times then left to stand for five minutes for reaction to go to completion and for the precipitate to settle to some extent. 5 mL of clear solution was removed and replaced by 5 mL concentrated sulfuric acid. After replacing the stopper the mixture was agitated until all the precipitate had dissolved and the solution had taken on a pale brown colour (of iodine). The mixture was transferred to a 500 mL conical flask and titrated with 0.0224 mol/L sodium thiosulfate solution using starch as indicator; 13.1 mL was required.

The reactions involved are Reactions 8.2, 8.3 and 8.4. Calculate the number of moles of iodine that were in the final solution, hence the number of moles of oxygen in the starting solution. Finally calculate the concentration of oxygen in the original sample in ppm.

- 9 A second sample of the same water as in Exercise 8 was collected in a 321 mL airtight bottle and stored in the dark at 20°C for 5 days. Then it was analysed for oxygen content as in Exercise 8. In the final titration 3.4 mL thiosulfate solution was needed. Calculate the BOD of the original water. Would you regard the original water as slightly, moderately or severely polluted or not polluted at all? Explain your answer and suggest possible sources of the pollution, if any.

## 8.7 MICROORGANISMS

Natural water can contain a wide range of microorganisms. Most are harmless but some can be extremely dangerous such as the pathogens that spread typhoid, cholera and dysentery. The elimination of such disease-causing agents from public water supplies has been the greatest contributor to public health in the last 200 years.

Because there are so many possible microorganisms that can be present in water, it is not possible to monitor all of them. Consequently scientists routinely monitor for an indicator organism that can signal the possible presence of pathogens. The chosen organism is *Escherichia coli*, commonly abbreviated to *E. coli*. This bacterium is generally quite harmless to humans and other animals, but is present in the intestinal tract (and so in faeces) of all animals. If it is found in water, it is a signal that the water is contaminated with sewage or animal wastes. People can be warned not to use the water while a search is made for the source of the contamination. Tests can also then be made for other organisms that are considered a particular threat to the locality.

To test for *E. coli* a sample is placed on a suitable nutrient bed and incubated for 12 to 24 hours, during which time the individual bacteria grow into colonies that are large enough to count by eye. Results are reported as *colony forming units* per 100 mL of water, CFU/100 mL. If there is more than 1 CFU/100 mL, the water is not suitable for drinking; if more than 200 CFU/100 mL, the water is unsafe for swimming.

An example will illustrate how the various tests described so far can be used to obtain information about the origin of water samples or about the pollution in them.



## Example

Some measurements on several water samples are shown in the following table.

Sample	L	M	N	P	Q	R	S
pH	6.5	6.9	7.8	6.6	9.2	3.4	7.6
DO <sup>a</sup> (ppm)	5.7	8.9	5.7	8.7	6.0	7.6	2.2
TDS <sup>a</sup> (ppm)	400	350	850	50	200	600	250
turbidity (NTU <sup>a</sup> )	90	50	15	4	30	60	65
<i>E. coli</i> (CFU <sup>a</sup> /100 mL)	35	0	0	0	15	0	150

*a DO = dissolved oxygen; TDS = total dissolved solids; NTU = nephelometric turbidity units; CFU = colony forming units*

Which of these samples would you consider to be from:

- a** a clean mountain stream
- b** a stream after it had flowed through an area that had recently been cleared of forest
- c** a stream that had flowed through a mixed farming area (cattle and grain crops)
- d** a stream polluted from run-off from a sulfide mine site
- e** an underground bore
- f** down stream from a raw sewage outlet?

To answer this question we need to be aware of the characteristics of each of the types of waterway listed.

- a** A clean mountain stream will be virtually unpolluted; its values for the various properties listed will be similar to those shown for clean water in Table 8.1. **Sample P** is the only one that meets these requirements.
- b** A stream running through a recently cleared forest area will have high turbidity (large amount of suspended solids) and high TDS, but its other properties will be close to those of clean water. **Sample M** is this stream, because its TDS and turbidity are high while pH, DO and *E. coli* are close to clean water values.
- c** A stream flowing through an area in which cattle graze will be contaminated with faecal coliforms (*E. coli*) and will probably have somewhat depleted DO, because of oxygen demanding wastes being washed into the stream. If crops are grown also, then we would expect high turbidity (erosion of suspended solids) and high TDS (again from run-off across ploughed ground). Samples L and S seem to meet these requirements (high *E. coli*, turbidity and TDS and low DO); however the DO in S is probably too low for just run-off from cattle droppings—it is more consistent with a genuine sewage discharge—so **Sample L** is the stream that flows through farm land. Q would be a candidate except that its pH is too high.
- d** Mine sites often suffer from acid drainage (conversion of sulfide on exposure to air and moisture to sulfuric acid) so we are looking for a stream with low pH. It may well have high TDS and turbidity (because of all the broken ground) but pH is the key. **Sample R** fits this profile.
- e** An underground bore will produce water with a high TDS and probably a somewhat low DO. pH may be a little higher than clean surface water, but other properties will be close to ‘clean’ values. **Sample N** meets these requirements; L, R and S also have high TDS but L and S have high *E. coli* which rules them out, and R has too low a pH.
- f** Discharge of raw sewage into a stream markedly lowers DO and increases *E. coli* counts; it also increases turbidity and TDS. These characteristics point us to S and L. However in L the DO is not excessively low and the *E. coli* not excessively high, so **Sample S** is the sewage-contaminated stream (particularly as we have the farmland option for L).

Sample Q does not fit any of the suggested categories. We can say that it is polluted, particularly with some alkaline waste and some microorganisms and has a low DO, suggestive of organic wastes also, but we cannot be more specific.

### Exercise

- 10 Some measurements on various water samples are shown in the following table.

Sample	A	B	C	D	E	F
TDS <sup>a</sup> mg/L	>10 <sup>4</sup>	900	80	150	>10 <sup>4</sup>	200
DO <sup>a</sup> (mg/L)	4.6	7.2	8.5	9.2	8.7	5.7
BOD <sup>a</sup> (mg/L)	60	1.6	4.2	2.5	1.8	75
coliforms (CFU <sup>a</sup> /100 mL)	500	0	30	3	0	250

a TDS = total dissolved solids; DO = dissolved oxygen; BOD = biochemical oxygen demand; CFU = colony forming units

Which of these samples would you consider to be

- a i sea water ii bore water iii fresh surface water
- b polluted with sewage
- c likely to be contaminated with parasites from animals
- d relatively unpoluted?

Give your reasons in each case.

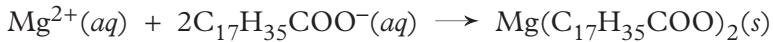
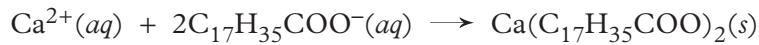


## 8.8 WATER HARDNESS

Hard water was defined in Section 8.1. Water is hard because of the presence of significant concentrations of calcium and magnesium ions. Water with very low concentrations of these ions is called *soft water*.

Soap is sodium stearate, C<sub>17</sub>H<sub>35</sub>COONa. It is a salt of the carboxylic acid, stearic acid (Section 5.16). We use soap because it makes water ‘wetter’. Technically it lowers the surface tension so that the water can stick to oily particles, and remove them from our skin or clothes.

The calcium and magnesium salts of stearic acid are insoluble in water. This means that if our tap water contains these cations, then a precipitate of calcium and magnesium stearates will form when soap is added to this water:



The formulae of the precipitates could equally well be written as (C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub>Ca or (C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub>Mg.

These precipitates appear as a grey scum on the surface of the water and often stick to the enamel of baths and handbasins. The formation of this scum removes soap from solution and hence spoils its cleaning power. The scum can often settle on fabrics being washed and discolour them, as it does not rinse away easily.

Sydney and Melbourne have relatively soft water. Brisbane water is moderately hard, while Adelaide’s water is very hard. Water from underground bores or from the downstream end of a very long river tends to be hard. This

is because it has been in contact with earthy materials for long periods and has been able to dissolve out calcium and magnesium salts. Rainwater is very soft.

An old solution to the problem of hard water was to fit a water softener to the household water supply. This is an ion exchanger which replaces calcium and magnesium ions with sodium ions. A disadvantage is that it needs to be regenerated regularly.

Another solution is to use synthetic detergents instead of soap. These do not form precipitates with calcium and magnesium ions. Hence synthetic detergents are more effective than soap in hard water. However, even detergents work better (clothes rinse more effectively) if the water is softened (e.g. by adding washing soda,  $\text{Na}_2\text{CO}_3$ , to precipitate the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions).

# Measuring the hardness of water

Water hardness is measured by determining the total concentration of calcium and magnesium ions in the water and expressing the result as milligrams of  $\text{CaCO}_3$  per litre.

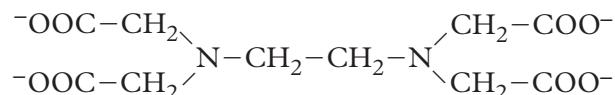
For example, for a sample of water containing  $1.0 \times 10^{-4}$  mol/L  $Mg^{2+}$  and  $2.5 \times 10^{-4}$  mol/L  $Ca^{2+}$ :

Total concentration of 'hardness' =  $(1.0 + 2.5) \times 10^{-4}$  mol/L  
 molar mass of  $\text{CaCO}_3$  = 100.1 g/mol

$$\text{So equivalent concentration of } \text{CaCO}_3 = 3.5 \times 10^{-4} \times 100.0 \text{ g/L} \\ = 3.5 \times 10^{-2} \text{ g/L} = 35 \text{ mg/L (or 35 ppm)}$$

Hardness of this water would be reported as 35 mg/L or 35 ppm.

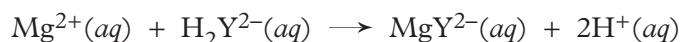
A volumetric titration is used for the analysis. It uses the fact that both calcium and magnesium ions in an ammonia, ammonium ion buffer (pH about 10) form a complex with the quadruply charged anion of ethylenediamine tetra-acetic acid, commonly called EDTA. The anion has the structure:



For simplicity in equations we often write EDTA as  $\text{H}_4\text{Y}$ . The titrant used is the disodium salt of EDTA,  $\text{Na}_2\text{H}_4\text{Y}$  (or  $(\text{Na}^+)_2(\text{H}_4\text{Y}^{2-})$ ). The reactions are:



and



The indicator used for this titration is another complexing agent Eriochrome Black T. In solution it has a blue colour but forms a reddish complex with  $Mg^{2+}$ . The equivalence point is when the solution changes from purple to blue (loses the last tinge of red). If a 0.0100 mol/L solution of  $Na_2H_2Y$  is used, then each mL of titrant corresponds to  $1.00 \times 10^{-5}$  mol of metal ion or to 1.00 mg of  $CaCO_3$  (molar mass 100 g/mol).

In the Sydney region, water from Warragamba Dam has a hardness of about 40 mg/L while that from dams closer to the source of the Nepean River (such as the Woronora and Cordeaux Dams) is only about 20 mg/L.

## Qualitative test for hardness

By trial and error it is determined how many drops of a soap solution need to be added to 5 mL distilled water in a test tube in order to produce a good lather (lots of bubbles or froth) when the mixture is shaken. This number of drops of soap solution is then added to 5 mL of the water to be tested and the mixture shaken. By comparing the amount of lather produced from the sample and the distilled water, it is decided whether the water is very hard (very little lather), moderately hard (significant amount of lather but well less than in the distilled water) or soft (similar amount of lather in the test sample as in the distilled water).

This test can be used to compare qualitatively the hardness of different samples of water but it cannot put a value to the hardness.

### Exercises

- 11 a When the quadruply charged anion of EDTA complexes with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , it forms six coordinate covalent bonds with the metal ion. Identify the six atoms which each contribute an electron pair for this.  
b EDTA titrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions are performed at a pH of about 10, because the complexing does not occur quantitatively at significantly lower pHs. Suggest a reason for this.
- 12 a Water from a particular source was quoted as having a hardness of 54 mg/L. Express this in total moles of calcium and magnesium ions per litre.  
b What is the hardness of water in which the calcium and magnesium ions have concentrations of  $3.7 \times 10^{-4}$  and  $0.9 \times 10^{-4}$  mol/L respectively?
- 13 When a 250 mL water sample was titrated with 0.0113 mol/L EDTA solution as described in Section 8.8, 18.4 mL was required. Calculate the hardness of the water (expressed in mg/L calcium carbonate). Why is it not necessary to determine  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  separately in order to calculate hardness?



## 8.9 TESTS FOR COMMON ANIONS

Anions that are generally present in fresh water are chloride and sulfate and to a lesser extent carbonate. Their presence can be detected by using the tests of Table 6.3. However because of the low concentrations likely to be present in unpolluted fresh water some modification may be needed.

### Carbonate

First check the pH of the water: carbonate is unlikely to be present in significant amounts if the pH is less than 6.5. Then heat the sample to about 80°C and carefully add drops of 0.1 mol/L hydrochloric acid: if colourless bubbles of gas form, carbonate is present. The high temperature is used to facilitate release of carbon dioxide which may remain in solution at low temperature. If there is evidence of significant amounts of carbonate, it may be estimated quantitatively by precipitating it as calcium carbonate from neutral or slightly alkaline solution (to ensure that hydrogen carbonate converts to carbonate and precipitates also).

## Chloride and sulfate

Chloride is detected qualitatively by adding a drop of silver nitrate solution. If chloride is present, the sample goes turbid (milky) because of the formation of insoluble silver chloride<sup>†</sup>.

Sulfate is detected by adding a drop of barium nitrate (or chloride) solution. If sulfate is present, the sample goes turbid because of the formation of insoluble barium sulfate. We can get a rough estimate of the concentration of chloride or sulfate in a sample by varying the amount of silver or barium ion added and seeing if turbidity is still produced as shown in Table 8.2

**TABLE 8.2 Semi-quantitative estimates of chloride and sulfate concentrations in water**

Amount of cation solution <sup>a</sup> added and volume of sample it is added to	If solution goes turbid, concentration (in mg/L) is	
	chloride	sulfate
1 drop $1.0 \times 10^{-2}$ mol/L to 10 mL	>0.2	>0.5
1 drop $1.0 \times 10^{-3}$ mol/L to 10 mL	>2	>5
1 drop $1.0 \times 10^{-3}$ mol/L to 100 mL	>20	>50
1 drop $1.0 \times 10^{-4}$ mol/L to 100 mL	>200	>500

a Ag<sup>+</sup> for chloride, Ba<sup>2+</sup> for sulfate.

## Phosphate

The best test for detecting the presence of phosphate at the low concentrations at which it is present in environmental water is the ammonium molybdate test, test 3 in Table 6.3. The water sample is acidified, then ammonium molybdate solution added and the mixture gently heated for a few minutes. The appearance of a yellow precipitate or just a yellow turbidity indicates the presence of phosphate.

Phosphate is generally the key nutrient involved in the formation of algal blooms (Section 8.12), so we often need to measure its concentration.

## Quantitative measurement of phosphate

Because of the low phosphate concentrations involved—often less than 1 ppm—a sensitive colorimetric method is used. A *colorimetric method* is one that relies on the quantitative measurement of the absorption of light by a coloured solution. Simple instruments for doing this are called *colorimeters*: they use filters to select the wavelength of light. More elaborate instruments are called *spectrophotometers*: they use monochromators to select the wavelength more precisely and so are generally more accurate.

To estimate phosphate quantitatively, a variation on the molybdate qualitative test is used. A measured quantity of a solution of ammonium molybdate with a catalyst is added to the sample followed by careful mixing. Then a measured quantity of solid ascorbic acid (Vitamin C) is added to this mixture. This

† Sulfate does not interfere with the chloride test here as it did in Sections 6.12 and 6.13, because in environmental water, sulfate concentrations never get high enough.

produces an intense blue colour (called molybdenum blue). By comparing the absorbance of this solution with that produced by a standard phosphate solution treated identically, we can calculate the concentration of phosphate. This method can be used for phosphate concentrations in the range 0.01 to 3 mg/L (ppm).

The yellow phosphomolybdate complex contains only Mo(VI). Ascorbic acid reduces some of this to Mo(V) and this causes the intense blue colour to develop.

## 8.10 CATIONS IN ENVIRONMENTAL WATER

In Sections 6.9 to 6.11 we looked at tests that could be used to identify six particular cations in solution:  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Table 8.3 lists some tests that can be used to identify some other cations that if present in water are of considerable concern to us.

**TABLE 8.3 Tests used to identify cations (additional to those in Table 6.1)<sup>a</sup>**

Cation	Tests
$\text{Hg}^{2+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a yellow or red precipitate of <math>\text{HgO}</math></li> <li>2 with KI forms a red precipitate, <math>\text{HgI}_2</math> which dissolves in excess KI</li> <li>3 acidify and add <math>\text{Na}_2\text{S}</math>: a black precipitate of <math>\text{HgS}</math> forms</li> </ol>
$\text{Cd}^{2+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a white precipitate of <math>\text{Cd}(\text{OH})_2</math> which does not dissolve in excess NaOH but it does dissolve in ammonia</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: a yellow precipitate of <math>\text{CdS}</math> forms</li> </ol>
$\text{Zn}^{2+}$	<ol style="list-style-type: none"> <li>1 with NaOH, forms a white precipitate of <math>\text{Zn}(\text{OH})_2</math> which dissolves in excess NaOH and also in ammonia (forming a colourless solution in both cases)</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: no precipitate forms. Make slightly alkaline and a white precipitate of <math>\text{ZnS}</math> forms</li> </ol>
$\text{Cr}^{3+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a grey-blue precipitate of <math>\text{Cr}(\text{OH})_3</math> which dissolves in excess NaOH (to form a green solution) but does not dissolve in ammonia</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: no precipitate forms. Make slightly alkaline and a grey-blue precipitate of <math>\text{Cr}(\text{OH})_3</math> forms<sup>b</sup></li> </ol>
$\text{Al}^{3+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a white precipitate of <math>\text{Al}(\text{OH})_3</math> which dissolves in excess NaOH (to form a colourless solution) but does not dissolve in ammonia</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: no precipitate forms. Make slightly alkaline and a white precipitate of <math>\text{Al}(\text{OH})_3</math> forms<sup>b</sup></li> </ol>

*a* None of these five cations forms a precipitate with chloride or sulfate.

*b* Chromium and aluminium sulfides in aqueous solution react with water (hydrolyse) to form hydroxides.

As was explained in Section 6.11, one cation can interfere with the test for another cation. In that section we overcame this problem by testing for the cations in a particular sequence and performing the tests on the filtrates left over from the previous tests (Figure 6.6). Similar schemes can be worked out for more comprehensive sets of cations but that is beyond the scope of this account. By carefully noting the results from several of the tests in Tables 6.2 and 8.3 you can probably work out just which cation(s) is(are) present in a given water sample.

## A simple test for heavy metals

In environmental contexts **heavy metals** are the transition metals plus lead, though in some contexts the semi-metal arsenic is also included.

The heavy metals that are of most concern, because of their detrimental health effects, are mercury, lead, cadmium, chromium, arsenic, and to a lesser extent, silver, zinc and copper.

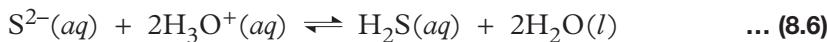
A solution of sodium sulfide can be used to get a quick indication of whether or not any heavy metals are present in a sample of water.

The water sample is acidified then drops of  $\text{Na}_2\text{S}$  solution are added: if a precipitate forms, then one or more of the following cations is present:  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^{3+}$ .

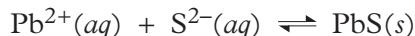
If no precipitate forms with acid present, the solution is made slightly alkaline. If this produces a precipitate, then one or more of the following cations is present:  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ . If a precipitate forms in acid solution, it should be centrifuged (or filtered) off and the remaining solution made alkaline to check whether any of this second group of cations is present.

### The chemistry involved

This heavy metal test is based on the facts that hydrogen sulfide is a very weak acid and that the two groups of cations have quite different solubilities in water (though all are insoluble). In acid solution the sulfide ion of sodium sulfide is almost completely converted to  $\text{H}_2\text{S}$ :



Only a minute concentration of  $\text{S}^{2-}$  is left in solution, but it is sufficient to precipitate extremely insoluble sulfides such as lead and copper; for example:



If a small amount of  $\text{PbS}$ , for example, can form, then that lowers the concentration of  $\text{S}^{2-}$  and this forces Reaction 8.6 to move to the left (Le Chatelier's principle) and so it keeps producing more  $\text{S}^{2-}$  until all the lead is precipitated.

The concentration of  $\text{S}^{2-}$  in acidified sulfide solution is too small to cause any precipitate with the cations that form *less insoluble* sulfides such as  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$ , so reactions such as



do not get started so do not affect Equilibrium 8.6 and so no precipitate forms.

However in alkaline solution Reaction 8.6 does not move very far to the right at all, and so there is a high enough  $\text{S}^{2-}$  concentration for Reaction 8.7 to move to the right and go to virtual completion and so we get a precipitate of zinc sulfide (and similarly for the other cations of that group).

If an appreciable amount of precipitate forms in either the acidic or alkaline test, then the tests of Tables 6.2 and 8.3 can be used to identify which heavy metals are present.

## Measurement of concentrations of cations

While knowing qualitatively that particular cations are present in water may be of some value, generally we need to know the concentrations of these cations in order to decide whether they present a risk to human health or to the environment.

A wide variety of methods is used to measure such concentrations. Traditional methods such as gravimetric analysis and titrations have limited use because of the low concentrations involved in environmental water samples. Instrumental methods are more commonly used. In Sections 6.18 and 6.19 we saw that atomic absorption spectroscopy is widely used for environmental monitoring. Mention was also made of atomic emission spectroscopy (Section 6.17): this is also widely used for monitoring water quality. This has the advantage of being able to analyse for several metals in the one measurement. With atomic absorption, metals must be measured one at a time because each requires a separate lamp.

## 8.11 FACTORS AFFECTING CONCENTRATIONS OF IONS

The ions present in natural water bodies (such as rivers, dams and oceans) and their concentrations depend upon the following factors:

### ■ The pathway from rain to water body

*Rain* contains very few ions—just small concentrations of carbonate (from dissolved  $\text{CO}_2$ ) and some  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions from sea spray that winds carry into clouds. When rain runs off bushland into streams, it picks up small amounts of nitrates and phosphates from natural nutrients on the surface and perhaps small amounts of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from decomposing minerals. In such cases TDS is generally below 50 ppm.

If, however, rain water soaks into the ground and flows through *underground aquifers* and then into a stream, it will contain increased amounts of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  by dissolving them from the soils and rocks that it flows through. For such water TDS will commonly be in the range 100 to 300 ppm.

If water percolates down to *deep underground aquifers* as in artesian basins and then comes to the surface centuries later for storage and use, it contains much higher levels of the above-mentioned ions and may contain various other cations such as  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . TDS values of 1000 ppm and above are common, though the higher TDS becomes, the less suitable the water is for humans and cattle and sheep.

### ■ The pH of the rain

Water from acid rain ( $\text{pH} < 5$ ) is better able to leach certain cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  from the soil it passes over or through and so concentrations of these ions increase.

### ■ The nature and amount of human activity in the catchment

*Land clearing* generally leads to more water rapidly running across disturbed land and into streams. This increases sediment loads (and so increases turbidity) and facilitates the dissolution of a variety of ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ .

*Agricultural pursuits* (growing crops and improving pastures) often lead to fertiliser run-off. This increases the concentration of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  in the water.

#### ■ Effluents discharged into the water bodies

Discharges of *raw and/or treated sewage* into rivers or oceans increase the concentrations of many ions, particularly phosphate and nitrate, but also many common ions such as those in the previous paragraph. Even good sewage treatment that removes nearly all suspended matter, BOD and pathogens can increase the TDS of the water by 200 ppm or more, this being made up of a wide variety of common ions.

*Storm water run-off* in urban areas can similarly increase the concentration of a variety of ions in water bodies.

*Industrial effluents*, if not carefully monitored and controlled, can discharge heavy metal ions into water bodies, ions such as  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .

#### ■ Leaching from rubbish dumps

When rain and storm water flow over and seep through poorly designed rubbish tips, they dissolve many harmful substances and carry them into waterways: the term for this is **leaching**. Dangerous cations such as cadmium from nickel–cadmium rechargeable batteries, mercury and lead from other batteries, zinc from old galvanised iron and anions such as nitrate and phosphate from decaying organic wastes are carried into streams.

## Oceans as well as rivers and dams

Because of their smaller volumes, rivers and dams are more vulnerable than oceans to increases in ion concentrations. Nevertheless discharge of poorly treated sewage from big cities (such as Sydney) and large run-offs from flooded rivers that flow through agricultural land can affect the ion concentrations in coastal ocean water quite significantly. The Great Barrier Reef off the north Queensland coast is being detrimentally affected by sediments, nutrients and possibly heavy metals that are being carried into the surrounding waters by coastal rivers flowing through agricultural and urban areas.

## Exercises

- 14 A group of students used the method described in Section 8.9 to determine the phosphate concentration in some environmental samples. First they calibrated their colorimeter by making up solutions of sodium phosphate of known concentration and ‘analysing’ them according to the above procedure and measuring the absorbance with the colorimeter. Results are shown below. Construct a calibration curve for this instrument of absorbance *versus* concentration of phosphate.

Concentration of phosphate (ppm)	0.030	0.060	0.100	0.150
Absorbance	0.07	0.16	0.25	0.41

Four environmental water samples were then put through the same test procedure. They gave the following absorbances:

Sample	A	B	C	D
Absorbance	0.14	0.36	0.48	0.025

Calculate the concentration of phosphate in each of these samples. Does the fact that two of these absorbances are outside the range of the calibration values make the results less accurate? Explain.

- 15** When 1 drop of 0.0010 mol/L silver nitrate solution was added to 10 mL of a sample of water and the mixture shaken, it went turbid. When the test was repeated with 100 mL of the same water, the mixture remained clear. When 1 drop of 0.010 mol/L barium nitrate solution was added to 10 mL of this water and the mixture shaken, the mixture went turbid. When the test was repeated using 0.0010 mol/L barium nitrate solution the mixture remained clear. With the aid of Table 8.2, what can you deduce about the concentrations of chloride and sulfate in this water?
- 16** Describe the tests you would perform (along with the results you would expect) to decide whether:
- a** a sample of fresh water was contaminated with sewage that also contained heavy metals
  - b** a creek was contaminated by acid drainage from a nearby coal mine (sulfides exposed to the air under certain conditions produce sulfuric acid)
  - c** the water in a stream just downstream of a partially-treated sewage discharge was a threat to the aquatic life of the stream
  - \*d** the sea water near a coastal chlor-alkali plant (which uses a lot of mercury) was contaminated with mercury
  - \*e** a river was contaminated with copper ions escaping from a nearby copper mine.

Explain why you used the particular test or tests that you chose.

- 17** A bore on a coastal farm draws water from a fresh water underground aquifer. It was suspected that sea water was encroaching into the aquifer. What test(s) would you perform to decide whether this was so?
- 18** What tests would you perform to decide whether the water in a river several kilometres downstream from the point at which treated sewage was discharged into the river was safe for human use? Explain why you would use the chosen tests.
- 19** When 1 drop of  $1.0 \times 10^{-3}$  mol/L silver nitrate solution was added to a 100 mL sample of water, it produced turbidity. What does this tell you about the chloride ion concentration in that water? How could you modify the test so that you could use the information in Table 8.2 to obtain a better estimate of the chloride ion concentration in the water?
- 20** **a** A river was contaminated with a heavy metal. How would you determine whether the contamination was chromium from a leather factory on one bank of the river or lead from a car battery manufacturer on the other bank?  
**b** A cadmium electroplating factory was accused of polluting a nearby creek with cadmium ions. The factory claimed that the heavy metal detected was zinc (leached out of the galvanising on the roofs of houses in the surrounding areas). Describe tests you would perform to decide whether the contaminant was zinc or cadmium ions.  
**\*c** How would you decide whether the heavy metal contaminant in a water sample was lead, silver or barium ion? Explain carefully how your test results prove the presence of one ion and the absence of the other two.

- \*21** Five major sources of water pollution are (1) sewage (treated and untreated) (2) urban storm water run-off (3) industrial effluents (4) agricultural run-off (crop growing, including irrigation, and grazing) (5) erosion from clearing forests and bushland.

Draw up a table that shows which water quality criteria (of those in Section 8.1) are affected, and in what ways, by each of these forms of pollution.

## 8.12 ALGAL BLOOMS AND EUTROPHICATION

So-called algal blooms, defined in Section 8.1, have presented a serious problem for many Australian rivers and dams in recent years. In the summer of 1991–2 an algal bloom made the water in a 1000 kilometre length of the Darling River unusable for people and livestock for many weeks.

Algal blooms lead to such deterioration of water quality that it becomes

unsuitable for its normal uses. For rivers and lakes such blooms can also lead to permanent degradation.

Algal blooms occur when nutrients are readily available in the water and when environmental conditions are favourable (warm temperatures, plenty of sunlight and not much water movement). The two nutrients which are normally in shortest supply to plants and which generally limit plant growth are nitrate and phosphate. Of the two, it is generally phosphate which is present in least amount and which therefore has the greatest control on growth rate.

If there is an abundant supply of phosphate in the water, then algae grow and multiply rapidly. Generally it appears as a greenish scum floating on the water surface. A great variety of aquatic species can be involved. Many species of green algae are commonly present; these are the green scum. Green algae, while a nuisance, are not toxic. However other species that are frequently present in algal blooms in fresh water are so-called *blue-green algae*. Actually these are not algae at all! They are types of bacteria called *cyanobacteria*. The cyano part of the name comes from the name of a particular colour, cyan, which is blue-green.



The algal bloom that occurred along the Darling River in the summer of 1991–2 extended for over 1000 km

### Detrimental effects

The detrimental effects of algal blooms are these:

- Cyanobacteria, if present, produce certain poisons that can kill livestock and cause serious illness in humans.
- The water becomes unsuitable for its normal uses because the high concentrations of non-poisonous algae are difficult to filter out, give the water an unpleasant taste and clog pumps used for moving water to irrigation land and animal drinking troughs.
- During the night algae consume dissolved oxygen from the water. This causes fish to suffocate and die, and in so doing make the river or dam very unpleasant (though during daylight hours algae, being plants, generate oxygen through photosynthesis).
- They lead to a build-up of sediments in the river or dam.

Sediments build up because eventually the uncontrolled growth of algae uses up all of one nutrient, so that there is insufficient to support its continued life; hence the algae die and decompose and in so doing use up any remaining dissolved oxygen. They then decay anaerobically (without oxygen); this creates a putrid mess which results in the death of any remaining life forms in the water.

This decay of the organisms produces much sediment which builds up on the floor of the river or dam.

Occasional algal blooms in a river or dam are reversible; the next flood or heavy rain flushes out the river or dam and it recovers. If algal blooms occur too frequently, then the river or dam does not fully recover after the next flood; sediments build up (which facilitates future algal blooms and the growth of rooted aquatic plants) and so the process of degradation continues and becomes very difficult to reverse.

A term often used in this context is *eutrophication*.

## Eutrophication

**Eutrophication** is the process in which a water body becomes enriched with nutrients such as phosphate and nitrate to such an extent that algal blooms become highly likely.

This enrichment of water bodies with nutrients followed by algal blooms is part of the natural process by which a clear stream or lake containing minimal amounts of living matter is converted into a swamp or marsh containing abundant life forms and eventually to meadow (dry land). In nature this is a slow process, taking tens of thousands of years. However human activity frequently accelerates the transition from a clear water body to a weed- and sediment-infested one by discharging nutrient-rich effluents into rivers and dams: such enrichment of nutrients as a result of human activity is called *cultural eutrophication*.

## Sources of nutrients

There are two main sources of nutrients in our waterways, sewage and farm fertilisers.

### Sewage

The organic matter in raw sewage contains significant amounts of phosphorus and nitrogen. The decomposition of organic matter whether in ‘normal’ sewage treatment works or in a waterway converts phosphorus to phosphate and some of the nitrogen to nitrate. In this way sewage increases the nutrient load of the water body. Tertiary sewage treatment removes much of the phosphate, but such treatment is rare in Australia (except for Canberra and a few other inland places).

Laundry washing powders often contain phosphates: they stop dirt re-settling onto the clothes and help maintain an optimum pH (act as a buffer). Since wash water generally ends up in the sewers, such washing powders contribute significantly to the phosphate load of the effluent from sewage treatment plants.

### Fertiliser

Fertiliser run-off is the most direct way that farming contributes to algal blooms. The main components of fertilisers are phosphate and fixed nitrogen, meaning nitrate and ammonia (in a variety of forms).

If too much fertiliser is used, the excess is washed away either by irrigation water or by rain and eventually drains into the nearest waterway and so into the overall river system.

## Monitoring for eutrophication

Because of the detrimental effects of the algal blooms that generally follow eutrophication, we need to monitor vulnerable water bodies on a regular basis. This means monitoring concentrations of the key nutrients, nitrate and phosphate. A colorimetric method for estimating phosphate was described in Section 8.9. There is also a colorimetric method available for estimating nitrate. Because in most Australian waterways phosphate is the growth-limiting nutrient, it is the best one to monitor to check for eutrophication.

An algal bloom is likely:

- in a dam or lake, if phosphate concentration > 0.05 ppm
- in a river or stream, if phosphate concentration > 0.1 ppm (a higher value because the water is more likely to be flowing). In other words, we say that a water body has become *eutrophic* if phosphate concentration > 0.05 ppm (dam or lake) or > 0.1 ppm (river).

### Exercises

\*22 Some test results on water samples taken from seven different streams are listed below.

Sample	A	B	C	D	E	F	G
turbidity <sup>a</sup> (NTU)	60	30	0.2	14	7	1	10
TDS <sup>a</sup> (mg/L)	620	200	45	450	120	150	180
pH	6.8	8.4	6.5	7.2	6.0	7.2	4.7
DO <sup>a</sup> (mg/L)	8.1	9.1	8.7	7.8	3.1	9.0	8.3
phosphate (ppm)	0.06	0.25	0.02	0.5	0.07	0.01	0.04

a NTU = nephelometric turbidity units: less than 1 is very clear water, 30 is quite turbid; TDS = total dissolved solids; DO = dissolved oxygen.

- a Which stream(s) would you consider to be relatively free of pollution?
- b Which sample(s) was(were) taken well downstream from the point where treated sewage was discharged into the stream?
- c Which stream if any has serious soil erosion upstream of the sampling point?
- d Which stream if any has suffered damage from acid drainage from a mine site?
- e Which stream(s) is(are) susceptible to an algal bloom?
- f Which stream is likely to contain very little aquatic life at the sampling point?

Give your reasons for each of your choices.

- \*23 a How would you decide that (i) a sluggish stream (ii) a storage dam was on the verge of producing an algal bloom? Why are the criteria slightly different in the two cases?
- b At sewage treatment plants that discharge their effluents into inland streams, phosphate is much more commonly removed (by precipitation with  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  or  $\text{Ca}^{2+}$ ) than is nitrate. Give two reasons for this being so.
- 24 Use the results in the table below to determine what, if any, types of pollution are affecting the streams from which the samples were taken. Indicate which, if any, stream you would expect to be vulnerable to an algal bloom. Give reasons for your decisions.

Sample	A	B	C	D	*E	*F	*G
turbidity (NTU <sup>a</sup> )	35	80	12	8	4	25	45
pH	8.2	6.6	9.7	7.1	6.5	7.2	3.7
DO <sup>a</sup> (mg/L)	3.1	7.2	8.5	8.2	8.7	8.3	6.5
BOD <sup>a</sup> (mg/L)	86	1.6	2.2	3	1.2	5	3
Na <sub>2</sub> S/H <sup>+</sup> test <sup>a</sup>	NR <sup>b</sup>	NR <sup>b</sup>	NR <sup>b</sup>	black ppt	NR <sup>b</sup>	NR <sup>b</sup>	black ppt
phosphate (mg/L)	0.35	0.04	0.03	0.02	0.01	0.23	0.02

a NTU = nephelometric turbidity unit; DO = dissolved oxygen; BOD = biochemical oxygen demand, Na<sub>2</sub>S/H<sup>+</sup> test is to add Na<sub>2</sub>S solution to an acidified sample of the water.

b NR = no reaction

#### WEBSITE

For a detailed survey of water pollution in NSW and steps being taken to alleviate it:

<http://www.epa.nsw.gov.au/soe/soe2003/Chapter5>

(this is the *State of the Environment Report* prepared by the NSW Environment Protection Authority; it treats nutrients, algal blooms and salinity (TDS) quite extensively)



## 8.13 WATER TREATMENT FOR DOMESTIC CONSUMPTION

The qualities that we expect of our drinking water were listed at the start of this chapter. To achieve these we need to protect the water catchment, and then to give the raw water an adequate treatment before piping it to homes and industries.

### Catchment

The geographic area from which all the streams and rainfall drain into a city's water storage dam is called its **catchment**. The first step in supplying good quality water is to protect the catchment. This means preserving the natural environment of the area as much as possible (no logging, land-clearing and minimal roads) and keeping out all human activity such as farming, grazing and mining. In that way the water that flows into the dam is relatively free of sediments and animal wastes (which often carry parasites or pathogens).

### Water treatment

In Australia water treatment generally means clarifying the water and sanitising it. 'Clarifying' means removing any turbidity or colour so that the water is sparklingly clear and colourless. 'Sanitising' means removing anything, particularly organisms, that would cause the water to be harmful to people.

Clarification is done by causing a precipitate to form in the water. Initially the precipitate forms as very small particles but as the water is gently stirred, these small particles stick together to form bigger ones in a process called **coagulation**. Sometimes the word **flocculation** is used for this process. Many of the other small particles that were originally present in the raw water adsorb onto the surface of these small precipitate particles and so get incorporated into the larger particles

that coagulation produces<sup>†</sup>. In this way the coagulated precipitate takes most of the suspended matter out of the water and is then filtered off, generally by passing the mixture through a coarse sand filter or sometimes through a mixture of sand and granulated anthracite (high quality coal). Anthracite with its high carbon content is able to adsorb much of the organic matter present in solution and this can remove odour and taste from the water.

This water treatment plant removes suspended particles by co-precipitation with an insoluble hydroxide followed by sand filtration before piping the water to domestic users

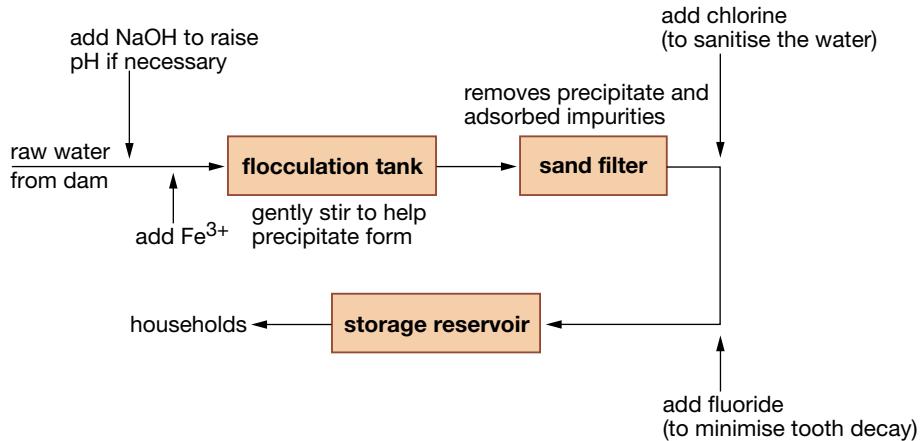


A precipitate that is widely used to clarify water is iron(III) hydroxide. This is formed first by adjusting (if necessary) the pH of the incoming water to above 7 (by adding lime or sodium hydroxide), then by adding a solution of an iron(III) compound such as iron(III) chloride. Iron(III) hydroxide is extremely insoluble and forms even at a pH as low as 7. Aluminium hydroxide is also widely used as the flocculating precipitate. Figure 8.4 is a flowchart for a typical water treatment plant.

After clarification the water is generally sanitised (sterilised) by having gaseous chlorine dissolved in it. Chlorine at a concentration of 1 or 2 ppm destroys bacteria and *some* viruses. Sufficient chlorine is added to the water (with careful monitoring) to ensure that the concentration stays slightly above 1 ppm until the water reaches the end user. If the starting water was reasonably clean and if the right amount of chlorine is used, there is no odour when it reaches the user.

Some water authorities add sodium fluoride (at a concentration of 1 ppm) to the water supply generally just downstream of the chlorination plant. Fluoride is added to strengthen tooth enamel in growing children: it is a form of enforced medication. It does not improve the safety of the water. The decision to add fluoride is made by each state or water authority.

<sup>†</sup> We previously met adsorption of impurities on to a precipitate in the sulfate analysis of Section 6.16. There it was a problem because it caused an error in our analysis; here the same adsorption is of great benefit to us.



**FIGURE 8.4**  
A flowchart for a water treatment plant

## How effective?

Like many other human enterprises, water treatment is a balance between cost and quality of the finished product. Sand filtration removes a high proportion of the particulate matter in the water after flocculation, but not the extremely small particles; and it is sufficiently fast to produce the volume of treated water that a big city needs. In addition chlorination is a cost-effective way of removing most disease-causing agents.

However as the *Giardia* and *Cryptosporidium* scare in the Sydney region in mid-1998 showed (when householders were advised to boil all water for human consumption because of fears that small amounts of these harmful parasites might have been present), there can be situations when sand filtration and chlorination are not adequate for removing such organisms. Use of membrane filters (Section 8.14) and/or ozone sterilisation would probably remove these parasites but at considerably increased costs. The present treatment methods coupled with better catchment management may be the more cost-effective approach.

## FOR INVESTIGATION

Prepare a report on your local city or town water supply. Include a map of the catchment and identify any likely sources of contamination in the catchment. Describe the purification processes used and list any additives that are put in the water and the reasons for adding them. Describe the testing that is done to monitor water quality, and assess the overall effectiveness of the purification and testing procedures. Include some comparisons of the quality of your town water with accepted national standards.



## Exercises

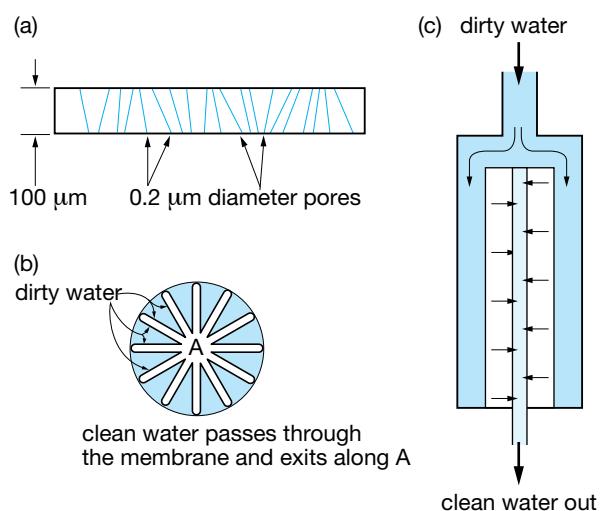
- 25 a** Write an equation for the formation of iron(III) hydroxide when iron(III) chloride is added to slightly alkaline water.
- b** Aluminium hydroxide is often used as a flocculating agent instead of iron(III) hydroxide. Write an equation for the formation of aluminium hydroxide.
- c** Why are aluminium and iron(III) hydroxides used in water clarification and not hydroxides of copper, zinc or magnesium?
- \*26** A first step in clarifying water by flocculation is to adjust the pH to above 7 before adding iron(III) chloride. Providing that the correct amount of iron(III) chloride is added, why is there no need to re-adjust the pH of the water after flocculation and filtration?



## 8.14 MEMBRANE FILTERS

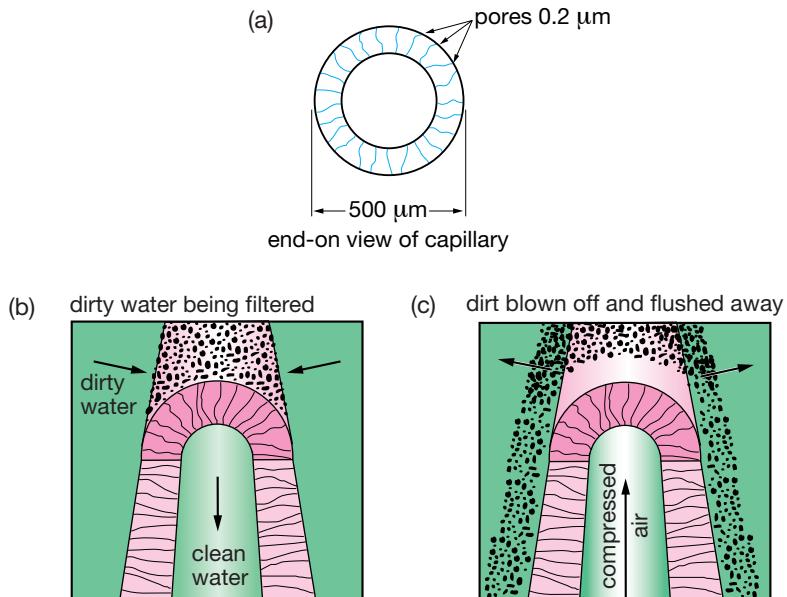
A **membrane filter** is essentially a thin film of a synthetic polymer through which there are pores (small holes) of fairly uniform size. This is shown schematically in Figure 8.5(a). Polymers that are commonly used are polypropylene, polytetrafluoroethylene and polysulphone. The simplest type of membrane filter is just a sheet of porous polymer that is pleated (folded) around a central rigid porous core and held in place with a surrounding mesh as in Figure 8.5(b). This filter cartridge is placed in a suitable housing (c) mounted in the water pipe and filters the water as it flows through it.

FIGURE 8.5  
A membrane filter: (a) the thin sheet of polymer with small pores through it; (b) the way a sheet is folded (pleated) to make a filter cartridge; (c) a cartridge in operation



Another type of membrane filter has the porous material made into hollow capillaries with an outside diameter of about 500 μm, inside diameter about 200 μm and a pore size of 0.2 to 0.5 μm, shown in cross-section in Figure 8.6(a); these are commonly called *hollow fibre* membrane filters. For each capillary dirty water flows from the outside through the wall of the capillary and clean water comes out of the inside as in Figure 8.6(b). Large numbers of such capillaries are bundled together to make a filtering unit with a very large surface area.

FIGURE 8.6  
(a) Cross-section of a hollow fibre (capillary) membrane filter; (b) how one capillary works; (c) backflushing (cleaning) a capillary



Many membrane filters, particularly hollow fibre ones, can be cleaned by blowing air from the clean side to dislodge trapped particles which are then washed away by the dirty water on the outside as shown in Figure 8.6(c). Figure 8.7 shows a bundle of such capillaries assembled into a filtering unit.



FIGURE 8.7  
Capillary membrane filters are bundled together parallel to one another as in the white cylinder in the middle of the photo; at the top left is a bundle that has been 'let loose' to show individual capillaries. The bundle is mounted in a housing that allows dirty water (under pressure) to pass over the outer surfaces of the capillaries; clean water flows through the walls of the capillaries as in Figure 8.6 and is collected from both ends

## Membrane filters compared with 'ordinary' filters

'Ordinary' filters such as (home or laboratory) filter papers or coarse sand filters (home swimming pools or water processing plants) consist of coarse material—fibres in filter papers, granules in sand filters—packed into a relatively thick bed. As the suspension seeps through this bed, big particles get trapped in it while small ones pass through. Such filters are called *depth filters*. A membrane filter consists of a solid film through which uniformly sized holes have been punched. Membrane filters are much thinner than depth filters and have a sharp cut-off in terms of diameter of particle they will let through—the diameter of the hole. While depth filters often have size ratings, stating the maximum size of particle they will let through, there is no sharp cut-off as is the case of membrane filters. Solutions pass through the thinner membrane filters much more quickly than through depth filters. Applying high pressure to depth filters is generally not effective, because it just pushes bigger particles through the matted filter material: high pressures can be used with membrane filters to speed up filtration, because the definite-sized holes do not let bigger particles through.

## Advantages

The advantages of membrane filters are:

- they can filter out much smaller particles than paper or sand filters can
- they filter out virtually all particles larger than their specified pore sizes

- they are quite thin and so liquids flow through them fairly rapidly
- they are reasonably strong and so can withstand pressure differences across them of typically 2 to 5 times atmospheric pressure
- they can be cleaned (back-flushed) and reused.

Membrane filters are widely used for filtering both drinking water and treated sewage (for reuse), though the latter not to any significant extent by public authorities in Australia. For drinking water, membrane filters can remove virtually all particles larger than  $0.2\text{ }\mu\text{m}$  including *Giardia* and *Cryptosporidium*.<sup>†</sup> Because of the relatively high quality of the raw water available for domestic use in the Sydney area, membrane filtration is currently considered too expensive for the relatively small improvement in water quality that it would provide.

It is impractical to use membrane filters to process untreated sewage, because it contains so much suspended matter that the filter pores would become clogged far too quickly. Before Sydney can consider using membrane filters to clean up sewage so the water can be re-used, good quality secondary treatment plants need to be added to the simple primary treatment plants that are currently used at the ocean outfalls (Manly, Bondi and Malabar). Membrane filtration is an effective form of tertiary treatment when it is desired to reuse the water for industry or for limited domestic purposes or before discharging the water into a river that is used by towns further downstream. Membrane filtration is widely used in industry, particularly for beverage preparation. Most bottled drinking water has been purified by passing it through a membrane filter. Membrane filters are used as a final stage in purifying recycled water at Olympic Park and the adjacent suburb of Newington in Sydney.

Although membrane filters can remove quite small suspended particles, typically ones larger than  $0.2\text{ }\mu\text{m}$  ( $= 200\text{ nm}$ ), they cannot remove substances that are actually dissolved in the water, because ions and other dissolved solids have diameters in the order of tens of nm, so they pass easily pass through membrane filters. This means that such filters cannot remove nitrate or phosphate or heavy metal ions from water.

An industrial scale capillary membrane filter plant similar to the one at Olympic Park in Sydney. The vertical grey cylinders in the middle left of the photo are the filter elements (shown in the foreground of Fig. 8.7)



<sup>†</sup> In Australia most water authorities ‘eliminate’ these parasites first by trying to keep them out of the storage dam, then if they are present, by drawing water from locations and depths in the dam where their concentrations are minimal. Sand filtration does remove some of these organisms.

## Important new terms

You should know the meaning of the following terms:

algal bloom (p. 263)  
biochemical oxygen demand (BOD) (p. 271)  
catchment (p. 289)  
coagulation (p. 290)  
electrolysis (p. 272)  
eutrophication (p. 287)  
flocculation (p. 290)

hard water (p. 263)  
heavy metals (p. 282)  
leaching (p. 284)  
membrane filter (p. 292)  
salinity (p. 268)  
secchi disc (p. 266)  
soft water (p. 263)  
total dissolved solids (TDS) (p. 267)  
turbidity (p. 266)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 List eight properties (criteria) that are used to assess water quality.
- 3 How would you measure the pH of water in a creek? If the water is environmentally clean, in what range should the pH lie?
- 4 How would you measure the turbidity of a sample of water? What does turbidity tell you about the water?
- 5 Describe two methods of determining **a** the total dissolved solids and **b** the concentration of dissolved oxygen in a sample of river water. For each property what are the advantages and disadvantages of each method? What range of values would you expect for each property for relatively clean environmental water?
- 6 Explain how you would measure the biochemical oxygen demand of a sample of river water. Why is such a measurement useful?
- 7 Why are we interested in the ‘hardness’ of water? How is hardness measured and in what form is it reported?
- 8 What are the two most abundant anions present in water in the environment? What three other anions are present in small but significant amounts? How would you test qualitatively for the two most abundant ones? How would you ensure that carbonate did not interfere with these tests?
- 9 Explain how you would test for the presence of **a**  $\text{Cu}^{2+}$  (as distinct from  $\text{Fe}^{3+}$ ) and **b**  $\text{Zn}^{2+}$  (as distinct from  $\text{Pb}^{2+}$ ) in separate samples of water.
- 10 Describe a test you could perform to determine whether there were any heavy metals in a water sample.
- 11 List five factors that affect the concentrations of ions in water bodies.
- 12 What four conditions are needed for an algal bloom to occur? What are the detrimental effects of algal blooms?
- 13 Explain how algal blooms form.
- 14 What procedures do most Australian cities follow in order to supply good quality tap water to their citizens? Explain how these procedures eliminate particular undesirable impurities.

- 15** Assess the effectiveness of the procedures in the previous question for supplying safe and high quality drinking water.
- 16** Describe the nature of membrane filters and list their advantages over paper or sand filters. Give several common uses of membrane filters.

# EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 3

MODULE  
**3**

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 Assess the importance of collaboration among chemists as they collect and analyse information in order to solve problems in the everyday world.   | 3     |
| 2 Explain why ozone in the stratosphere is beneficial to humans while ozone in the lower atmosphere is a problem for us.  | 3     |
| 3 Outline the process used for the industrial synthesis of ammonia. List three or four factors the designers and operators of the plant would need to consider to produce significant quantities of ammonia as cheaply as possible. | 8     |
| 4 Evaluate the usefulness of flame tests for identifying elements in samples.   | 4     |
| 5 Describe experiments (both qualitative and quantitative) that you have performed to assess the quality of different water samples.  | 7     |
| 6 Evaluate the work of Fritz Haber and Carl Bosch in developing an industrial process for the synthesis of ammonia, both at the time they did it and over the next 100 years.   | 4     |
| 7 Compare the physical properties and general chemical reactivity of ozone and molecular oxygen. Interpret the difference in terms of molecular structure.  | 5     |
| 8 Assess the impact of atomic absorption spectroscopy upon the study of trace elements in biological systems.   | 4     |
| 9 Describe a chemical process in which different products are formed when different experimental conditions are used. Outline how you would ensure that the process formed the maximum amount of desired product.                   | 5     |
| 10 Explain why the water supplies in different towns often contain different concentrations of ions such as $Mg^{2+}$ , $Ca^{2+}$ , $Na^+$ , $Cl^-$ , $SO_4^{2-}$ and $HCO_3^-$ .   | 4     |
| 11 Identify five major air pollutants and their main sources.   | 5     |
| 12 Compare the structures of membrane filters and ordinary filters (such as filter paper) and identify two advantages of membrane filters.  | 5     |
| 13 Assess the success of international agreements that aim at reducing concentrations of chlorofluorocarbons (CFCs) in the atmosphere.  | 4     |
| 14 Evaluate the effectiveness of monitoring phosphate concentration in a water body as a method of predicting the likelihood of an algal bloom.   | 3     |
| 15 Explain how chlorofluorocarbons (CFCs) have a detrimental effect upon ozone concentrations in the stratosphere, particularly over the Antarctic in spring.   | 7     |

- 16** Assess the effectiveness of procedures used to clarify and sanitise your local town water supply. **5**
- 17** Outline the benefits and shortcomings of Le Chatelier's principle in predicting yields of chemical reactions, using the reaction between hydrogen and nitrogen as an example. **4**
- 18** Evaluate the effectiveness of current methods of monitoring the so-called ozone hole. **4**
- 19** Explain why in atomic absorption spectroscopy **a** a different lamp is used for each element to be analysed, and **b** the technique only provides an estimate of the amount (concentration) of a particular element in the sample but no information about the compound the element is present in. **4**
- 20** In recent years chlorofluorocarbons (CFCs) have been replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Evaluate the effectiveness of these substitutions for minimising damage to the ozone layer in the stratosphere. **5**

# REVISION TEST FOR MODULE 3

MODULE  
**3**

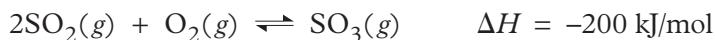
**Total marks: 50 Suggested time: 90 minutes**

The table of solubility data inside the back cover of this book may be used if needed.

## MULTIPLE CHOICE QUESTIONS (1 mark each)

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

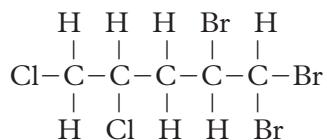
- 1** The equilibrium reaction:



is an important step in the industrial synthesis of sulfuric acid. One way of increasing the percentage conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is to:

- a** increase the temperature
- b** lower the total pressure
- c** increase the concentration of  $\text{O}_2$  in the reaction mixture
- d** add a high pressure of  $\text{N}_2$  to the reaction mixture

- 2** The correct name for the compound having the structure



is:

- a** 4,5-dichloro-1,1,2-tribromopentane
  - b** 4,4,5-tribromo-1,2-dichloropentane
  - c** 1,1,2-tribromo-4,5-dichloropentane
  - d** 1,2-dichloro-4,4,5-tribromopentane
- 3** The table below shows the results of some tests performed on environmentally clean water and on two samples of polluted water.

	Clean water	Sample P	Sample Q
dissolved oxygen (ppm)	9.0	2.8	8.5
total dissolved solids (ppm)	50	340	650
micro-organisms (CFU/100 mL <sup>a</sup> )	2	350	5
phosphate (ppm)	0.02	2.0	0.55

*a CFU = colony forming units*

The most likely sources of the pollution in the two samples are:

- a** land-clearing for P and a spill from a mine-site for Q
  - b** grazing land run-off for P and factory discharges for Q
  - c** treated sewage for P and cotton-field run-off for Q
  - d** raw sewage for P and farmland erosion for Q
- 4** When excess barium chloride solution was added to a solution made by dissolving 2.51 g of commercial lawn food in 250 mL water, 1.03 g barium sulfate was formed. The percentage sulfate in the lawn food is:

- a** 10.0%      **c** 24.1%  
**b** 16.9%      **d** 41.0%
- 5** Of the species,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{Ag}(\text{NH}_3)_2^+$ , the one that does *not* involve a coordinate covalent bond is:
- a**  $\text{O}_2$       **c**  $\text{Ag}(\text{NH}_3)_2^+$   
**b**  $\text{CO}$       **d**  $\text{N}_2\text{O}$
- 6** A sample of water known to contain only *one* of the cations  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  was divided into three portions for testing with solutions of hydrochloric acid, sulfuric acid and sodium hydroxide respectively. A precipitate was formed in each case. The cation present in the solution is:
- a**  $\text{Pb}^{2+}$       **c**  $\text{Cu}^{2+}$   
**b**  $\text{Ba}^{2+}$       **d**  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$
- 7** In the Haber process for synthesising ammonia an iron catalyst (reduced magnetite) is used because:
- a** it moves the equilibrium in the desired direction  
**b** it decreases the formation of unwanted by-products  
**c** it removes unwanted oxygen and so prevents a hydrogen–oxygen explosion  
**d** it allows a lower temperature to be used for the process
- 8** The table below compares some measurements on the air from three polluted areas with those of clean air.

	Clean air	Sample L	Sample M	Sample N
Hydrocarbons (ppm)	0.1	0.05	2.6	1.8
$\text{NO}_x$ (ppm)	0.01	0.3	0.4	0.12
CO (ppm)	0.5	1	3	10
$\text{SO}_2$ (ppm)	0.02	0.2	0.15	0.03
particles ( $\mu\text{g}/\text{m}^3$ )	20	200	350	80

- The most likely causes of the pollution are:
- a** L from motor cars, M from heavy industry and N from electricity generation  
**b** L from mining, M from dust storms and N from heavy industry  
**c** L from electricity generation, M from heavy industry and N from motor cars  
**d** L from motor cars, M from mining and N from electricity generation
- 9** Of the compounds,  $\text{CCl}_2\text{F}_2$ ,  $\text{CH}_3-\text{CCl}_3$ ,  $\text{CH}_2\text{F}-\text{CF}_3$ ,  $\text{CBrClF}_2$ ,  $\text{CF}_3-\text{CHCl}_2$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CCl}_4$ ,  $\text{CF}_3-\text{CF}_3$  the ones that have no detrimental effect upon the stratosphere are:
- a**  $\text{CH}_2\text{F}-\text{CF}_3$  and  $\text{CH}_2\text{F}_2$   
**b**  $\text{CH}_2\text{F}-\text{CF}_3$ ,  $\text{CH}_2\text{F}_2$  and  $\text{CF}_3-\text{CF}_3$   
**c**  $\text{CH}_3-\text{CCl}_3$ ,  $\text{CH}_2\text{F}-\text{CF}_3$ ,  $\text{CF}_3-\text{CHCl}_2$ ,  $\text{CH}_2\text{F}_2$   
**d**  $\text{CBrClF}_2$ ,  $\text{CCl}_4$
- 10** A simple way of detecting ozone in polluted air is to bubble the air through a potassium iodide solution. Ozone oxidises colourless iodide to yellow-brown iodine. The correct equation for this reaction is:

- a**  $2\text{O}_3(g) + 2\text{I}^-(aq) \rightarrow \text{I}_2(aq) + 3\text{O}_2(g)$
- b**  $\text{O}_3(g) + 2\text{I}^-(aq) + 3\text{H}^+(aq) \rightarrow \text{I}_2(aq) + 3\text{OH}^-(aq)$
- c**  $\text{O}_3(g) + 2\text{I}^-(aq) + 2\text{H}^+(aq) \rightarrow \text{I}_2(aq) + \text{H}_2\text{O}(l) + \text{O}_2(g)$
- d**  $\text{O}_3(g) + 2\text{I}^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{I}_2(aq) + 3\text{OH}^-(aq)$

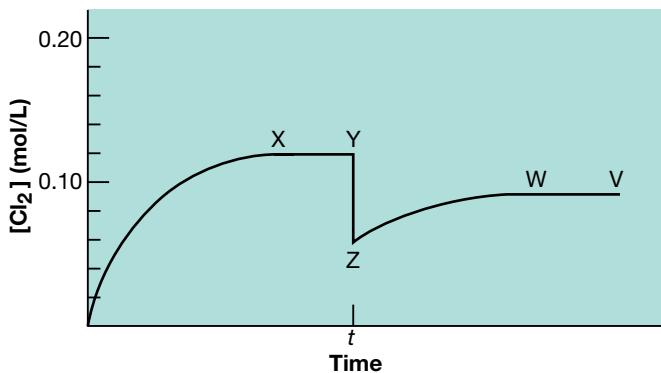
### SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

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    |
|---|----------|
| <b>11</b> Ammonia is synthesised industrially by passing a stoichiometric mixture of $\text{N}_2$ and $\text{H}_2$ over a catalyst at a pressure of about $2.5 \times 10^4 \text{ kPa}$ and a temperature of $400^\circ\text{C}$ .                            |          |
| <b>a</b> Write a balanced equation for the reaction and name the catalyst used.   | <b>1</b> |
| <b>b</b> Explain why:   |          |
| <i>i</i> a high pressure is used  |          |
| <i>ii</i> a significantly higher or lower temperature is <i>not</i> used  | <b>2</b> |
| <b>c</b> Explain how <i>all</i> of the reactant mixture is eventually converted to ammonia, even though at equilibrium there is only a 40% conversion of reactants to ammonia.  | <b>1</b> |
| <b>12</b> <b>a</b> Draw electron dot structures for an oxygen atom and for an ozone molecule.   | <b>1</b> |
| <b>b</b> Explain how ozone is produced in photochemical smog.   | <b>2</b> |
| <b>13</b> Describe, with at least one chemical equation, an experiment you have performed to measure the sulfate content in a lawn fertiliser. Identify several possible sources of error in your experiment and outline the steps you took to minimise them. | <b>7</b> |
| <b>14</b> Gaseous phosphorous pentachloride decomposes at elevated temperatures to phosphorous trichloride and chlorine:  |          |



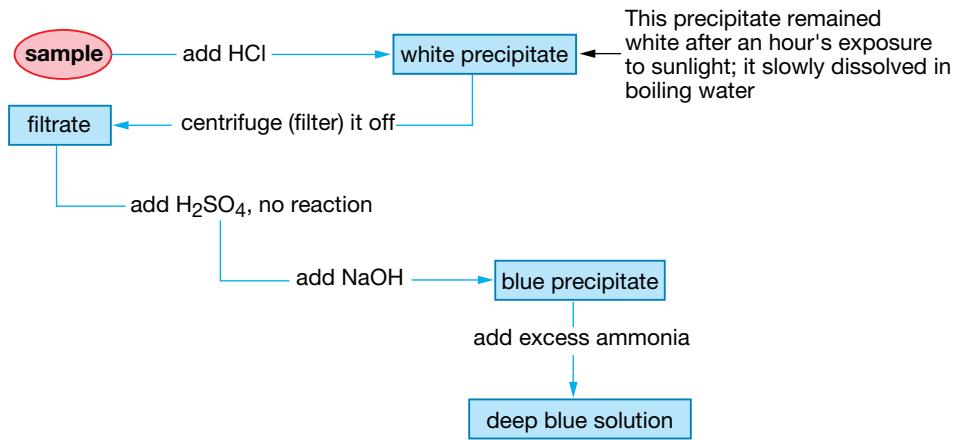
At a fixed temperature 0.020 mol  $\text{PCl}_5$  was placed in a large syringe with the volume adjusted to 0.100 L. The concentration of chlorine as a function of time is shown in the diagram. At time  $t$ , the volume available to the gas mixture was suddenly increased to 0.200 L. The diagram shows the variation in chlorine concentration at and also after that time.



- a** Explain why the chlorine concentration remained constant from X to Y and why it did not get to 0.20 mol/L.

- b Why did the concentration decrease suddenly to Z (at time  $t$ )?
  - c Why did the concentration of chlorine increase from Z to W and why did it remain constant from W to V?
  - d Suppose that the volume had been decreased to 0.050 L at time  $t$  (instead of being increased). Copy the diagram from time zero to  $t$  into your workbook then sketch the curve you would have expected for chlorine concentration after point Y.
  - e On the diagram you drew in (d), draw the curve for concentration of chlorine that you would have expected if a catalyst had been used.
- 4

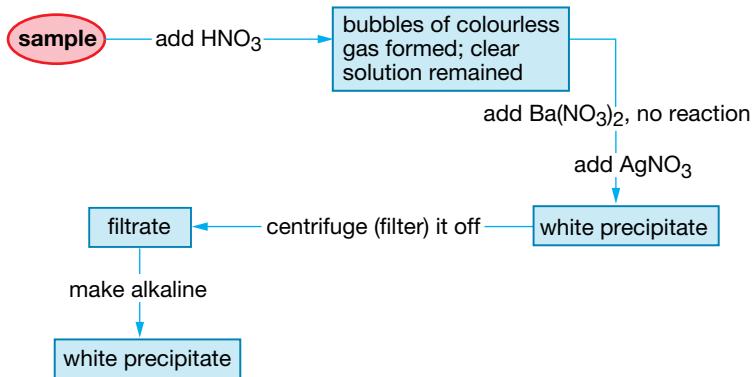
- 15 a** In order to determine the cation(s) present in a solution a chemist performed the tests in the following chart.



What cation(s) is(are) present in the solution? Write chemical equations for two of the reactions involved in this analysis.

3

- b Our chemist then determined the anion(s) present in a second sample by performing the tests in the next chart.



What anion(s) is(are) present in the solution? Explain your reasoning.

3

- 16 a** Describe the effect chlorofluorocarbons (CFCs) are having on stratospheric ozone. Write equations for all important chemical reactions that you mention, and include explanations for the facts that:
- i quite small amounts of CFCs can have very large effects
  - ii CFCs have this effect while many other halogenated compounds do not

- |     |   |   |
|-----|---|---|
| iii | the problem is most severe over the Antarctic and in spring   | 6 |
| b   | Assess the effectiveness of the way that the world is trying to solve this problem.   | 3 |
| 17  | List six properties (or criteria), excluding temperature and pH, that are used to assess the quality of water in the environment. For <i>four</i> of these outline how various forms of pollution cause values to be different from those of environmentally clean water. | 7 |

# MODULE 3 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 3 of the New South Wales Higher School Certificate HSC Course.

## Syllabus content

The following table lists (for Module 3) 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 3

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.4.1 Much of the work of chemists involves monitoring the reactants and products of reactions and managing reaction conditions</b>	
■ outline the role of a chemist employed in a named industry or enterprise, identifying the branch of chemistry undertaken by the chemist and explaining a chemical principle that the chemist uses	6.1, 6.2
■ identify the need for collaboration between chemists as they collect and analyse data	6.4
■ describe an example of a chemical reaction such as combustion, where reactants form different products under different conditions and thus would need monitoring	6.5
<b>9.4.2 Chemical processes in industry require monitoring and management to maximise production</b>	
■ identify and describe the industrial uses of ammonia	6.6
■ identify that ammonia can be synthesised from its component gases, nitrogen and hydrogen	6.7
■ describe that synthesis of ammonia occurs as a reversible reaction that will reach equilibrium	6.7
■ identify the reaction of hydrogen with nitrogen as exothermic	6.7
■ explain why the rate of reaction is increased by higher temperatures	6.7
■ explain why the yield of product in the Haber process is reduced at higher temperatures using Le Chatelier's principle	6.7
■ explain why the Haber process is based on a delicate balancing act involving reaction energy, reaction rate and equilibrium	6.7
■ explain that the use of a catalyst will lower the reaction temperature required and identify the catalyst(s) used in the Haber process	6.7
■ analyse the impact of increased pressure on the system involved in the Haber process	6.7

Syllabus reference Students learn to	Sections where found in CCHSC
■ explain why monitoring of the reaction vessel used in the Haber process is crucial and discuss the monitoring required	6.7
<b>9.4.3 Manufactured products, including food, drugs and household chemicals, are analysed to determine or ensure their chemical composition</b>	
■ deduce the ions present in a sample from the results of tests	6.8 to 6.14
■ describe the use of atomic absorption spectroscopy (AAS) in detecting concentrations of metal ions in solutions and assess its impact on scientific understanding of the effects of trace elements	6.18, 6.19
<b>9.4.4 Human activity has caused changes in the composition and the structure of the atmosphere. Chemists monitor these changes so that further damage can be limited</b>	
■ describe the composition and layered structure of the atmosphere	7.1, 7.2
■ identify the main pollutants found in the lower atmosphere and their sources	7.3
■ describe ozone as a molecule able to act both as an upper atmosphere UV radiation shield and as a lower atmosphere pollutant	7.4, 7.5
■ describe the formation of a coordinate covalent bond	7.6
■ demonstrate the formation of coordinate covalent bonds using Lewis electron dot structures	7.6
■ compare the properties of the oxygen allotropes O <sub>2</sub> and O <sub>3</sub> and account for them on the basis of molecular structure and bonding	7.7
■ compare the properties of the gaseous forms of oxygen and the oxygen free radical	7.8
■ identify the origins of chlorofluorocarbons (CFCs) and halons in the atmosphere	7.10
■ identify and name examples of isomers (excluding geometrical and optical) of haloalkanes up to eight carbon atoms	7.10
■ discuss the problems associated with the use of CFCs and assess the effectiveness of steps taken to alleviate these problems	7.9, 7.11 to 7.13
■ analyse the information available that indicates changes in atmospheric ozone concentrations, describe the changes observed and explain how this information was obtained	7.14
<b>9.4.5 Human activity also impacts on waterways. Chemical monitoring and management assists in providing safe water for human use and to protect the habitats of other organisms</b>	
■ identify that water quality can be determined by considering: <ul style="list-style-type: none"> <li>– concentrations of common ions</li> <li>– total dissolved solids</li> <li>– hardness</li> <li>– turbidity</li> <li>– acidity</li> <li>– dissolved oxygen and biochemical oxygen demand</li> </ul>	8.1 to 8.10

■ identify factors that affect the concentrations of a range of ions in solution in natural bodies of water such as rivers and oceans	8.11
■ describe and assess the effectiveness of methods used to purify and sanitise mass water supplies	8.13
■ describe the design and composition of microscopic membrane filters and explain how they purify contaminated water	8.14

## 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 3

Experiment	Location in CCHSC BLM	Related material in CCHSC <sup>a</sup>
1 Perform tests, including flame tests, to identify a range of cations and anions.	Module 3 Worksheets 2 and 3 (pp. 120 and 125)	Sections 6.9 to 6.14 Chapter 6 Exercises 9 to 26 interpret results from these tests
2 Measure the sulfate content of a lawn fertiliser.	Module 3 Worksheet 5 (p. 135)	Section 6.16 Chapter 6 Exercises 27 and 31 Revision Test Question 13
3 Perform qualitative and quantitative tests to analyse and compare the quality of water samples.	Module 3 Worksheets 9 and 10 (pp. 144 and 150)	Sections 8.2 to 8.10 Chapter 8 Exercises 3 to 20 interpret or calculate results from these tests Exam-style Question 5

<sup>a</sup> 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 3 activities

Syllabus item	Relevant material in CCHSC
<b>9.4.1</b> ■ gather, process and present information ... about the work of practising scientists ...	Sections 6.2 and 6.3
<b>9.4.2</b> ■ gather ... information ... to describe the conditions under which Haber developed the industrial synthesis of ammonia and evaluate its significance ...	First paragraph in Section 6.7 gives a start for this
<b>9.4.3</b> ■ Experiment 1 (see previous table)	
■ gather ... information to describe and explain evidence for the need to monitor levels of one of the above ions ...	Section 6.15
■ Experiment 2 (see previous table)	
■ analyse information to evaluate the reliability of the results ... and to propose solutions to problems ...	Section 6.16 Revision Test Question 13
■ gather ... information to interpret ... AAS measurements and evaluate the effectiveness of this in pollution control	Uses and Example 2 in Section 6.18
<b>9.4.4</b> ■ present information ... to write the equations ... involving CFCs ... to demonstrate the removal of ozone from the atmosphere	Sections 7.11 and 7.12
■ gather ... information ... including simulations, molecular model kits or ... to model isomers of haloalkanes	Figure 7.5 shows photos of some molecular models
■ present information ... to identify alternative chemicals used to replace CFCs and evaluate the effectiveness of their use ...	Section 7.13
<b>9.4.5</b> ■ Experiment 3 (see previous table)	
■ gather ... information on the range and chemistry of the tests used to:	Sections 8.10 and 8.12
– identify heavy metal pollution ... – monitor possible eutrophication ...	
■ gather ... information on the features of the local town water supply in terms of ...	Section 8.13 and the For investigation box in that section

## Prescribed focus areas

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

As with most modules, the material of Module 3 (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. This module has a strong emphasis on applications and use, ranging from the application of chemical principles to the industrial synthesis of ammonia to the use of a wide range of chemical tests for assessing water quality.

However Module 3, with its emphasis on air and water pollution, also relates strongly to area 4, implications for society and the environment. Problems such as the ozone hole and pollution of urban atmospheres should grab students'

attention and interest, particularly as they have enough background knowledge to be able to understand the chemistry involved in these problems. General societal concerns about water quality should stimulate students to delve into the questions of water pollution and why our water bodies are under such threat. Salinity is such a topical and urgent issue nationally that a short section on it is included (though it is on the margins of the syllabus).

Much of the air and water pollution material that supports area 4 can also, with a slightly different emphasis, provide opportunities to develop area 5, current issues, research and development, particularly the current issues aspect.

There is not much scope for involving area 1, the history of chemistry, in this module, apart from the historical consequences of the development of the Haber process in Germany just before World War I and possibly the story of Alan Walsh's development of atomic absorption spectroscopy.