

Chapter

ENVIRONMENTAL 7 POLLUTION AND ACIDITY



Figure 7.1

A lightning strike causes chemical changes in the atmosphere. Ozone is formed from oxygen, and nitrogen and oxygen combine to form nitrogen oxides. Some nitrogen oxides are acidic.

Introduction

Before the seventeenth century, the cause of acidity was not properly understood. Antoine Lavoisier undertook a series of experiments with various oxides of non-metals. These experiments led him to believe that acidity was caused by the presence of the element oxygen in a compound. In this chapter we examine acid–base chemistry in the context of oxides in the environment.

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7.1 OXIDES AND ACID RAIN

Remember

Before beginning this section, you should be able to:

- classify common substances as acidic, basic or neutral
- construct word and balanced formulae equations of chemical reactions.

Key content

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

- identify oxides of non-metals which act as acids, and describe the conditions under which they act as acids
- analyse the position of these non-metals in the periodic table and outline the relationship between position of elements in the periodic table and acidity/basicity of oxides
- identify natural and industrial sources of sulfur dioxide and oxides of nitrogen
- describe, using equations, examples of chemical reactions that release sulfur dioxide, and chemical reactions that release oxides of nitrogen
- assess the evidence that indicates increases in atmospheric concentrations of oxides of sulfur and nitrogen
- explain the formation and effects of acid rain
- analyse information from secondary sources to summarise the industrial origins of sulfur dioxide and oxides of nitrogen, and evaluate reasons for concern about their release into the environment.

Chlorine (VII) oxide is a colourless, oily liquid that is explosive. It reacts with water to form perchloric acid, which is a fuming, colourless liquid and one of the four strongest acids.

Acidity and basicity of oxides

Oxides are chemical compounds formed when an element reacts with oxygen.

In the school laboratory, a metal such as magnesium or a non-metal such as phosphorus can be burned in a gas jar of oxygen. The magnesium burns with a brilliant white flame to generate an oxide. In the case of magnesium a white powder is formed. This is magnesium oxide.



When red phosphorus is ignited in air or oxygen, it burns with a yellow flame to form a white smoke. Depending on the amount of oxygen present, oxides such as P_4O_6 (phosphorus (III) oxide) or P_4O_{10} (phosphorus (V) oxide) will form.



The acid–base properties of these oxides can be investigated using indicators. When magnesium oxide is added to water containing universal indicator the indicator changes from green to blue-violet. This shows that magnesium oxide is a basic oxide. This reaction occurs because of the presence of water. The magnesium oxide dissolves in the water to generate magnesium hydroxide. The hydroxide ions that are released cause the colour change of the indicator.

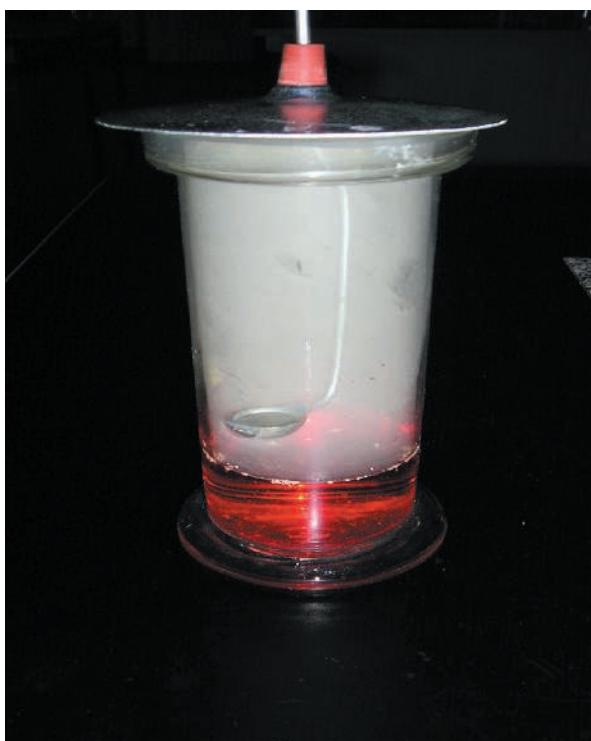


Figure 7.2

When sulfur burns in oxygen, sulfur dioxide is formed. The sulfur dioxide dissolves in water to produce an acidic solution as shown by the universal indicator turning red.

When the white oxides of phosphorus are dissolved in water containing universal indicator, the mixture turns from green to red. Thus phosphorus oxides are acidic. Once again the presence of water is essential. The phosphorus oxides partly dissolve in the warm water to produce phosphoric acid. This acid releases hydrogen ions that cause the change in colour of the indicator.

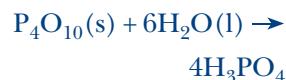


Figure 7.3

Phosphorus burns in oxygen and produces a white smoke. This smoke consists of solid particles of the oxides of phosphorus.



neutralisation: the reaction between an acid and a base to produce a new compound that usually has neither acidic nor basic properties

salt: the ionic compound formed when a base is neutralised by an acid

Some oxides, however, are not soluble in water, so indicators cannot be used to determine their acidity or basicity. In order to determine whether any oxide is acidic or basic we need to investigate whether it reacts with strong acids such as hydrochloric acid or strong bases such as sodium hydroxide. The reaction that occurs is classified as a **neutralisation** reaction. In the process of neutralisation the acidic and basic properties are destroyed and a new compound called a '**salt**' is formed.

Neutralisation



SYLLABUS FOCUS

15. NOMENCLATURE OF SALTS

The ionic compound that forms when a base is neutralised by an acid is commonly called a salt. Sodium chloride is such an example. It forms when sodium hydroxide is neutralised by hydrochloric acid. Salts are named after their parent acid, as shown in the table below. The metal ion of the base is named first, followed by the name of the anion of the parent acid.

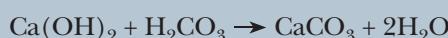
Parent acid	Name of salt anion
hydrochloric acid	chloride
sulfuric acid	sulfate
nitric acid	nitrate
acetic acid	acetate
phosphoric acid	phosphate
carbonic acid	carbonate
nitrous acid	nitrite

Examples:

1. Barium hydroxide + phosphoric acid \rightarrow barium phosphate + water



2. Calcium hydroxide + carbonic acid \rightarrow calcium carbonate + water



Basic oxides

An oxide that dissolves and reacts with a strong acid is said to be a *basic oxide*.

Example:

Copper (II) oxide reacts and dissolves in hydrochloric acid to form copper (II) chloride and water. Copper (II) chloride is the salt.



Acidic oxides

An oxide that dissolves and reacts with a strong basic solution such as sodium hydroxide is said to be an *acidic oxide*.

Example:

Sulfur trioxide reacts with sodium hydroxide solution to form sodium sulfate and water. Sodium sulfate is the salt.



Amphoteric oxides

In some cases, the oxide reacts with both strong acids and strong bases. Such oxides are classified as *amphoteric*. Aluminium oxide is an example of an **amphoteric oxide**. It reacts with hydrochloric acid to produce aluminium chloride.



Aluminium oxide also reacts with sodium hydroxide solution to form sodium aluminate (NaAlO_2 or NaAl(OH)_4).



or,



Generalisations

The following generalisations can be made on the basis of the experiments described above.

- Most metallic oxides are basic oxides.
- Most non-metallic oxides are acidic oxides.
- Some oxides are neutral.
- Some oxides have both basic and acidic properties.

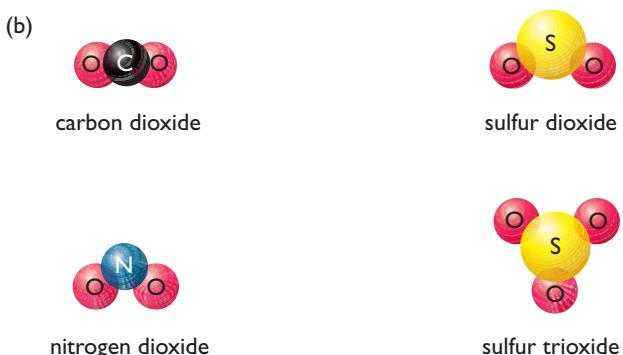
Table 7.1 shows some common examples of acidic, basic, amphoteric and neutral oxides.

Table 7.1 Oxides and their acidity

Acidic oxides	Basic oxides	Amphoteric oxides	Neutral oxides
Cl_2O_7	Na_2O	Al_2O_3	CO
SO_3	K_2O	ZnO	NO
SO_2	CaO	SnO	N_2O
NO_2	BaO	PbO	
CO_2	MgO	Sb_2O_3	



Figure 7.4
 (a) CO_2 molecule
 (b) Most non-metal oxides are acidic oxides.

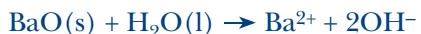


Oxides and the periodic table

The generalisations discussed previously allow us to demonstrate the trends in acidity and basicity of the oxides in the periodic table.

The metals of Groups I and II all form basic oxides. The basicity of these oxides increases down each group. Thus barium oxide is a stronger base than magnesium oxide.

Example:



Most non-metals (other than the noble gases) form acidic oxides. The acidity of these oxides decreases down each group as the elements become more metallic in character. In addition the non-metallic oxides with the highest oxidation states in the non-metal tend to be more acidic. Thus, sulfur trioxide (SO_3) is more acidic than sulfur dioxide (SO_2). Dichlorine heptoxide (Cl_2O_7) is more acidic than dichlorine oxide (Cl_2O).

Example:



SAMPLE PROBLEM 7.1

SOLUTION

When dichlorine heptoxide dissolves in water it reacts to form perchloric acid (HClO_4).

- Write a balanced equation for this reaction.
- Determine the oxidation state of the chlorine in this compound.



- (b) H has an oxidation state of +I and O has an oxidation state of -II.

Let the oxidation state of Cl = x .

Thus (+I) + (x) + 4(-II) = 0.

Thus $x = +\text{VII}$.

The oxidation state of chlorine is +VII.

Figure 7.5 is an outline diagram of the periodic table. This diagram shows the location of basic, acidic, amphoteric and neutral oxides. In many cases an element may have a basic or acidic or amphoteric oxide due to the *different oxidation states* of the element. Generally, the higher the oxidation state of the metal or semi-metal, the more amphoteric or acidic the oxide. The effect of differing oxidation states on the acidity of oxides makes it difficult to make generalisations and to discuss trends in acidity and basicity in the oxides of the elements of the periodic table.

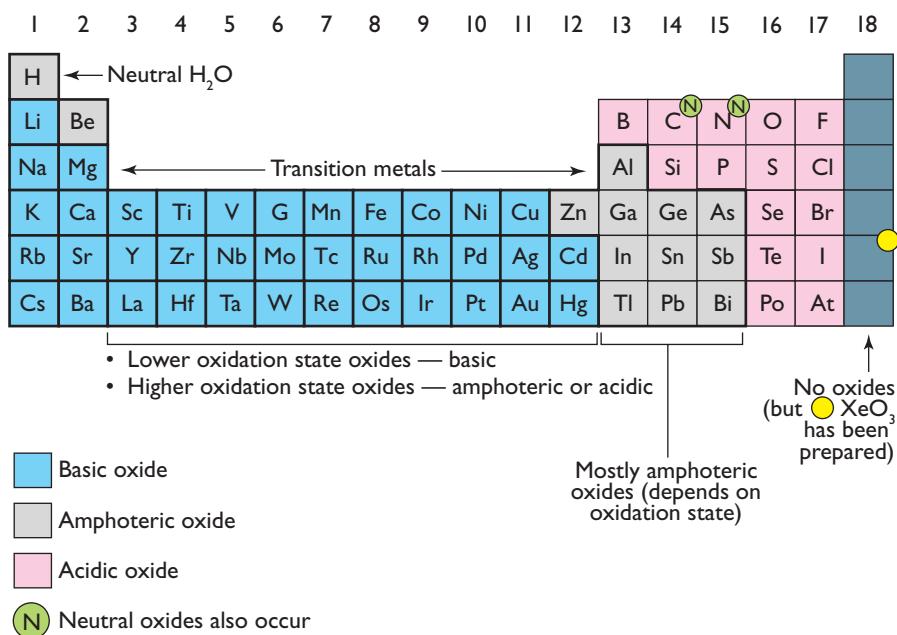


Figure 7.5

The periodic table shows that metallic oxides are mostly basic and that non-metallic oxides are mostly acidic. The elements with amphoteric oxides lie between these two groupings.

Table 7.2 Examples of transition metal oxides

Vanadium oxides	Chromium oxides	Manganese oxides
VO — basic	CrO — basic	MnO — basic
V_2O_3 — basic	Cr_2O_3 — amphoteric	MnO_2 — amphoteric
VO_2 — basic to amphoteric	CrO_3 — acidic	Mn_2O_7 — strongly acidic
V_2O_5 — amphoteric to acidic		

Table 7.3 Examples of the oxides of Groups III, IV and V

Group (III) oxides	Group (IV) oxides	Group (V) oxides
B_2O_3 — acidic	CO — neutral;	NO — neutral
Al_2O_3 — amphoteric	CO_2 — acidic	N_2O — neutral
Ga_2O_3 — amphoteric to basic	SiO_2 — weakly acidic	NO_2 — acidic
In_2O_3 — amphoteric to basic	GeO — basic to amphoteric	N_2O_5 — strongly acidic
Tl_2O_3 — amphoteric to basic	GeO_2 — amphoteric to slightly acidic	P_4O_6 — acidic
	SnO — amphoteric	P_4O_{10} — acidic
	SnO_2 — amphoteric	As_2O_3 — amphoteric
	PbO — basic to amphoteric	As_2O_5 — amphoteric to acidic
	PbO_2 — amphoteric	Sb_2O_3 — amphoteric
		Sb_2O_5 — amphoteric to acidic
		Bi_2O_3 — basic
		Bi_2O_5 — amphoteric to acidic

Note: Some oxides behave in different ways in different chemical environments so have more than one classification (such as amphoteric to basic).

Periods 2 and 3 (Figure 7.6) of the periodic table show interesting trends in the acid–base properties of the oxides. As we move from left to right the basicity of the oxides decreases until an amphoteric oxide is reached. Beryllium oxide and aluminium oxide are amphoteric. The oxides then show increasingly acidic properties as we move along each period to Group VII. This trend is readily related to the decreasing metallic character of the elements across each period. The trend is also related to the type of crystal lattice that each oxide forms. The basic oxides of period 3 (Na_2O and MgO) are ionic compounds. The aluminium oxide lattice is also ionic and the compound is quite insoluble in water. The silicon dioxide lattice is a giant covalent network, and this compound is also very insoluble in water. The remaining oxides all form covalent molecular lattices. These differences in bonding affect the behaviour of each oxide with water. The high solubility of sodium oxide allows the oxide ion to interact with the water and form hydroxide ions. Similarly, the high solubility of sulfur trioxide in water allows a chemical change to occur which leads to the formation of acidic hydrogen ions. The two oxides that are very insoluble in water (Al_2O_3 and SiO_2) exhibit their amphoteric and weakly acidic properties respectively, only in the presence of strong acids and bases.

Figure 7.6

From left to right, the basicity of the oxides decreases till an amphoteric oxide is reached; the acidity then increases.

	I	II	III	IV	V	VI	VII
Period 2	Li_2O Basic	BeO Amphoteric	B_2O_3 Weakly acidic	CO_2 Acidic	NO_2 Acidic	O_2 Neutral	F_2O Neutral
Period 3	Na_2O Strongly basic	MgO Basic	Al_2O_3 Amphoteric	SiO_2 Weakly acidic	P_4O_{10} Acidic	SO_3 Strongly acidic	Cl_2O_7 Very strongly acidic

Acidic oxides and pollution

Our atmosphere is a sink for many pollutants. Some of these pollutants are oxides. Volcanoes and geysers release many different gases into the atmosphere, including sulfur dioxide. Carbon monoxide, carbon dioxide and sulfur dioxide are also formed during the combustion of organic matter during bushfires. Bacterial decomposition can also release sulfur dioxide into the environment. Lightning storms produce toxic nitrogen oxides as nitrogen and oxygen molecules react together.

The activities of human beings result in the release of oxides into the atmosphere. Industries generate a variety of oxides such as carbon monoxide, carbon dioxide, sulfur dioxide and the oxides of nitrogen.

Oxides of carbon

The natural cellular respiratory processes of animals and plants produce carbon dioxide, which is ultimately released into the atmosphere. Green plants utilise the carbon dioxide for photosynthesis. Large amounts of carbon monoxide and carbon dioxide are also produced during bushfires. The process of incomplete combustion produces carbon monoxide, whereas carbon dioxide is the product of complete combustion. The combustion of fossil fuels such as petrol, kerosene and diesel oil releases large amounts of the carbon oxides into the atmosphere. Coal-fired power plants also release vast amounts of carbon oxides into the atmosphere. The increasing levels of carbon dioxide in the atmosphere are often linked to global warming. Carbon monoxide does not build up over time in the atmosphere as it is rapidly removed by the action of soil organisms or by oxidation to carbon dioxide.

Oxides of sulfur

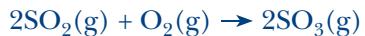
The oxides of sulfur are irritating, poisonous gases. These gases particularly affect people who suffer from respiratory problems such as asthma and emphysema. About 50% of the sulfur dioxide that enters our atmosphere is derived from the oxidation of hydrogen sulfide (H_2S) produced from bacterial decomposition. The remainder is produced by human activity. Sulfur dioxide is produced by the combustion of fuels such as coal and diesel oil. In Australia considerable quantities of coal are burnt to generate most of our electricity (~75%). Fossil fuels usually contain small quantities of sulfur minerals (e.g. FeS_2) although the bituminous coal from eastern NSW is lower in sulfide minerals (~0.3–1.0%) than coal from other locations. These sulfide minerals in coal are oxidised during combustion, and sulfur dioxide is released.



Metal smelters that convert sulfide minerals into metals are also a major source of sulfur dioxide pollution. For example, the smelting of chalcopyrite ($CuFeS_2$) during the production of copper results in the release of sulfur dioxide. Towns near these smelters can suffer from sulfur dioxide pollution. In regions such as the lower Hunter, about 95% of SO_2 emissions are associated with power and smelting industries.

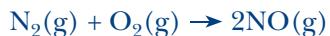


Sulfur trioxide is produced mainly by oxidation of sulfur dioxide in the atmosphere. Dioxygen and ozone are the oxidants involved in this oxidation process.

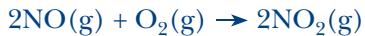


Oxides of nitrogen (NO_x)

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the most common atmospheric oxides of nitrogen found in urban air. They are collectively referred to as NO_x . In Sydney, about 86% of the total emissions of NO_x comes from the engines of motor vehicles and other transport. The nitric oxide (a colourless gas) is formed when nitrogen and oxygen react at high temperatures. Nitric oxide is a neutral oxide.



NO_2 is a brown gas and is produced by oxidation of NO . The rate of NO_2 formation depends on the concentration of NO in the air. Up to 10% of the total NO_x in air is NO_2 . Nitrogen dioxide is an acidic oxide.



NO_x is also derived from other sources, including industries, electrical power production and oil refining. NO_2 is of concern as it causes damage to the respiratory system of humans as well as irritating the eyes. Young children and older people are particularly susceptible. Un-flued gas heaters and kerosene heaters also contribute to NO_2 pollution of the air inside houses.

Monitoring SO₂ and NO₂ levels

During the industrial revolution of the 19th century, large amounts of coal were burnt to provide power for factories and their machines. Vast quantities of carbon dioxide and sulfur dioxide poured into the air. Iron smelters generated large volumes of sulfur dioxide as they produced the growing quantities of steel required for industry. The atmosphere of large industrialised cities in Europe and the USA became highly polluted with acidic gases. The increased use of motor vehicles in the 20th century (particularly after 1945) increased oil consumption. Emissions of sulfur dioxide doubled in the 25-year period following World War II. Adding to this pollution burden on the atmosphere was the increasing production of nitrogen oxides in internal combustion engines.

Following numerous deaths (about 4000) in London in 1952 due to heavy acidic smogs, pollution controls began to be introduced to clean up the air of these large cities. High levels of photochemical smog (produced by the action of sunlight on air containing moisture, ozone, hydrocarbons and NO_x) in cities such as Los Angeles and Tokyo in the 1960s accelerated the push for emission controls on motor vehicles. In the 1970s the development of more sensitive gas analysis technologies allowed chemists to monitor the global increase in sulfur dioxide emissions due to the expansion of industries in Asia.

In recent years the air quality has improved in most westernised countries. In Europe, the sulfur dioxide emissions dropped by about 45% in the 1990s. In the same period, nitrogen dioxide emissions dropped by about 20%. However, due to increasing population and usage of motor vehicles, the levels of pollutants have stabilised rather than continuing to decrease. The rapid industrialisation of Asia (particularly China) has led to huge increases in sulfur dioxide emissions. It is predicted that sulfur dioxide emissions in Asia will triple in the 20-year period from 1990.



Figure 7.7

The air in major cities is often highly polluted with particulates as well as acidic and toxic gases. Photochemical smog is a particular problem in large urbanised areas.

The Environmental Protection Agency of NSW (EPA) monitors the levels of pollutant gases in the atmosphere in many regions across NSW. The 2003 report reveals the following information.

- The peak 1-hour measurements of sulfur dioxide in Sydney air are now less than 25% of the National Environmental Protection Council (NEPC) standard (0.20 ppm).

- NO_2 concentrations have remained fairly stable over the last decade, with concentrations rarely above the NEPC 1-hour peak standard of 0.12 ppm. In Sydney, typical levels have been much lower than 0.08 ppm over the last decade. This compares favourably to the 1980s when the standard was exceeded over many days in the winter.

Table 7.4 shows EPA data for various suburbs of Sydney in winter (June 2005). The data shows how the heavy traffic in the central-west suburbs of Sydney contributes to NO_2 pollution.

Table 7.4 Maximum 1-hour levels of SO_2 and NO_2 in various monitoring sites in Sydney on 24 June 2005 (winter)

Monitoring site	Maximum 1-hour concentration of SO_2 (ppm)	Maximum 1-hour concentration of NO_2 (ppm)
Randwick (east)	0.06	0.13
Chullora (central west)	0.01	0.23
Richmond (north-west)	0	0.12
Bringelly (south west)	0.01	0.06

Source: <http://www2.nsw.epa.gov.au>

The NSW Department of Environment and Conservation prepares quarterly reports on air quality. The data in Table 7.5 compares information for June in the reports for the years 2000, 2002 and 2004. This data confirms that the air quality in Sydney with respect to SO_2 and NO_2 is high when compared with NEPC standards. The data shows no discernible trends overall across the 5-year period.

Table 7.5 Average SO_2 and NO_2 concentrations at various sites during June in 2000, 2002 and 2004 (1-hour averages)*

(a) Sulfur dioxide (NEPC standard = 0.20 ppm)			
Monitoring site	2000	2002	2004
Randwick (east)	0.04	0.02	0.08
Woolooware (south)	0.03	0.02	0.03
Richmond (north-west)	0.02	0.01	0.03
Bringelly (south-west)	0.01	0.02	0.01

(b) Nitrogen dioxide (NEPC standard = 0.12 ppm)			
Monitoring site	2000	2002	2004
Randwick (east)	0.032	0.030	0.031
Woolooware (south)	0.024	0.026	0.026
Richmond (north-west)	0.016	0.015	0.017
Bringelly (south-west)	0.016	0.016	0.016

* Source: Quarterly reports on air quality from the NSW Department of Environment and Conservation for June in 2000, 2002 and 2004

The air in Sydney compares favourably with that of much larger cities overseas. The large industrialised cities of China, the USA and Europe have much higher levels of atmospheric NO_2 and SO_2 than Sydney's. Peak 1-hour levels of NO_2 of 0.13 ppm to 0.46 ppm in London, and 0.24 ppm to 0.47 ppm

in Los Angeles, have been recorded. In most major centres in Europe and the USA the emission controls that have been instituted by government environmental agencies have improved air quality since the 1950s.

In order to reduce emissions of sulfur dioxide and nitrogen oxides there are a number of options available. These include:

- reducing the amount of coal being burnt—this can be achieved if people use appliances that are more energy-efficient; as individuals we can help by reducing our own personal use of electricity
- power companies burning low-sulfur coal rather than high-sulfur coal—they can also switch to natural gas, which produces very little sulfur dioxide on combustion
- reducing our reliance on fossil fuels—developing other forms of power production such as hydroelectricity and solar power
- collecting the sulfur dioxide produced by smelting metal sulfides and using it to make sulfuric acid
- reducing acidic emissions from smoke stacks by a process called ‘scrubbing’—the acidic gases are passed through a slurry of a base such as calcium oxide; the sulfur dioxide reacts with the calcium oxide to form solid calcium sulfite
- ensuring that exhausts from motor vehicles pass through a catalytic converter—nitrogen oxides are then converted back to nitrogen gas.



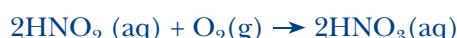
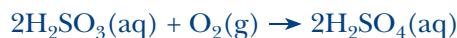
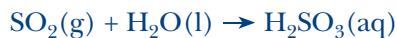
Acid rain

When all gases are removed from pure water, its pH is 7.0 (neutral) at 25°C. However, natural water contains dissolved gases including carbon dioxide, which makes the water weakly acidic (due to the presence of carbonic acid). This has a typical pH of 6.0–6.5.



When the atmosphere is polluted with acidic oxides such as sulfur dioxide and nitrogen dioxide, rainwater can become quite acidic (pH 4.0–5.0) due to the high solubility of these gases in water. Rain that has such a low pH is called **acid rain**. Acid rain with a pH of 3.6 has been recorded in many severely polluted industrialised areas in Europe and the USA. The term ‘acid rain’ comes from the title of a book published in 1872 by Angus Smith. Acid precipitation, however, had been observed in the seventeenth century and its causes related to industrial emissions.

When the oxides of sulfur and nitrogen dioxide dissolve in water they produce solutions of various acids. Sulfur dioxide forms weak sulfurous acid (H_2SO_3) whereas sulfur trioxide produces strong sulfuric acid (H_2SO_4). Sulfurous acid can be catalytically oxidised to produce sulfuric acid. Nitrogen dioxide produces weak nitrous acid (HNO_2) and strong nitric acid (HNO_3) when it dissolves in water. In the presence of water and oxygen the nitrous acid is catalytically oxidised to nitric acid.



acid rain: rain that has a pH lower than 5

Effects of acid rain

When you visit the ancient cities of Europe you may observe that many marble statues and building facades are eroded. Acid rain is partly responsible for this problem. When the calcium carbonate of the marble is attacked by the sulfuric acid in acid rain, the surface of the marble is converted into insoluble calcium sulfate.



The wet calcium sulfate crystallises to form a porous and crumbly mineral called gypsum (calcium sulfate dihydrate). Over several centuries the soot from coal burning, as well as various dusts, have collected in the pores of the gypsum and turned the marble black.

Acidic rain can also attack metallic structures composed of iron and steel. The iron is oxidised by the hydrogen ions in the acid and becomes chemically weathered.



Acid rain has had a devastating effect on many northern hemisphere forests. The famous Black Forest in Germany has been significantly damaged by acid rain. Pine needles lose their waxy coating and turn brown, and the trees become denuded of foliage. In the 1980s up to 50% of European forests had been affected by acid rain. The sugar maples of Quebec have also been damaged by acid rain that has formed due to sulfur dioxide emissions from the industrialised north-east of the USA.



Figure 7.8

Marble is a metamorphic form of limestone. It is attacked by acid rain, and the surface erodes.

Acid rain also affects the soil, and the acidified soils inhibit the growth of plant seedlings. Basic minerals in the soil (such as dolomite and limestone) are attacked and dissolved by acidic water. Many types of sandstone have grains that are cemented together with calcite (calcium carbonate). The acid rain will dissolve this cement and so cause significant chemical weathering and erosion.

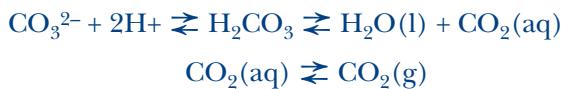


Figure 7.9

These pine trees in Europe have been damaged by acid rain, leading to a loss of foliage.

Mineral nutrients such as potassium, calcium and magnesium that are required for plant growth can be removed when acid rain soaks into the ground. Some insoluble minerals can also be dissolved by the acidified water and cause a release of toxic levels of metal ions. High levels of aluminium ions (formed when clay minerals are attacked by acid) in the soil interfere with normal mineral uptake by plant roots. Nitrogen fixing bacteria that are vital to a healthy soil are also affected by increasing acidification.

A 1997 study by high school students around the world showed that acid rain with a pH between 4 and 5 was most common in Eastern Europe, where there are fewer controls on sulfur dioxide emissions from industries. When acid rain drains into lakes, it can significantly acidify them. Scandinavian lakes have become acidified due to the sulfur dioxide emissions carried from the industrialised zones of Eastern Europe. As the lake water becomes more acidic the populations of aquatic organisms become stressed. The presence of acidic hydrogen ions interferes with the carbon dioxide/carbonate equilibrium in the water. The amount of dissolved carbon dioxide in the water drops as carbonate ions are removed. This leads to stresses on photosynthetic organisms.



Many aquatic invertebrates cannot reproduce in an acidic environment. Most fish eggs will not survive in water if the pH drops below 5.5. Below a pH of 5 adult fish will die as they cannot extract sufficient calcium from the water to maintain their skeletons. Studies in the 1970s showed that acidified lakes also had high levels of toxic heavy metals. The increased acidity of the lakes leads to chemical leaching of heavy metals from bedrock and soil into the lakes. Thus the death of many fish can also be attributed to heavy metal poisoning. The drop in fish numbers affects all parts of the food chain. In some locations, small acidified lakes have been restored to normal by large scale 'liming'. This involved adding large amounts of hydrated calcium oxide or sodium carbonate to the lake to raise the pH back to 7. It has been estimated that by the mid-twenty-first century, the world's oceans will have become significantly acidic due to the absorption of the acidic greenhouse gas carbon dioxide. If liming were to be used to neutralise this acidity then engineers would need to quarry a block of limestone 60 km square and 100 m deep every year and sprinkle the powdered limestone across all the oceans.

SYLLABUS FOCUS

16. USING INSTRUCTION TERMS CORRECTLY

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

'Discuss'

This verb requires you to identify issues and provide points for and against.

Example:

Discuss the issues associated with programs to reduce acid rain in industrialised cities.

Answer:

Industrialisation has been associated with the use of energy for industry, mining and transport. In most countries this energy is derived from the combustion of fossil fuels. Their combustion products produce acidic gases (carbon dioxide, sulfur dioxide, nitrogen dioxide) that lead to the formation of acid rain. The acid rain is an environmental hazard in many ways. It causes chemical erosion and disturbs food chains. Currently there is little choice for industry other than to continue to use fossil fuels as energy sources. Solar energy and other alternative energies cannot currently provide the level of energy for industrialised societies. Consequently, the only achievable programs are those in which acidic gases are removed from the combustion gases before they are vented into the environment.

7.1 Questions

1. Identify the acidic oxide.
 - A MgO
 - B P₄O₁₀
 - C NO
 - D CO
2. Sulfur is allowed to burn in oxygen, and the gaseous product is allowed to dissolve in water containing universal indicator. The indicator will turn
 - A blue.
 - B green.
 - C violet.
 - D red.
3. Identify the names of the products formed when KOH is neutralised by H₃PO₄.
 - A Potassium phosphate and water
 - B Potassium phosphide and phosphorus (V) oxide and water
 - C Water
 - D Potassium phosphate and hydrogen
4. Identify the set that contains an acidic oxide, an amphoteric oxide and a basic oxide.
 - A Al₂O₃, CaO, CuO
 - B Na₂O, ZnO, FeO
 - C Cl₂O₇, BaO, ZnO
 - D CO₂, SO₂, Al₂O₃
5. A major source of atmospheric sulfur dioxide is
 - A lightning storms.
 - B combustion of coal.
 - C bushfires.
 - D combustion of unleaded petrol.
6. (a) Identify the cause of large increases in sulfur dioxide emissions in the 25 years following World War II.
(b) Describe the human health problems associated with sulfur dioxide pollution of the atmosphere.
7. (a) Identify the gases that are collectively referred to as 'NO_x'.
(b) Explain why the production of NO_x is an environmental concern.
8. Dolomite is a natural carbonate mineral. Its chemical formula is MgCO₃.CaCO₃. Acid rain containing sulfuric acid attacks samples of dolomite.
 - (a) Identify the pollutant gas that forms sulfuric acid with water.
 - (b) Write a balanced equation for the reaction between the dolomite and the acid rain sample.
9. Beryllium oxide is an amphoteric oxide.
 - (a) Define the term 'amphoteric oxide'.
 - (b) Solid beryllium oxide reacts with potassium hydroxide solution to form a solution containing the beryllate ion (Be(OH)₄²⁻). Write a balanced ionic equation for this reaction.
(c) The solution in (b) is slowly acidified with dilute hydrochloric acid until excess acid is present. Write a balanced ionic equation for this reaction.

10. (a) Classify the acid–base properties of the oxides of the elements of Group (II) of the periodic table.
- (b) Describe the trend in the acid–base properties of the following oxides down Group (IV): CO_2 ; SiO_2 ; GeO_2 ; SnO , PbO .
- (c) Identify the acidic oxides, amphoteric oxides and basic oxides of the elements of period 3.
11. A 1997 study by school students showed that the rain in Melbourne had a pH between 4.5 and 5.0.
- (a) Explain whether this rain could be classified as acid rain.
- (b) Identify some of the effects of such rain on the local environment.
12. The roasting of copper (I) sulfide in oxygen produces molten copper metal and sulfur dioxide.
- (a) Write a balanced equation for this reaction.
- (b) Aqueous solutions of sulfur dioxide are oxidised by oxygen to form sulfuric acid. Write a balanced equation for this reaction.
- (c) Explain how acid rain that contains sulfuric acid can lead to the chemical weathering and erosion of marble statues. Illustrate your answer with an equation.

7.2 ACIDS AND EQUILIBRIA

Remember:

Before beginning this section, you should be able to:

- identify oxides of non-metals which act as acids, and describe the conditions under which they act as acids.

Key content

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

- define Le Chatelier's principle
- identify factors which can affect the equilibrium in a reversible reaction
- describe the solubility of carbon dioxide in water under various conditions as an equilibrium process, and explain the process in terms of Le Chatelier's principle
- calculate volumes of gases given masses of some substances in reactions, and calculate masses of substances given gaseous volumes, in reactions involving gases at 0°C and 100k Pa or 25°C and 100 kPa
- identify data, plan and perform a first-hand investigation to decarbonate soft drink and gather data to measure the mass changes involved, and calculate the volume of gas released at 25°C and 100 kPa .

Chemical equilibrium

In the Preliminary Course, we examined examples of chemical equilibrium in relation to saturated solutions of salts in water. We shall now develop these concepts further, and look at examples of equilibria involving acids and bases.

When you add a small chip of calcium carbonate to a beaker of dilute hydrochloric acid, you see a lot of fizzing as the calcium carbonate dissolves. The gas that is released into the air is carbon dioxide. At the end, all the calcium carbonate has dissolved. We can write a balanced equation for this reaction:



This reaction is an example of one that proceeds to completion if the correct proportions of reactants are present. The reactants are totally consumed.

Not all reactions proceed to completion. In many reactions, the final reaction mixture consists of both products and reactants. Let us look at a simple example of these types of reaction.

Example: Dissolution of iodine in water

If we place crystals of iodine in a Petri dish containing water, we find that the iodine slowly starts to dissolve, and the solvent becomes more yellow-orange over time. A lid is placed on the dish to prevent evaporation. The presence of some alcohol in the water speeds up the dissolution. We can use time-lapse photography to monitor the increasing depth of colour in the iodine solution that is forming. Eventually the solution reaches a constant orange-red colour, even though there are crystals of solid iodine still present in the dish. We can write an equation for this dissolution reaction:





Figure 7.10

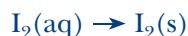
Carbon dioxide dissolves in water to produce carbonic acid. Carbonic acid slowly dissolves calcium carbonate to produce solutions of calcium hydrogen carbonate. As these solutions evaporate, calcium carbonate is deposited and stalactites and stalagmites form.



Figure 7.11

As iodine dissolves in water, the solution becomes more yellow-orange. The colour deepens over time until a point is reached when there is no further change.

When the colour of the solution is no longer changing, the water has become saturated in iodine. The system appears static, but a further experiment can show that this is not the case. The experiment involves preparing a saturated solution of radioactive iodine. A small amount of this solution is added to the previous non-radioactive saturated solution. No change in colour occurs. Over the next few hours, some of the iodine crystals are removed, washed and dried. They are then checked for radioactivity using a Geiger counter. The test shows that the crystals become increasingly radioactive over time. This can only be explained by radioactive molecules in solution forming crystals or crystallising on the surfaces of other crystals. We can write an equation for this crystallisation reaction:



As the colour of the solution does not change, we must assume that non-radioactive iodine crystals undergo dissolution at the same rate that radioactive molecules crystallise. Thus this system is dynamic rather than static. This example shows us that chemical reactions are reversible. We show this reversibility by using reversible arrows \rightleftharpoons . The arrow pointing to the right designates the forward dissolution reaction; the arrow pointing to the left designates the reverse crystallisation reaction.



Conditions for chemical equilibrium

The previous example showed that chemical equilibria are dynamic and not static. All systems in chemical equilibria exhibit the following characteristics.

- The system is closed. This means that atoms, molecules or ions cannot leave or enter the system. Thus the reaction of calcium carbonate with hydrochloric acid in a beaker is not a closed system as the carbon dioxide escapes. Water in a capped bottle will not continue to evaporate, because an equilibrium eventually becomes established between the liquid water and the water vapour.

Figure 7.12
In a closed system the air above liquid water becomes saturated in water vapour at a fixed temperature. A dynamic equilibrium is established.

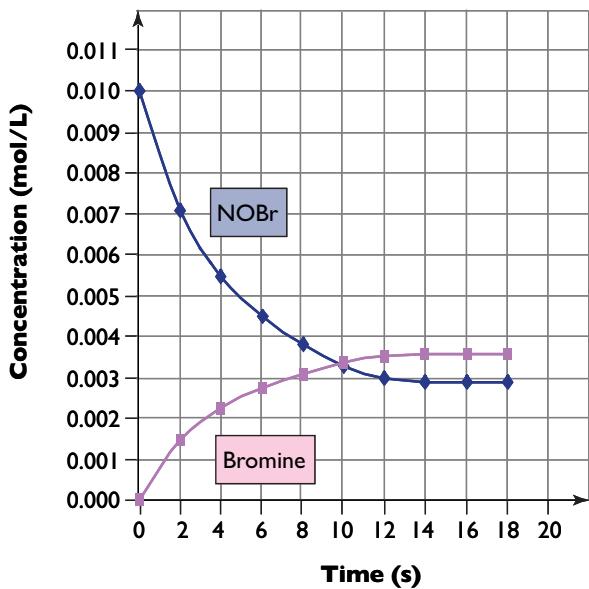
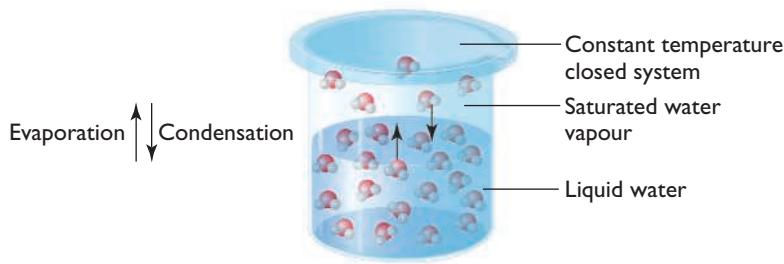


Figure 7.13

Initially, the reaction vessel contains 0.01 mol/L of NOBr. Equilibrium is achieved after 14 seconds. The graph shows the rising concentration of bromine.

- The observable or measurable properties of the system are constant. These properties are often called *macroscopic* properties and they include colour, electrical conductivity, concentration and gas pressure.
- The concentrations of reactants and products are constant once equilibrium is achieved.
- The rate of the forward reaction equals the rate of the reverse reaction. Thus the system is dynamic.

The following example illustrates these equilibrium principles.

Example: Decomposition of nitrosyl bromide

Experimental data has been collected for the decomposition of nitrosyl bromide (NOBr) as a function of time at constant temperature in a closed system. The reaction equilibrium is:



Figure 7.13 shows the change in concentration of NOBr and Br₂ with time.

The following features should be noted from Figure 7.13.

- The slope of the graph at any point is a measure of reaction rate. The graph shows that the concentration of NOBr decreases more rapidly in the initial few seconds than it does at 10 seconds. Thus the initial rate of NOBr decomposition is high, and this rate decreases as the system approaches equilibrium. At this point the NOBr concentration is constant and remains so.
- Initially there is no bromine present. Its concentration increases rapidly at first, but this rate decreases as the system approaches equilibrium. At this point the bromine concentration is constant.
- Although the equilibrium concentrations of NOBr and Br₂ are not equal, the rate of the forward reaction is equal to the rate of the reverse reaction after 14 seconds.

This system can also be observed using a macroscopic property to determine when equilibrium has been achieved. Colour cannot be used easily as both NOBr and Br₂ are reddish-brown in colour. Gas pressure can be used, however, as the pressure rises as the reaction proceeds towards equilibrium. This occurs because there are more product particles than reactant particles. Once the gas pressure reaches a constant value then equilibrium has been attained. It is vital that the temperature be held constant as temperature will influence both the gas pressure and the position or extent of the equilibrium.

SAMPLE PROBLEM 7.2

SOLUTION

Blue copper sulfate crystals are added to 20 mL of water in a jar, and the mixture thoroughly stirred and allowed to stand with the lid on. Eventually a saturated solution of copper sulfate forms. Identify two macroscopic properties that could be used to demonstrate that the system has reached equilibrium.

Equilibrium is reached when there is no further change in measurable macroscopic properties. Two properties that could be used are:

- colour — the solution will reach a constant blue; this can be measured instrumentally using a colorimeter
- electrical conductivity — the number of ions in solution will rise as the solid dissolves; eventually the solution becomes saturated in ions, so there will be no further rise in electrical conductivity.

Changing the position of the equilibrium

In the 1880s, the French chemist Henri Le Chatelier studied many chemical equilibria. From these studies he developed a principle that helps chemists to predict the effect of any disturbance on the system in equilibrium.

Le Chatelier's principle

'If a system is at equilibrium and a change is made that disturbs the equilibrium, then the system responds in such a way as to counteract the change and eventually a new equilibrium is established.'

Le Chatelier's early research involved the chemistry of cement and plaster. He developed new instruments, including a high temperature platinum-rhodium thermocouple. He wrote over 500 articles, books and scientific papers on metallic alloys, clays and ceramics.

The factors that may cause a disturbance to a chemical system in equilibrium are:

- temperature
- concentration (or gas partial pressure)
- total gas pressure (in gaseous equilibria).

It should be noted at this point that catalysts do not alter the position of a system already in equilibrium. Also, if a system is not at equilibrium then catalysts reduce the time to reach equilibrium; however, the final equilibrium position is the same whether the catalyst is present or not.

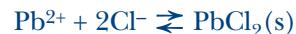
Temperature

Reactions can be classified as endothermic or exothermic on the basis of whether heat is absorbed or released in the forward reaction. Using Le Chatelier's principle, the following predictions can be made.

- For endothermic equilibria, an increase in temperature causes the equilibrium to shift to favour the products.
- For exothermic equilibria, an increase in temperature causes the equilibrium to shift to favour the reactants.

Example:

The reaction of colourless lead (II) ions and colourless chloride ions to form a white precipitate of lead (II) chloride is an exothermic equilibrium.



Experiment: The effect of temperature on this equilibrium can be demonstrated by adding drops of lead (II) nitrate solution to a sodium chloride solution in a beaker until a faint white suspension of

lead (II) chloride appears. Mix thoroughly. Divide this mixture into two test tubes. Place one tube in iced water or leave it at room temperature, and place the other in a beaker of hot water. Allow the systems to adjust to the temperature change.



Figure 7.14

The precipitation of lead (II) chloride decreases with increasing temperature. This demonstrates a shift in an exothermic equilibrium.

Observations: More precipitate is present in the tube at the lower temperature. In the hot water, the precipitate should reduce in amount, or even dissolve completely.

Explanation: Heat is a product of the forward reaction. If the tube is cooled, heat is removed. This disturbs the equilibrium and so a change occurs to oppose the disturbance. The equilibrium moves to the right to make more heat; consequently, more white precipitate forms. If the tube is heated, the system responds to remove some of the added heat by shifting the equilibrium to the left. Thus, more precipitate dissolves in the heated tube.

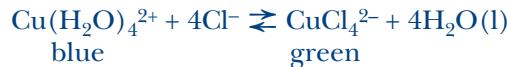
Concentration

Increasing or decreasing the concentration of reactants or products can shift the position of a chemical equilibrium. Using Le Chatelier's principle, the following predictions can be made.

- Increasing the concentration of reactants or decreasing the concentration of products shifts the equilibrium to favour the products.
- Decreasing the concentration of reactants or increasing the concentration of products shifts the equilibrium to favour the reactants.

Example:

The reaction of hydrated copper (II) ions ($\text{Cu}(\text{H}_2\text{O})_4^{2+}$) with chloride ions to form green CuCl_4^{2-} ions and water can be used to demonstrate the effect of changing concentrations on a chemical equilibrium.



Experiment: Prepare a mixture containing 2 mL of water and a small spatula tip of sodium chloride in a small beaker. Add 1–2 scoops of crystals of blue, hydrated copper (II) sulfate to this mixture. Stir to produce a slurry. Add crystals of sodium chloride to saturate the solution in chloride ions. Finally, add water slowly with stirring.



Figure 7.15

The hydrated copper ion is blue. As the concentration of chloride ion increases the colour of the solution changes from blue to green.

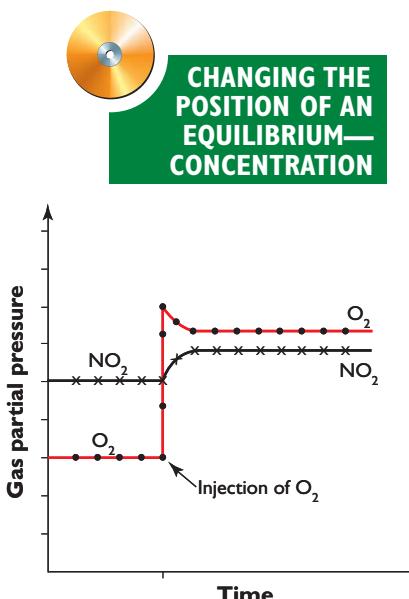


Figure 7.16

The injection of oxygen raises its partial pressure. This partial pressure decreases as the equilibrium shifts to the right.

Observations: The blue mixture turns green as the salt is added. When water is added to the green mixture it turns green-blue then blue.

Explanation: The high concentration of chloride ions disturbs the equilibrium, and the system responds to counteract the change. The equilibrium shifts to the right to use up some of the additional chloride ions. Thus the solution becomes greener.

When water is added to the green mixture, the disturbance causes the equilibrium to shift to counteract the change. The equilibrium shifts to the left to use up some of the added water. Thus, the solution becomes bluer and less green.

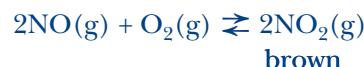
Gas partial pressure

In a mixture of gases, the total gas pressure is the sum of the individual pressures of each component gas. This individual gas pressure is called the *partial pressure* of the gas. Partial pressure is therefore a measure of the concentration of the gas within the total gas mixture. Using Le Chatelier's principle the following predictions can be made.

- Increasing the partial pressure of a reactant gas shifts the equilibrium to favour the products.
- Increasing the partial pressure of a product gas shifts the equilibrium to favour the reactants.

Example:

An equilibrium mixture consisting of colourless NO, colourless O₂ and brown NO₂ is held at a constant temperature. The mixture is pale brown due to NO₂.



Experiment: A gas syringe was used to inject oxygen gas into the equilibrium mixture. The mixture turns from light brown to darker brown.

Explanation: The increase in the oxygen partial pressure has disturbed the equilibrium; to counteract the change, the equilibrium has shifted to the right to reduce the amount of O₂ in the mixture. Thus the depth of brown colour has increased.

Total gas pressure

A simple way to investigate the effect of changing the total gas pressure on a gaseous equilibrium is to use a gas syringe as a reaction vessel. The gas mixture to be examined is placed in the syringe. The volume of the gas can be increased or decreased by moving the plunger. In the seventeenth century, Robert Boyle was able to prove experimentally that the pressure of a gas (at constant temperature) is inversely proportional to its volume. Thus if the volume of a gas is decreased by compression then its pressure will increase.

Experiment: A sample of NO₂ is introduced into a gas syringe held at constant temperature. The gas eventually comes to equilibrium with its dimer, N₂O₄.



The plunger is then pulled out to double the volume. This is equivalent to halving the gas pressure. The partial gas pressures or concentrations of each species also halve.



Observations: The brown colour of the gas mixture initially lightens as the volume suddenly rises. The pale brown mixture then slowly darkens in colour.

Explanation: The initial lightening of the brown colour is due to the doubling in volume and the spreading out of the gaseous particles. This change has disturbed the equilibrium and halved the partial pressures of each gas in the reaction vessel. The system responds by shifting to the left to counteract the change. This shift to the left increases the number of particles in the syringe and as these particles are brown, the brown colouration intensifies.

Figure 7.17 shows a graph of the partial pressures of the gaseous components as the system responds to this disturbance.

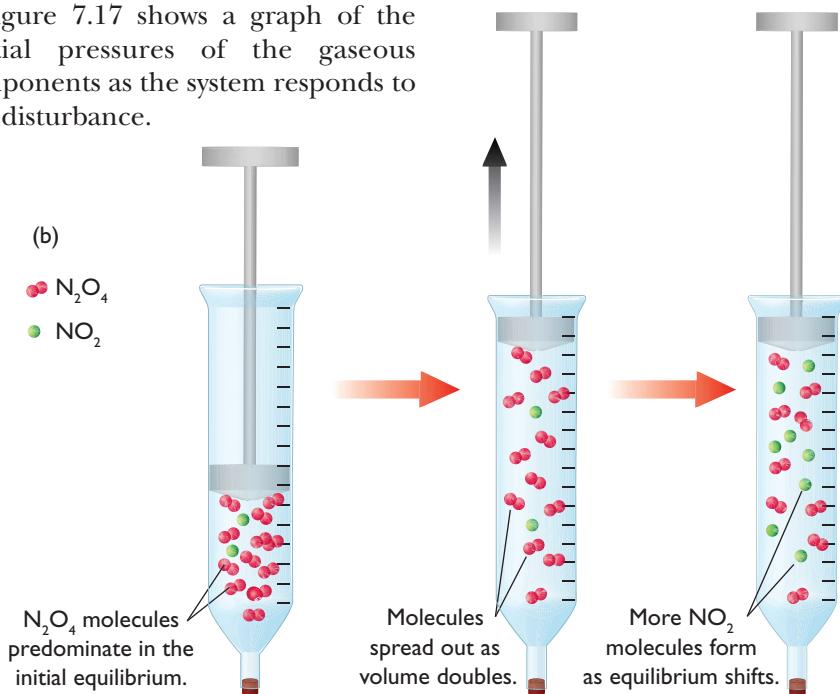
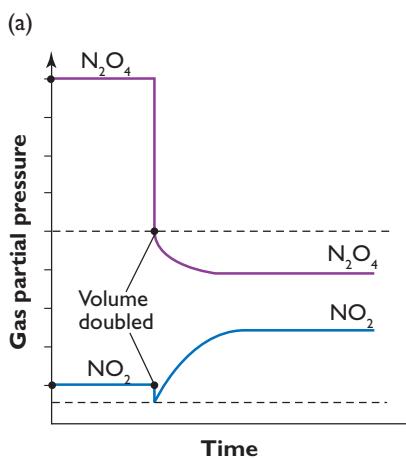


Figure 7.17

(a) Doubling the gas volume halves the total pressure. (b) The colour of the gas mixture initially lightens due to the increase in volume. As the system establishes a new equilibrium the brown colour deepens a little.

SYLLABUS FOCUS

17. USING INSTRUCTION TERMS CORRECTLY

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

'Demonstrate'

This instruction word requires you to show that a statement, concept or record is true or consistent by example or calculation.

Example:

Demonstrate that Le Chatelier's principle is consistent with the observation that limestone decomposes into lime more readily in an open furnace than a closed furnace.

Answer:

The open furnace allows carbon dioxide to escape as it forms.



The open furnace prevents carbon dioxide from reacting with $\text{CaO}(\text{s})$ and forming $\text{CaCO}_3(\text{s})$ in a reversible equilibrium. In a closed furnace an equilibrium is established. Le Chatelier's principle is demonstrated by this example, as the continual removal of gaseous carbon dioxide, forces the equilibrium to continuously shift to the right.

Carbon dioxide equilibrium in aqueous systems

Carbon dioxide is an acidic oxide. It dissolves in water to produce a solution of carbonic acid (H_2CO_3). Carbonic acid is in equilibrium with hydrogen ions and hydrogen carbonate ions as shown in the following equations.



This dissolution reaction is exothermic.

Let us examine these equilibria using carbonated soft drinks as an example.



Figure 7.18

The loss of gaseous carbon dioxide above the liquid in the open container causes an equilibrium shift, and the carbon dioxide comes out of solution. The soft-drink ultimately goes 'flat'.

Carbonated soft drinks

Soda water and other carbonated soft drinks are manufactured by dissolving carbon dioxide in water under pressure (~400–500 kPa). The water is supersaturated in carbon dioxide. The system will remain this way only if the bottle is sealed so as to maintain the high carbon dioxide gas pressure in the gas space under the cap. The increase in carbon dioxide gas pressure has significant effects on the gaseous equilibria. Equilibrium (1) is shifted to the right to reduce the gas pressure. Thus more carbon dioxide is dissolved. This in turn affects equilibrium (2), which is also pushed to the right to make more carbonic acid. The increase in carbonic acid concentration shifts equilibrium (3) to the right and thus the acidity increases as more H^+ ions are formed. Thus, soda water tastes sour or tart. Its pH is about 4.

When the cap of a soft-drink bottle is unscrewed, there is a rapid effervescence observed (Figure 7.19). The soft drink eventually goes 'flat' and tastes less sour due to the reversal of these three equilibria. The escape of the gaseous carbon dioxide has caused equilibrium (1) to shift to the left in the open system. The other two equilibria in turn shift to the left.

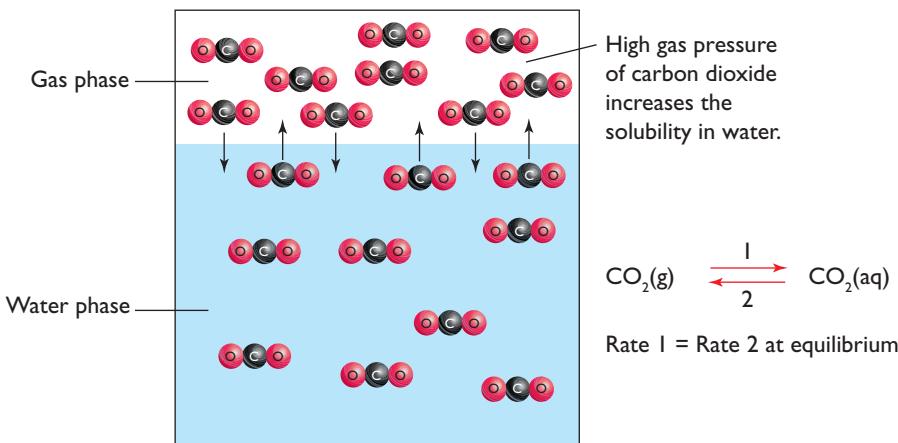
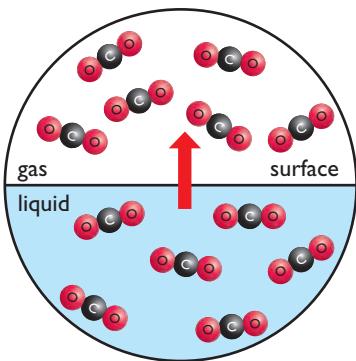


Figure 7.19 The solubility of carbon dioxide in water depends on the carbon dioxide partial pressure above the water. As this pressure increases, more carbon dioxide dissolves in the water.

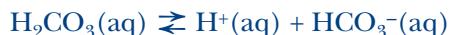
The carbon dioxide equilibrium in water can be further investigated by changing the conditions.

Changing the pH

Experiment: Drops of lemon juice are injected into the soda water.

Observation: The soda water degasses.

Explanation: The addition of the lemon juice increased the hydrogen ion concentration of the soda water. This caused the carbonic acid equilibrium to shift to the left to use up some of the added acid.



The increase in carbonic acid levels causes the following two equilibria to reverse and produce more gaseous carbon dioxide.



Changing the temperature (at constant pressure)

Experiment: Warm a sample of soda water (in a gas syringe).

Observation: The soda water degasses.

Explanation: The dissolution of carbon dioxide in water is exothermic. Heat is therefore a product of the reaction.



If heat is added, the equilibria shift to the left to counteract the change. This causes the soda water to de-gas.

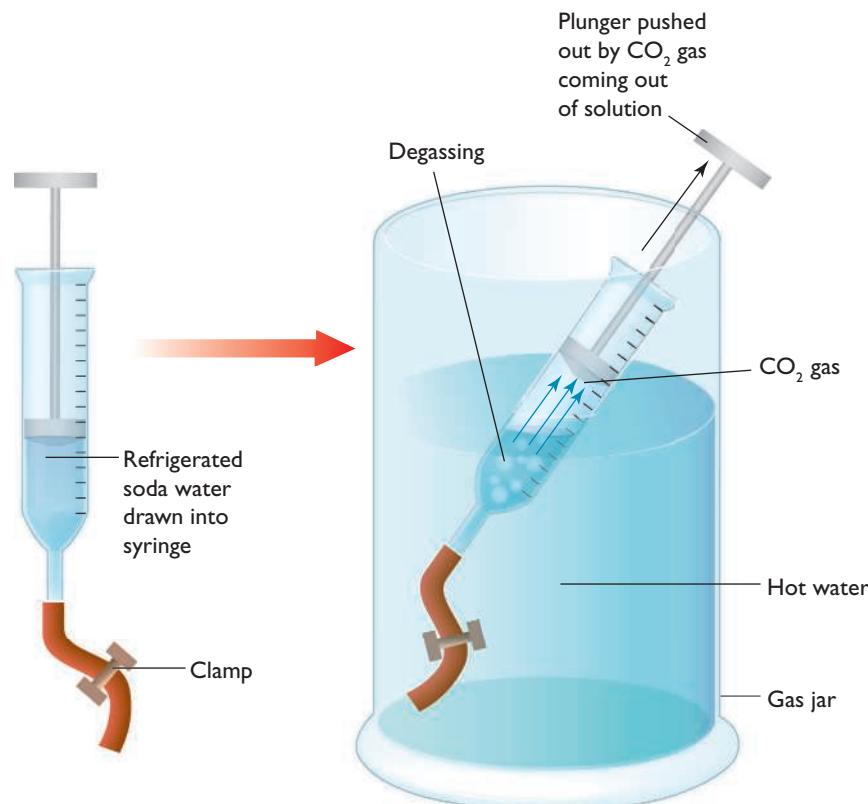


Figure 7.20

Soda water degasses as it is heated, as the dissolution equilibrium is exothermic.

This decreased solubility of carbon dioxide in water with increasing temperature is shown in Table 7.6.

Table 7.6. Solubility of carbon dioxide in water as a function of temperature (total pressure = 1 atm)

Temperature (°C)	0	20	25	30	40
Solubility of carbon dioxide (g/kg water)	3.35	1.69	1.45	1.26	1.10

Mass–volume calculations involving gases

Avogadro's Law

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

SAMPLE PROBLEM 7.3

Figure 7.21 shows two 1-litre vessels (A and B) at the same temperature and pressure. Vessel A contains oxygen (O_2) gas, and vessel B contains an unknown gas (X_2). The mass of gas in vessel A is 9.600 g, and the mass of gas in vessel B is 11.400 g. Identify the gaseous element present in vessel B.

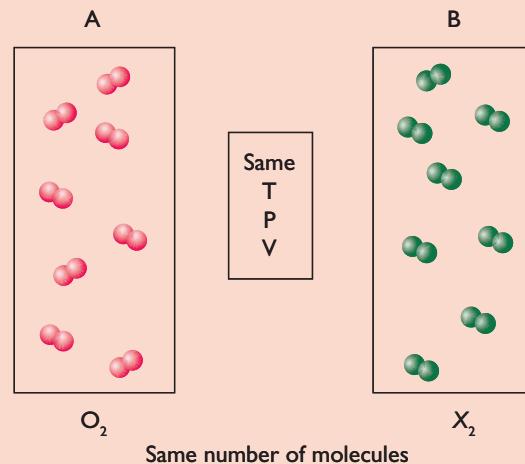


Figure 7.21 Each vessel contains the same number of molecules

According to Avogadro's Law, the same volume of gas (at the same temperature and pressure) contains the same number of molecules. Thus, 9.600 g of oxygen contains as many molecules as 11.400 g of X_2 .

$$\text{Molecular weight of } O_2 = 32.00$$

$$\text{Let the atomic weight of } X = x.$$

$$\text{Molecular weight of } X_2 = 2x$$

The ratio of the molecular weights will be equal to the mass ratio of each gas.

Thus,

$$9.600 : 11.400 = 32.00 : 2x$$

Solve for x .

$$x = 19.0$$

The gaseous element that has an atomic weight of 19.0 is fluorine. The gas in vessel B is therefore fluorine (F_2).

Volumes of gases at standard temperatures and pressures

Gas volumes vary as the temperature and pressure change. As a consequence, gas volumes need to be reported along with the temperature and pressure of the gas. To simplify matters the following standard conditions are used.

- Pressure = 100 kPa
- Temperature = 0°C or 25°C

When one is dealing with 1 mole of any gas, that volume of gas is called its *molar volume*. Unlike the term *molar weight*, which varies from one chemical substance to another, the molar volume is constant for all gases. This is understandable in terms of the particulate nature of gases. Most of the space occupied by a gas is empty and the actual volume of each gas molecule is very small compared with the total gas volume. It is only when gases are highly compressed that this rule is not strictly true.

The molar volume (V_M) of any gas has the following values at the stated temperatures and pressures:

- At 0°C and 100 kPa: $V_M = 22.71 \text{ L/mol}$
- At 25°C and 100 kPa: $V_M = 24.79 \text{ L/mol}$

The relationship between the number of moles (n) of a gas and its volume (V) is:

$$n = V/V_M$$

This equation can be used to solve problems involving the quantities of gases involved in chemical changes.

SAMPLE PROBLEM 7.4

A 0.60 g ribbon of magnesium is dissolved completely in sulfuric acid. Calculate the volume of dry hydrogen produced at 100 kPa and 25°C.

SOLUTION

Step 1. Calculate the number of moles of magnesium that have reacted.

$$n(\text{Mg}) = m/M = 0.60 / 24.31 = 0.02468 \text{ mol}$$

Step 2. Write a balanced equation for the reaction.



Step 3. Determine the number of moles of hydrogen formed.

The balanced equation shows that 1 mole of magnesium produces 1 mole of hydrogen.

$$\text{Thus: } n(\text{H}_2) = n(\text{Mg}) = 0.02468 \text{ mol}$$

Step 4: Calculate the volume of hydrogen.

$$\begin{aligned}V(\text{H}_2) &= n(\text{H}_2) \times V_M \\&= (0.02468)(24.79) \\&= 0.612 \text{ L}\end{aligned}$$

SAMPLE PROBLEM 7.5

Sulfur dioxide gas and water vapour form when hydrogen sulfide gas is oxidised by oxygen.

- (a) Write a balanced equation for this reaction.
- (b) Calculate the mass of sulfur dioxide formed when 100 mL of hydrogen sulfide (at 0°C and 100 kPa) is reacted with excess oxygen.

SOLUTION >>>>

- (a) $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + 2\text{SO}_2(\text{g})$
 (b) Step 1. Calculate the number of moles of hydrogen sulfide.

Convert the volume of the gas to litres (0.100 L)

$$n(\text{H}_2\text{S}) = V/V_M = 0.100/22.71 = 4.403 \times 10^{-3} \text{ mol}$$

Step 2. Use the balanced equation to determine the number of moles of sulfur dioxide formed.

Two moles of hydrogen sulfide form two moles of sulfur dioxide (1 : 1 mole ratio).

$$\begin{aligned} n(\text{SO}_2) &= n(\text{H}_2\text{S}) \\ &= 4.403 \times 10^{-3} \text{ mol} \end{aligned}$$

Step 3. Calculate the mass, m , of sulfur dioxide

$$M(\text{SO}_2) = 64.07 \text{ g/mol}$$

$$m = nM$$

$$\begin{aligned} m(\text{SO}_2) &= nM(\text{SO}_2) \\ &= (4.403 \times 10^{-3})(64.7) \\ &= 0.282 \text{ g} \end{aligned}$$

SAMPLE PROBLEM 7.6 >>

The Apollo-13 spacecraft suffered an explosion on the outward journey to the moon in April 1970. Critical levels of carbon dioxide began to build up in the cabin. Above 2% CO_2 , the astronauts would feel nausea and giddiness. The astronauts constructed a temporary air purifier using lithium hydroxide to remove carbon dioxide from the air. Lithium hydrogen carbonate was formed as the carbon dioxide was absorbed.

- (a) Write a balanced equation for the reaction between carbon dioxide gas and lithium hydroxide.
 (b) Calculate the number of carbon dioxide molecules that can be removed from the air by 100 g of lithium hydroxide.
 (c) Determine the volume of this carbon dioxide at 25°C and 100 kPa.



- (b) Step 1. Calculate the number of moles of LiOH

$$M(\text{LiOH}) = 23.949 \text{ g/mol}$$

$$n(\text{LiOH}) = m/M = 100/23.949 = 4.176 \text{ mol}$$

Step 2. Use the balanced equation to calculate the number of moles of CO_2 that will react.

The balanced equation shows a 1:1 mole stoichiometry:

$$n(\text{CO}_2) = n(\text{LiOH}) = 4.176 \text{ mol}$$

Step 3. Calculate the number of carbon dioxide molecules (N)

$$\text{Use } n = N/N_A$$

$$N = nN_A = (4.176)(6.022 \times 10^{23}) = 2.51 \times 10^{24} \text{ molecules of carbon dioxide.}$$

- (c) Use $V = nV_M$
 $= (4.176)(24.79)$
 $= 103.6 \text{ L}$

7.1 PRACTICAL ACTIVITIES



Decarbonating soda water

7.2 Questions

- Green copper (II) chloride crystals are dissolved in water to produce a saturated solution. The macroscopic property that can be used to determine when the system has reached equilibrium is
 - A gas pressure.
 - B volume.
 - C colour.
 - D solubility.
- When aqueous ammonia is added to copper (II) sulfate solution, the mixture turns from pale blue to deep blue.



Once equilibrium is established, identify a change that will cause the equilibrium to shift to the left.

- A Dilution with water
 - B Addition of additional ammonia
 - C Addition of copper (II) sulfate crystals with stirring
 - D Removal of the water as it forms
- An equilibrium mixture of brown NO_2 gas and colourless N_2O_4 was placed in three separate glass tubes.



The tubes were sealed. One tube was cooled in ice water. The second was held at room temperature. The third was heated using hot water.

The first tube turned very pale. The second tube remained pale brown. The final tube turned deep brown.

The conclusion that can be made about this equilibrium is:

- A the forward reaction is endothermic.
 - B the forward reaction is exothermic.
 - C that pressure increases as a result of heating have caused the equilibrium to shift to the right to make more N_2O_4 .
 - D the reverse reaction is exothermic.
- A few drops of methyl orange indicator were added to 10 mL of water in a beaker. The mixture appeared yellow. Drops of dilute acetic acid were then added until the mixture just turned red.



Identify the change that can be made to turn the indicator colour back to yellow.

- A Add drops of hydrochloric acid.
- B Remove acetate ions by precipitation.
- C Reduce the volume of the vessel by half.
- D Add sodium acetate crystals with stirring.

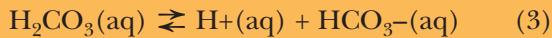
- A saturated solution of white calcium carbonate in water was prepared.



Crystals of calcium chloride were then added to this saturated solution, and the mixture stirred for five minutes. Identify the observation that would be made on addition of the calcium chloride.

- A Additional white solid precipitated out.
- B The solid calcium carbonate completely dissolved.
- C The mixture started to fizz.
- D No visible changes were observed.

- The following equilibria are relevant to the carbon dioxide equilibria in soda water.



Describe how the solubility of carbon dioxide in water is affected by each of the following changes.

- Addition of drops of sodium hydroxide solution
- Increasing the partial pressure of carbon dioxide above the soda water
- Adding nitrogen gas to raise the total gas pressure above the soda water

- Calculate the mass and volume (at 25°C and 100 kPa) of sulfur dioxide produced by the complete combustion of 4.0 moles of sulfur in excess oxygen.

- A 3.007 g sample of a hydrocarbon gas occupies 2.271 L at 100 kPa and 0°C. Calculate the molar weight of this gas and identify the hydrocarbon.

- A sample of 10.0 g of impure calcium carbonate is dissolved in excess dilute hydrochloric acid, and the carbon dioxide evolved is collected and dried. Its volume at 25°C and 100 kPa is 2.41 L. Assume that the impurity in the calcium carbonate is inert. Calculate the percentage by weight of pure calcium carbonate in the original sample.

10. The weathering of limestone caves results in the formation of stalactites and stalagmites.
- The water dripping into crevices on the outside of the cave has a pH of 6. Explain why the pH of the water is not 7.
 - Once the water percolates through cracks into the cave roof it begins to drip. Measurements of the pH of this dripping water show it to be about 7.5. Explain why the pH has risen.
 - This dripping water is saturated with calcium ions. Use an equation to explain why the water is rich in calcium ions.
 - If the dripping water evaporates, it leaves a white crusty deposit. Explain this observation in terms of Le Chatelier's principle.



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SUMMARY

- Generally, metallic oxides are basic and non-metallic oxides are acidic. There are some exceptions to these generalisations.
- Some oxides are amphoteric: they can behave as either an acid or a base.
- The acidity or basicity of oxides can be related to the position of elements in the periodic table.
- When an acid neutralises a base, a salt and water are formed.
- Salts are named after the anion of their parent acid.
- Various acidic oxides such as sulfur dioxide and nitrogen dioxide have polluted the atmosphere.
- In Western countries acidic oxide pollution is controlled, whereas in some poorer nations or emerging economies such as China, the amount of gaseous acidic oxides entering the air is increasing.
- The presence of acidic oxides in the air leads to the formation of acid rain.
- Acid rain causes damage to the built and natural environments.
- Various factors affect the position of a chemical equilibrium, including temperature, pressure and concentration.
- If a system is in equilibrium and a change is made which upsets the equilibrium, the system alters in such a way as to counteract the change and a new equilibrium is established (Le Chatelier's Principle).
- The formation of limestone caves is related to acid-base and solubility equilibria involving carbon dioxide and carbonic acid.
- The carbon dioxide/carbonic acid equilibria in carbonated beverages can be used to illustrate Le Chatelier's principle.

PRACTICAL ACTIVITIES

7.1 PRACTICAL ACTIVITIES

DECARBONATING SODA WATER

Aim

To investigate the amount of carbon dioxide lost when a carbonated beverage is degassed

Background

Carbon dioxide is far less soluble in salt water than in normal fresh water. This information allows us to degas a soft drink and use the change in mass to calculate the amount of carbon dioxide released. The results from all work groups will be used to ensure improved reliability.

Materials

- 300 mL soda water bottle (1 per group) (refrigerated)
- 500 mL beaker
- glass rod
- clock glass
- 6 g salt
- electronic balance

Safety

- Wear safety glasses throughout this experiment.
- Identify other safety precautions relevant to this experiment by reading the method.

Method

1. Weigh an unopened soda water bottle on an electronic balance.
2. Weigh a clean, dry 500 mL beaker with a glass rod inside.
3. Remove the beaker from the balance. Unscrew the lid of the soda water bottle and slowly pour all its contents into the beaker. Place the beaker, rod, soda water and lid on the balance. Record the new weight.
4. Weigh out 6.0 g of salt onto a clean clock glass and add it slowly to the soda water. Stir with the rod to assist the degassing.

5. After 10 minutes, weigh the beaker and its contents. Continue to stir for several minutes. Repeat weighing after 30 minutes, by which time the soda water should have gone flat.
6. Meanwhile, wash and dry the soda water bottle and cap. Reweigh the empty bottle and cap.

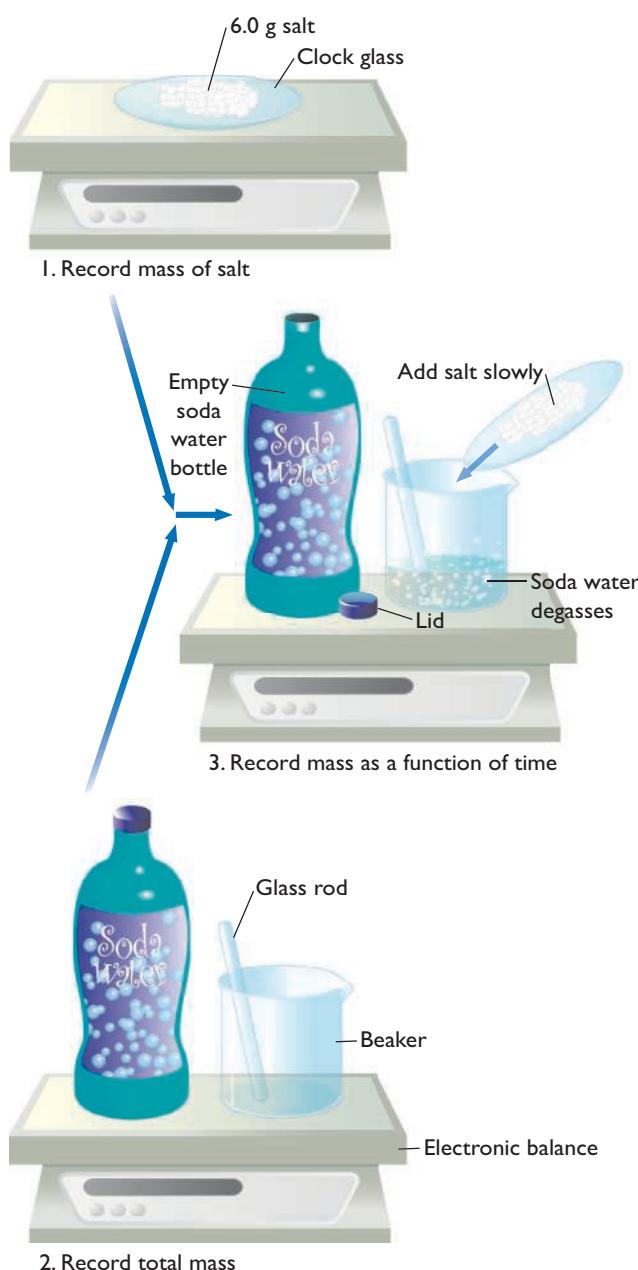


Figure 7.22 The salting-out procedure releases a large amount of dissolved carbon dioxide from the soda water.

PRACTICAL ACTIVITIES

Results

Tabulate your results.

Analysis

Use your tabulated results to perform the following calculations.

1. Calculate the mass of soda water used in the experiment.
2. Calculate the change in mass after salting out the soda water.
3. Assuming that the change in mass is due to the loss of carbon dioxide alone, calculate the number of moles of carbon dioxide lost.

4. Calculate the volume of this evolved carbon dioxide at 25°C and 100 kPa.
5. Discuss whether it is likely that the soda water is fully degassed.
6. Explain how the reliability of the investigation can be improved.
7. Explain whether or not the accuracy of the experiment would have been improved if we had used 600 mL of soda water and 12 g of salt.

Conclusion

Write an appropriate conclusion for this experiment.

DATA ANALYSIS

7.2 DATA ANALYSIS

INDUSTRIAL ORIGINS OF SULFUR DIOXIDE AND NITROGEN OXIDES

The following data tables provide information about the sources of sulfur dioxide and nitrogen oxide emissions into the air.

Examine this data and answer the questions that follow.

Table 7.7 Port Phillip (Victoria) air-shed data from the National Pollution Inventory (2003–2004)

Pollutant	Industry emissions (%)	Transport emissions (%)	Diffuse emissions from other sources (%)
sulfur dioxide	38	2	60
NO _x	4	72	24

Table 7.8 Sulfur dioxide emission sources in Australia

Source	Examples
industry	coal burning power plants; wood pulping; paper manufacture; petroleum refining; metal refining; metal smelting
transport	motor vehicles (cars, trucks, buses); planes; shipping
diffuse	textile bleaching; food preservation; wineries; fumigation

Table 7.9 Annual emissions on NO_x in Sydney (1992 data)

Transport emissions (%)	Major industry emissions (%)	Domestic and commercial emissions (%)
82	13	5

Table 7.10 Breakdown of transport NO_x emissions

Transport	%
cars	49
heavy duty vehicles	39
light commercial vehicles	8
other vehicles	4

Questions

- Identify industries that can contribute to high sulfur dioxide emissions.
- Present the data in Table 7.7 as a sulfur dioxide divided bar graph.
- Identify the major source of nitrogen oxide pollution in both Melbourne and Sydney.
- Use Tables 7.9 and 7.10 to calculate the percentage of NO_x in the annual emissions that are contributed by cars.
- Present the data in Tables 7.9 and 7.10 as pie graphs.
- Use the information from this chapter to evaluate reasons for concern over the release of SO₂ and NO_x into the environment.