

Chapter

13 ATMOSPHERIC CHEMISTRY



Figure 13.1

The Earth is surrounded by a layer of gases that we call the atmosphere. In the last 150 years, human activities have led to significant changes to the atmosphere.

Introduction

Our atmosphere is an important layer that not only provides various gases such as oxygen, nitrogen and carbon dioxide to sustain life, but also provides a protective barrier against some of the harmful radiation from our Sun and outer space. The atmosphere insulates the Earth from extreme temperature changes. Our atmosphere is a dynamic system whose composition has changed continuously over the last 4 billion years. The activities of humans and the pollutants they produce have had a great influence on the composition of our atmosphere.

In this chapter

- 13.1 Chemistry of atmospheric pollution
and ozone depletion

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13.1 CHEMISTRY OF ATMOSPHERIC POLLUTION AND OZONE DEPLETION

Remember

Before beginning this section, you should be able to:

- identify IUPAC names for carbon compounds as they are encountered
- explain that energy is required to break bonds and energy is released when bonds are formed
- describe the energy needed to begin a chemical reaction as activation energy
- identify the sources of pollution that accompany the combustion of organic compounds and explain how these can be avoided
- explain the role of catalysts in changing the activation energy and hence the rate of chemical reactions.

Composition and structure of the atmosphere

The atmosphere is a thin gaseous layer that extends to a distance of about 600 km above the Earth's surface. Figure 13.2 shows the layered structure of the atmosphere and the temperature gradient with altitude. It is the changes in the temperature gradient that mark the boundaries between the atmospheric layers.

Troposphere (0–15 km)

The troposphere is the layer closest to the ground. About 75% by mass of the atmosphere is concentrated in the troposphere. The air pressure is also highest at the surface (~100 kPa) and decreases with altitude to about 10 kPa at 15 km altitude. The gases of the troposphere are well mixed due to transfer of heat energy via convection currents that circulate the gases and particles. The troposphere cools with increasing altitude from about 15°C at the surface to about –50°C to –60°C at the stratospheric boundary which is called the *tropopause*. The rate of transfer of gases or pollutants across the tropopause is very slow. Water vapour that reaches the tropopause condenses to ice crystals and this prevents loss of water into the stratosphere. The tropopause is at a higher altitude at the equator than at the poles due to the expansion of hot air.

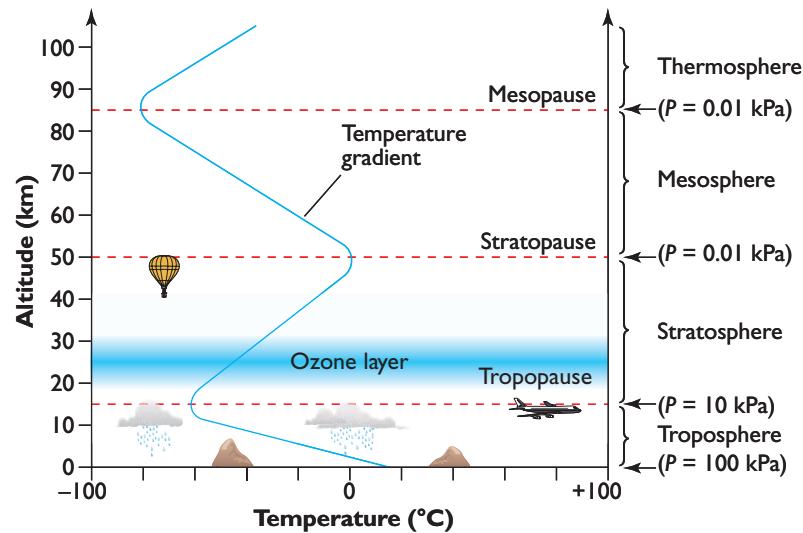


Figure 13.2

Humans live in the troposphere, which is the layer of the atmosphere at ground level.

Stratosphere (15–50 km)

Air pressure continues to decrease with altitude and in the stratosphere the air pressure drops from about 10 kPa to about 0.1 kPa at the *stratopause*, which is the boundary between the stratosphere and mesosphere. The first 9 km of the stratosphere has a fairly uniform temperature. Thereafter the temperature increases with altitude. Within the stratosphere we find the main zone of the **ozone layer** (which extends from an altitude of 10 km to the stratopause). The greatest concentration of ozone (O_3) occurs at about 25 km altitude (8–10 ppm). The higher regions of the ozone layer are warmer than the upper troposphere as ozone absorbs

Key content

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

- describe the composition and layered structure of the atmosphere
- identify the main pollutants found in the lower atmosphere and their sources
- describe ozone as a molecule able to act both as an upper-atmosphere UV radiation shield and a lower atmosphere pollutant
- describe the formation of a coordinate covalent bond
- demonstrate the formation of coordinate covalent bonds using Lewis electron dot structures
- compare the properties of the oxygen allotropes O_2 and O_3 , and account for them on the basis of molecular structure and bonding
- compare the properties of the gaseous forms of oxygen and the oxygen free radical
- identify the origins of chlorofluorocarbons (CFCs) and halons in the atmosphere
- identify and name examples of isomers (excluding geometrical and optical) of haloalkanes up to eight carbon atoms
- discuss the problems associated with the use of CFCs and assess the effectiveness of steps taken to alleviate these problems
- analyse the information available that indicates changes in atmospheric ozone concentrations, describe the changes observed and explain how this information was obtained
- present information from secondary sources to write the equations that show the reactions involving CFCs and ozone to demonstrate the removal of ozone from the atmosphere
- gather, process and present information from secondary sources including simulations, molecular model kits or pictorial representations to model isomers of haloalkanes
- present information from secondary sources to identify alternative chemicals used to replace CFCs, and evaluate the effectiveness of their use as a replacement for CFCs.

low wavelength solar radiation such as UV-B (wavelength 280–320 nm) and some UV-C (200–280 nm).

There is very little vertical mixing of gases in the stratosphere as the temperature increase with altitude in this layer prevents convection currents. The air in the stratosphere is therefore very dry and stable, and the ozone in this region does not migrate into the troposphere. Pollutants that enter the stratosphere usually remain there for long periods of time. About 99.9% of the Earth's atmosphere is present in the troposphere and stratosphere. The temperature at the stratopause is about -2°C to 0°C .

Mesosphere (50–85 km) and thermosphere (85 km–600 km)

Air pressure continues to decrease in the mesosphere from about 0.1 kPa to 0.01 kPa. The temperature in this zone decreases with altitude and reaches about -90°C at the **mesopause** at an altitude of 85 km. Few molecules in this zone absorb radiation, so the zone is very cold.

Above the mesopause the temperature rises once again in a zone called the *thermosphere*. This is due to absorption of very high frequency radiation. The thermosphere extends out to about 600 km. The ionosphere is a region in which some atoms and molecules are converted to gaseous ions (e.g. O^+ , O^{2+} , NO^+). The region where ions are produced is called the *ionosphere* and includes part of the mesosphere as well as the thermosphere. The temperature of the thermosphere can reach over 1700°C ; however, because the air is so thin, a thermometer would find it difficult to record these temperatures because air molecules are so far apart that they would rarely strike the thermometer bulb.

There is no distinct end to the atmosphere. It fades gradually into the very low pressures of space.

Composition of the atmosphere

The composition of the atmosphere is essentially constant at all altitudes. Although the concentration of total gas particles drops with increasing altitude, the relative proportions of atmospheric components remains fairly constant. Table 13.1 shows the composition of tropospheric gases near sea level. The amount of water vapour in the atmosphere typically varies from 1–5%.

Table 13.1 Composition of the (sea level) troposphere (dried)

Gas	Concentration % (v/v)	Gas	Concentration % (v/v)
nitrogen	78.09	methane	0.000 16
oxygen	20.94	krypton	0.000 12
argon	0.934	hydrogen	0.000 05
carbon dioxide	0.037	carbon monoxide	0.000 01
neon	0.001 8	ozone	0.000 002
helium	0.000 5	xenon	0.000 008 7

For most gases the concentrations are best expressed in parts per million (ppm). (Note: 1 ppm = 1 millilitre per kilolitre.)

Lower atmospheric pollutants

The atmosphere becomes polluted by both natural processes and the activities of humans. Volcanoes can release toxic gases including sulfur dioxide. Lightning produces toxic nitrogen oxides and ozone.

Let us examine some gases that pollute the lower atmosphere. Lower atmospheric pollutants often include particulates such as soot from forest fires and the exhaust from industry. Metal dusts and concrete dusts also are atmospheric pollutants, as are vapours from solvents used in industry and domestically.

SAMPLE PROBLEM 13.1

SOLUTION

Calculate the concentrations of argon and hydrogen in the atmosphere in parts per million.

Use the data from Table 13.1 to solve this problem.

Convert the % (v/v) data to mL/kL.

$$\text{Argon: } c(\text{Ar}) = 0.93\% \text{ (v/v)}$$

$$= 0.93 \text{ mL}/100 \text{ mL}$$

$$= 0.93 \times 10000 \text{ mL/kL}$$

$$= 9300 \text{ ppm}$$

$$\text{Hydrogen: } c(\text{H}_2) = 0.00005\% \text{ (v/v)}$$

$$= 0.00005 \times 10000 \text{ mL/kL}$$

$$= 0.5 \text{ ppm}$$



Figure 13.3

Natural and man-made pollutants:
(a) The energy of a lightning flash is sufficient for some oxygen molecules to react with other oxygen molecules or nitrogen molecules to form toxic ozone and nitrogen monoxide.
(b) Particulates from industrial exhaust pollute the atmosphere.



Carbon dioxide

The concentration of carbon dioxide has shown a gradual increase during the twentieth century. The burning of fossil fuels such as coal and oil products has caused this gradual increase in carbon dioxide levels. This increase in carbon dioxide is one of the factors that scientists believe has added to global warming. This is sometimes referred to as the 'enhanced greenhouse effect'. Carbon dioxide absorbs infrared (IR) radiation that is re-radiated by the Earth's surface.

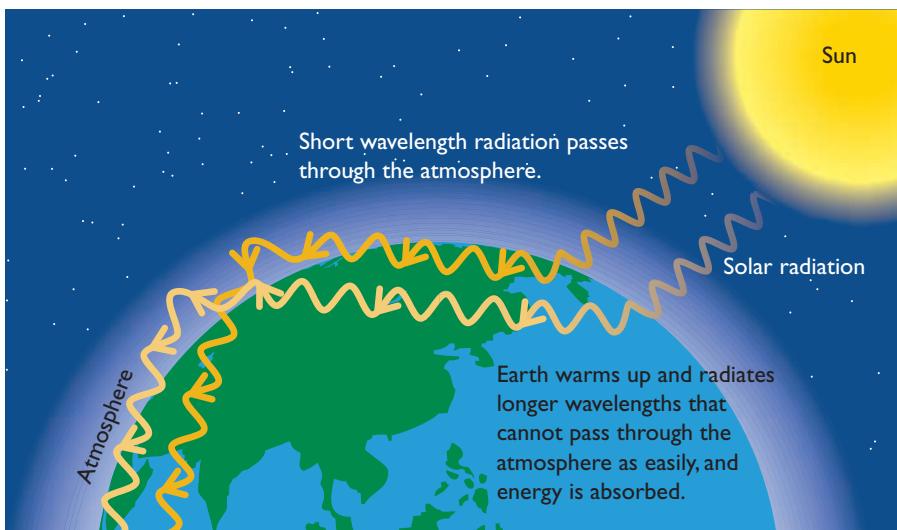


Figure 13.4

Short wavelength radiation from the sun passes through the atmosphere to the ground. The wavelengths re-radiated are longer and are absorbed by some of the molecules in the atmosphere (e.g. carbon dioxide, water vapour). The atmosphere becomes hotter as a result. Increases in carbon dioxide trap the heat in the atmosphere.

This process is vital in ensuring that the Earth does not lose too much heat and become a cold, lifeless planet. Too much carbon dioxide, however, leads to higher heat retention with consequent changes to the abiotic and biotic environment. Figure 13.5 shows the increasing concentration of carbon dioxide in the troposphere over time.

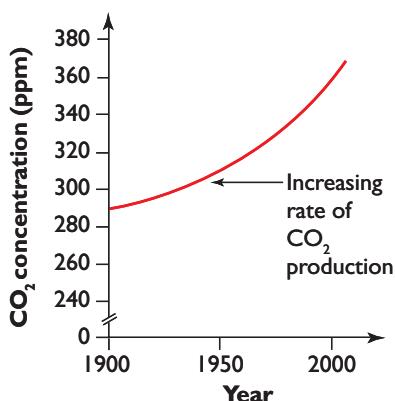


Figure 13.5

Global warming is believed to be increased by the rise in carbon dioxide levels in the atmosphere.

Carbon monoxide

Carbon monoxide is a lower-atmospheric pollutant. Road traffic emissions account for up to 90% of carbon monoxide emissions, although much of the remainder is generated during bushfires. Carbon monoxide is produced by the process of incomplete combustion. The gas is toxic because it is readily absorbed by haemoglobin molecules and transported by the blood. Carbon monoxide binds to haemoglobin over 200 times more efficiently than oxygen does. This causes tiredness, headache and eventual death as less oxygen is transported.



Carbon monoxide does not build up in the atmosphere as it is rapidly removed by the action of soil organisms or by oxidation to carbon dioxide. Its natural concentration in the troposphere is about 0.1 ppm, but this may rise 500 times in locations where there is a high density of automobile traffic.

Nitrogen oxides (NO_x)

Emissions from road traffic are the principal sources of nitrogen oxides such as NO and NO_2 . In the combustion chamber, nitrogen and oxygen combine in the presence of a spark to form nitric oxide (NO). This gas in turn reacts with oxygen to form NO_2 . The conversion to nitrogen dioxide is catalysed by carbon compounds and sunlight. NO can also react with any tropospheric ozone (O_3) to produce NO_2 .

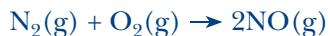


Figure 13.6 shows a graph of NO, NO₂, O₃ and hydrocarbon concentrations during a sunny day in city air.

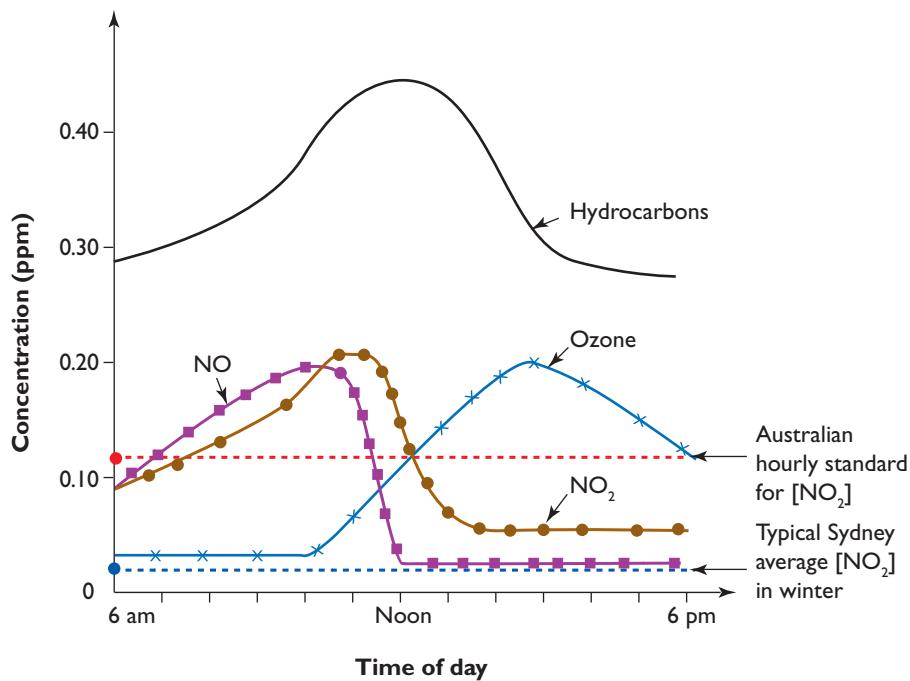


Figure 13.6

The levels of NO_x and O₃ in the atmosphere change throughout the day as the amount of sunlight changes.

free radical: atoms or molecules with one or more unpaired valence electrons

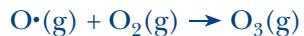


Figure 13.7

The pine trees in some parts of Europe have been severely damaged by acidic gases (such as NO₂) that dissolve in rainwater to produce acid rain.

Atmospheric studies show that the concentration of nitrogen oxides in the air in cities is greatest when traffic volume peaks. In smog, concentrations of 0.2 ppm of NO₂ have been recorded. Levels of NO₂ in Sydney air are normally below the Australian hourly standard of 0.12 ppm.

Nitrogen dioxide is an irritant to the respiratory system. It reacts with hydrocarbons (e.g. unburnt fuel) in the presence of sunlight to produce photochemical pollutants including ozone. UV photons cause photo-dissociation of NO₂ with the formation of reactive species called **free radicals**. The oxygen free radical (O[•]) that forms, rapidly reacts with oxygen molecules to produce ozone. Thus the formation of ozone is highest when the UV levels peak and the concentration of NO₂ is high.



The ozone that is produced has excess energy, which is removed from the system by the release of photons or by transfer to a molecule of nitrogen in the air.

Nitrogen dioxide is also oxidised to form nitric acid, which contributes to acid rain.

Ozone

Ozone is a pollutant in the lower atmosphere. Tropospheric ozone represents about 10% of all the atmospheric ozone. It is generated as shown by the equation in the previous section (*Nitrogen oxides*). The higher UV levels in summer lead to greater photochemical smog problems at this time. The natural background level of ozone in the troposphere is about 0.02 ppm whereas in photochemical smog the level may rise to 0.3 ppm or higher. Measurements of ozone levels in Australian capital cities over the last 30 years show that following an initial decline in the 1980s, the levels

have remained fairly steady (~0.13 ppm average maximum hourly levels in Sydney) rather than declining.

Ozone is very poisonous at levels above 20 ppm. It readily oxidises organic tissue and thus disrupts normal biochemical reactions in the body. It irritates the eyes and causes breathing difficulties. Ozone is also toxic to plants, including agricultural crops. It is a much stronger oxidising agent than oxygen, especially in acidic environments. It readily attacks rubber and plastics. In some areas in the USA, air pollution (as ozone alone, or ozone in combination with sulfur dioxide and nitrogen oxides) is responsible for 90% of crop damage.

Volatile organic compounds (VOC)

Volatile organic compounds are released in the exhaust gases of vehicles. The major compounds of concern are benzene and 1,3-butadiene, as they are known carcinogens (cancer-causing agents). They also irritate the lungs. The benzene that is produced is a minor petrol component, and also enters the atmosphere during petroleum refining. The 1,3-butadiene is produced by fuel combustion in diesel and petrol vehicles.

Sulfur dioxide

Sulfur dioxide is an irritating, poisonous gas that is produced by the combustion of fuels (such as coal and oil) that contain sulfur minerals. Power stations and metal smelters are the principal sources of sulfur dioxide pollution. Maximum hourly sulfur dioxide levels in the air around smelting sites such as at Mt Isa have reached 0.5 ppm. The Australian maximum one-hour standard is 0.2 ppm. Mt Isa has achieved yearly average emissions lower than those of the Australian standard of 0.02 ppm. Sulfur dioxide levels in cities are well below the national standards.

In nature, sulfur dioxide is also generated naturally by volcanoes and by bacterial action. It is an acidic oxide that contributes to the formation of acid rain.



Figure 13.8

In many cities, photochemical smog is a significant problem. It is caused by the emissions of nitrogen oxides and hydrocarbons, and the action of sunlight, which together produce a mixture of molecules that cause breathing difficulties.

coordinate bond: a covalent bond in which one atom provides both electrons to form the bonding pair

Coordinate bonding

Coordinate bonding is a special example of covalent bonding. For this reason it is sometimes called *coordinate covalent bonding*. A **coordinate bond** forms when one atom provides both electrons for the shared pair. Once the coordinate bond is formed it is identical to a normal covalent bond.

A covalent bond symbol with an arrow tip (\rightarrow) is often used to designate a coordinate bond.

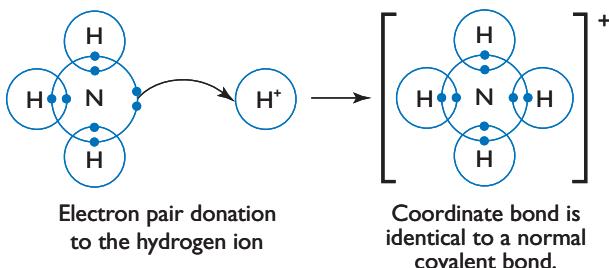


Figure 13.9
A coordinate bond forms when an ammonia molecule reacts with a hydrogen ion.

Let us now examine some common molecules in which coordinate bonding is present.

Ammonium ions (NH_4^+)

Ammonium ions form when ammonia molecules react with hydrogen ions. The non-bonding pair of electrons on the nitrogen atom is shared with the hydrogen ion to form the bond.

Hydronium ions (H_3O^+)

The oxygen atom in water has two non-bonding electron pairs. Hydronium ions form when one of these non-bonding pairs is shared with a hydrogen ion. The hydronium ion is of particular importance in acid-base systems.

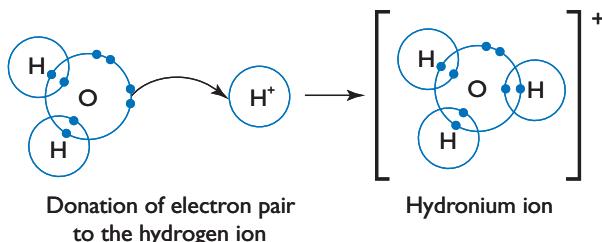


Figure 13.10
A coordinate bond forms when a water molecule reacts with a hydrogen ion.

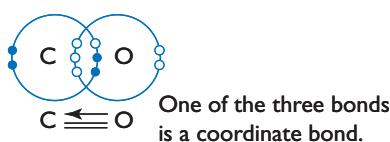


Figure 13.11
The carbon and oxygen atoms in CO are linked by covalent and coordinate covalent bonds.

Carbon monoxide (CO)

Both covalent and coordinate bonds are present in a carbon monoxide molecule. Figure 13.11 shows the formation of these bonds as the carbon monoxide bond forms from carbon and oxygen atoms.

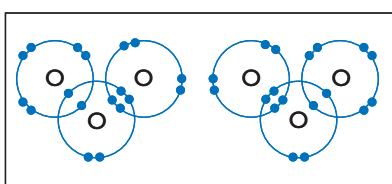
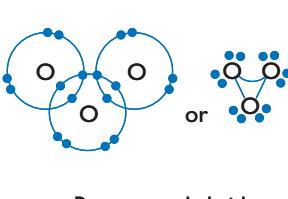


Figure 13.12
Covalent and coordinate bonding are involved in the linking of the three oxygen atoms in ozone.



Ozone is a 'bent' molecule. The bond angle is 117° , and each bond is the same length (128 pm). Figure 13.12 shows two Lewis electron dot structures for ozone. In each case both covalent and coordinate bonds are shown. Neither diagram adequately explains the equal length of both bonds.

The actual molecule of ozone is a *resonance structure* which is a composite of the two, as indicated in the third diagram in Figure 13.12.

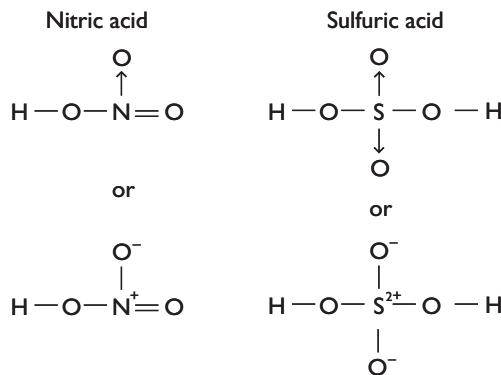


Figure 13.13
There are many examples of coordinate bonding in molecules.

Oxygen was discovered by Karl Scheele in Sweden, and Joseph Priestley in England, in 1773. It was Antoine Lavoisier who gave this gas the name 'oxygen'.

allotropic forms: different structural forms of an element in the same state

Oxygen and ozone

Oxygen (O_2) is required by all aerobic organisms. In particular, it is used to oxidise nutrients to release energy. Our atmosphere has not always contained such high levels of oxygen. Three billion years ago there was very little oxygen in the primitive atmosphere. The fossil record shows us that when photosynthetic organisms such as cyanobacteria appeared they utilised the oxygen that was produced by photosynthesis to oxidise iron and sulfur compounds in the lithosphere. Eventually, sufficient oxygen was produced that some began to collect in the atmosphere. As oxygen levels increased, new aerobic life forms evolved — life forms that could use this gas to generate energy.

Allotropes of oxygen

Oxygen exists in two **allotropic forms**: O_2 and O_3 . Trioxygen or ozone (O_3) is pale blue in the gaseous state whereas dioxygen (O_2) is colourless. Liquid ozone (b.p. = $111^\circ C$) is deep blue whereas liquid dioxygen is pale blue (b.p. = $-183^\circ C$). Solid ozone is black-violet (m.p. = $-193^\circ C$). In comparison, solid diatomic oxygen (m.p. = $-219^\circ C$) is pale blue in colour. Diatomic oxygen has a density similar to that of air, whereas ozone is about 1.5 times as dense as air. Although both gases are sparingly soluble in water, ozone is more soluble than diatomic oxygen.

Diatomic oxygen has many uses in industry. These include its involvement during oxyacetylene welding and, in the steel industry, in the conversion of iron to steel. In medicine, compressed oxygen bottles are vital for sustaining patients during operations, as well as those suffering from respiratory diseases. In the space industry liquid oxygen is used as an oxidiser for the liquid hydrogen fuel in rockets and the space shuttle. Ozone is a more powerful oxidant than oxygen. Ozone is an excellent bleaching agent and can be used to bleach wood pulp in the preparation of paper. Because it kills micro-organisms, ozone can be used to disinfect water.

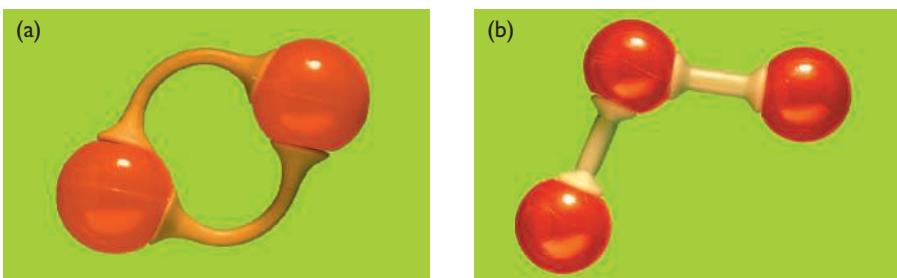


Figure 13.14

- (a) Dioxygen consists of two oxygen atoms and (b) ozone consists of three oxygen atoms.

bond energy: the energy required to break a chemical bond

Diatomeric oxygen (O_2)

Diatomeric oxygen (dioxygen) consists of two oxygen atoms linked by a double covalent bond. This double bond is very strong and has a high bond energy (498 kJ/mol). Such bond stability makes it less reactive than ozone, which has a lower **bond energy** (445 kJ/mol).

Diatomeric oxygen supports combustion and rekindles a glowing splint of wood. This test is commonly used as a test for oxygen. Hot metals such as magnesium burn in oxygen to form metallic oxides.



Active metals burn in diatomic oxygen to form peroxides or superoxides rather than oxides. Sodium burns in oxygen to produce yellow sodium peroxide (Na_2O_2) whereas potassium reacts to form yellow

potassium superoxide (KO_2). The peroxide ions (O_2^{2-}) and superoxide ion (O_2^-) are molecular ions. They are powerful oxidising agents.

Non-metals react with diatomic oxygen to form covalent molecular oxides. Red-hot carbon burns brightly in a gas jar of oxygen to form carbon dioxide. Yellow sulfur burns in oxygen to form sulfur dioxide gas.

Triatomic oxygen (O_3)

Ozone consists of three oxygen atoms arranged to form a bent molecule with bonds of equal length. Simple Lewis electron dot diagrams do not adequately explain its structure and properties. Each bond in ozone can be considered as being intermediate between a single bond and a double bond.

Ozone is a pungent and poisonous gas. It is a very powerful oxidising agent and as a consequence is able to oxidise living tissue. In its reactions it is able to split off a reactive oxygen atom (or radical), because its bond energy is lower than that of diatomic oxygen. This free oxygen atom then rapidly combines with the material that is being oxidised. Ozone very rapidly oxidises metals to form metal oxides with the release of oxygen gas.

Ozone can be made by a silent electrical discharge between metal gauzes in an atmosphere of oxygen.



Ozone readily oxidises sulfides to form sulfates.



SYLLABUS FOCUS

26. 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:

'Compare'

This instruction word requires you to show how things are similar or different.

Example:

Compare the bonding in oxygen and ozone molecules.

Answer:

In both molecules the oxygen atoms are linked by covalent bonds. In dioxygen, the covalent bond is a double covalent bond. In ozone the bonds between oxygen atoms are intermediate between single and double covalent bonds.

Oxygen (O_2) and the oxygen free radical ($\text{O}\bullet$)

Oxygen atoms have 8 electrons and an electron configuration of 2, 6. In its lowest energy state (or ground state) the valence shell contains three pairs of electrons. When oxygen atoms combine to form oxygen molecules (O_2), a pair of valence electrons from each atom are shared to form a double covalent bond that links the two atoms together.

When oxygen molecules are split into separate oxygen atoms (e.g. by the absorption of UV light in the stratosphere) the atoms of oxygen formed are called *oxygen free radicals*. These radicals are different from oxygen atoms in their ground state. They have two paired electrons and two unpaired electrons in their valence shell. The presence of these unpaired electrons makes oxygen free radicals extremely reactive. The unpaired electrons exist in higher energy states (or excited states) than the ground

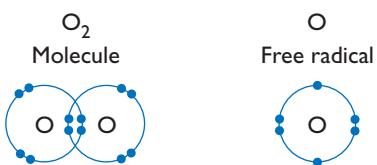


Figure 13.15

The oxygen free radical consists of two paired electrons and two unpaired electrons in the valence shell.

state. These oxygen free radicals exist only briefly in the lower layers of the atmosphere before they react with other radicals or molecules. In the thermosphere, oxygen free radicals are formed when far UV photons cause photodissociation of oxygen molecules. The great separation of particles in the thermosphere allows radicals to predominate.

The dot notation is used for free radicals. The symbol $\text{O}\cdot$ is used to represent the oxygen free radical.

Oxygen free radicals are even more reactive than ozone.

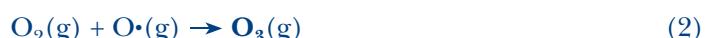
The ozone shield

Ozone is classified as a toxic gas in the troposphere. In the stratosphere, however, it is vital to life on Earth. In the stratosphere the ozone molecules absorb ultraviolet radiation (wavelength band 200–320 nm), which is harmful to the cells of living organisms.

The ozone in the stratosphere is constantly being formed and decomposed. The following information summarises the formation and decomposition cycles which involve the absorption of UV-B and UV-C radiation. In these processes the UV radiation is converted to heat energy, which warms the stratosphere. Because of the ozone shield only a small fraction of the UV-B radiation from space reaches ground level. Most of the UV-A radiation (320–400 nm) reaches the Earth's surface. This is important as UV-A promotes the production of vitamin-D in our skin.

Natural formation of ozone

Stratospheric oxygen absorbs ultraviolet light (UV-C wavelengths < 242 nm) and photodissociation occurs leading to the formation of oxygen free radicals. These reactive radicals combine with oxygen molecules to form an energised ozone molecule. This excess kinetic energy of the ozone molecule is transferred to another molecule such as nitrogen or oxygen, or photons may be released. This process prevents energised ozone molecules decomposing.



Note: Species in **bold** are energised molecules.

Energetic ozone molecules decompose back to oxygen (reverse of equation 2) unless collisions with other molecular species are able to transfer the vibrational kinetic energy away from the ozone molecule. These collisions are more frequent at lower altitudes. If the altitude is too low, however, insufficient UV radiation can penetrate to initiate reaction (1). Because of these opposing factors the maximum rate of ozone production occurs at an altitude of 50 km.

Natural decomposition of ozone

There are many processes that lead to the decomposition of ozone in the upper atmosphere. Some of these are discussed below.

Ozone molecules absorb radiation strongly in the 200–310 nm range (UV-C and most of the UV-B). As a result, the ozone decomposes back to oxygen molecules and oxygen free radicals. No other atmospheric molecules absorb the solar radiations in this range. Without ozone, these high-energy photons would reach the Earth's surface and damage the DNA in living cells. Additional UV radiation would also degrade



FORMATION AND DECOMPOSITION OF OZONE

synthetic plastic polymers used as structural materials. Thus, the ozone layer provides a necessary shield to protect life. As ozone decomposes, the reactions which led to its formation are reversed.



About 25% of the oxygen free radicals formed in (4) directly combine with ozone to produce diatomic oxygen molecules.



Most of the ozone decomposition is caused by catalytic reactions with other free radicals found in the upper atmosphere. These include $\text{OH}\cdot$, $\text{NO}\cdot$ and $\text{Cl}\cdot$. The following equations illustrate the reactions involving $\text{NO}\cdot$ radicals. Note that the sum of equations (6) and (7) is equal to equation (5).



The net result of the formation and decomposition cycle of ozone is that solar energy is converted to heat energy. In addition, atmospheric turbulence produces an ozone gradient in the atmosphere, which leads to its maximum concentration at an altitude around 25 km. Figure 13.16 summarises the ozone formation and decomposition reactions.

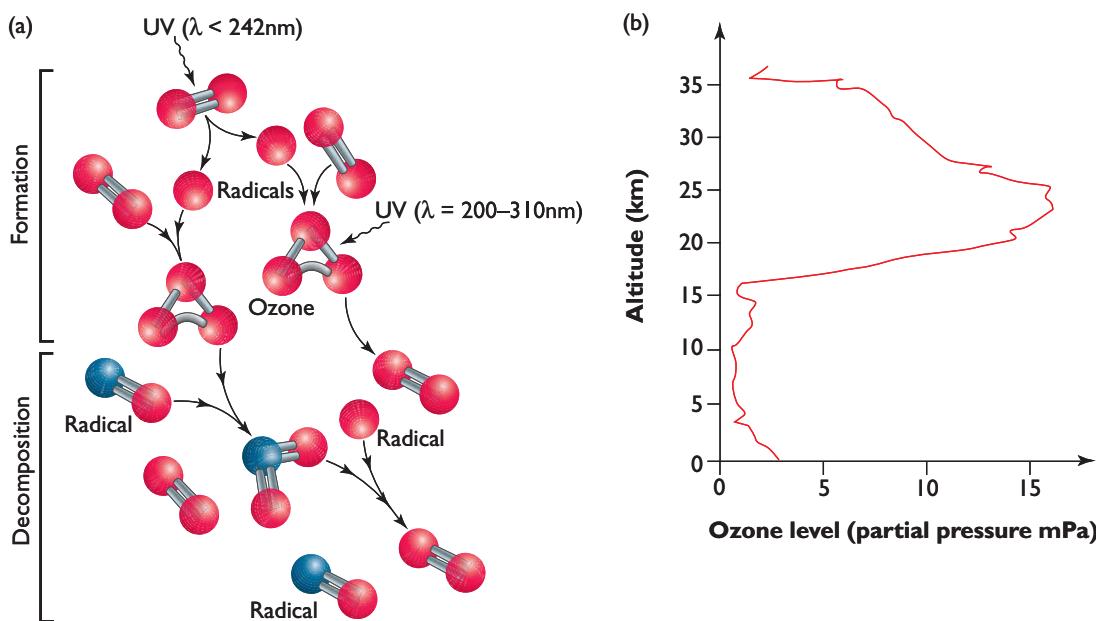


Figure 13.16

(a) Ozone forms and decomposes in the upper atmosphere. A steady state is attained unless other processes occur to upset this steady state. (b) Ozone gradient changes with altitude.

Haloalkanes, CFCs and halons

When alkanes react with halogens (members of Group VII of the periodic table) they form new compounds that are collectively called **haloalkanes**.

The current IUPAC nomenclature rules are used to name haloalkanes. These rules are summarised on the following page.

haloalkanes: alkane molecules in which one or more hydrogen atoms have been substituted by halogen atoms (e.g. F, Cl, Br, I)

Nomenclature rules for haloalkanes

1. The halogen functional groups are named using prefixes placed in front of the name of the alkane:
F: fluoro- Cl: chloro- Br: bromo- I: iodo-
2. Select the longest unbranched hydrocarbon chain in the haloalkane molecule. Count the number of carbons in this chain. This number will decide the stem name of the alkane.
3. Number the chain from the end that produces the lowest set of locants (numbered positions) for all the functional groups including any alkyl functional groups that may also be present along the chain. (*Note:* The lowest set of locants is the set which, when compared term by term with other locant sets, each cited in order of increasing value, has the lowest term at the first point of difference.)
4. In naming the haloalkanes, the functional groups are named alphabetically using the locants to designate positions (disregard prefixes such as di-, tri- etc. in this alphabetical ordering).
5. If the previous rules lead to more than one possible name, then the correct name is the one in which the lowest locant is assigned to the functional group cited first as a prefix.

SAMPLE PROBLEM 13.2a ➤

Use the nomenclature rules to name the following haloalkane.



SOLUTION ➤➤➤➤➤

1. The ‘chloro’ is the only functional group present in this molecule.
2. The longest unbranched chain contains 6 carbon atoms. Thus the parent alkane is hexane.
3. The chain will be numbered from the right-hand end as this will give the ‘chloro’ group a locant of 3 on the chain rather a locant of 4 if numbering from the left.
4. The name of the molecule is 3-chlorohexane.

SAMPLE PROBLEM 13.2b ➤

Use the nomenclature rules to name the two haloalkanes in Figure 13.17.



Figure 13.17 Haloalkanes A and B

SOLUTION ➤➤➤➤➤

Haloalkene A

1. There are two ‘chloro’ and one ‘fluoro’ functional groups.
2. The longest unbranched chain contains three carbon atoms. Thus the parent alkane is propane.
3. Naming of functional groups is done alphabetically. Ignore the prefix ‘di’ in determining alphabetical order. Chloro groups are named before the fluoro group.

4. Numbering the chain from the left gives the functional groups locants of 1, 2 and 3.

Numbering the chain from the right gives the functional groups locants of 1, 2 and 3. Thus the set of locants is the same from either end.

To give a unique name to this molecule we then apply the last rule to give the prefix cited first the lowest locant (i.e. chlorine); thus the chain is numbered from the left. Consequently, 'fluoro' is at locant 3 and the two 'chloro' groups are at locants 1 and 2.

The name of the molecule is 1,2-dichloro-3-fluoropropane.

Haloalkene B

1. There is one 'bromo' and one 'chloro' functional group.
2. The longest unbranched chain contains five carbon atoms. Thus the parent alkane is pentane.
3. 'Bromo' is named before 'chloro'.
4. Numbering the chain from the left gives the functional groups locants of 2 and 4.

Numbering the chain from the right gives the functional groups locants of 2 and 4.

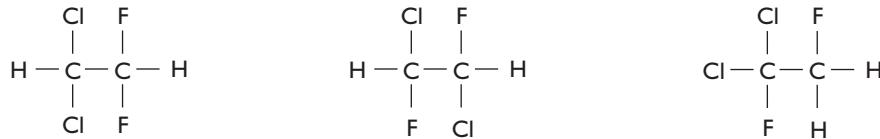
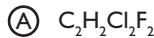
The set of locants is the same from either end.

To give a unique name to this molecule we then apply the last rule to give the prefix cited first the lowest locant (i.e. bromine); thus the chain is numbered from the left. Consequently, 'bromo' is at locant 2 and 'chloro' is at locant 4.

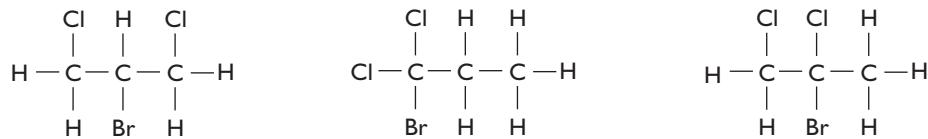
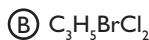
The name of the molecule is 2-bromo-4-chloropentane.

Isomers

Haloalkanes often exist in isomeric forms. The variable location of the halogen functional groups within the molecule leads to the formation of isomers. Figure 13.18 shows examples of isomers of selected haloalkanes together with their systematic names. Check that the nomenclature rules are in agreement with these names.



1,1-dichloro-2,2-difluoroethane 1,2-dichloro-1,2-difluoroethane 1,1-dichloro-1,2-difluoroethane



2-bromo-1,3-dichloropropane 1-bromo-1,2-dichloropropane 2-bromo-1,2-dichloropropane

Figure 13.18

Check that each isomer has the same molecular formula.

chlorofluorocarbons (CFCs): haloalkane molecules in which all the hydrogen atoms have been replaced by fluorine or chlorine atoms

halon: haloalkane molecules in which all the hydrogen atoms have been replaced by bromine, chlorine and/or fluorine atoms

13.1 PRACTICAL ACTIVITIES



Modelling haloalkanes

Chlorofluorocarbons and halons

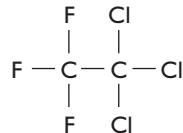
Chlorofluorocarbons (CFCs) and **halons** are examples of haloalkanes. CFCs were originally developed to replace toxic ammonia as a refrigerant gas. CFCs had several advantages over ammonia in that they were unreactive and non-toxic, and readily liquefied on compression. Thousands of tonnes of CFCs were manufactured for use as refrigerants in air conditioners and refrigerators as well as propellants in spray cans (such as deodorants and insecticides). These CFCs also found wide use as ‘blowing’ agents to make expanded plastics such as polystyrene foam as well as solvents for cleaning electronic circuits and dry cleaning.

Chlorofluorocarbons typically contain only ‘chloro’ and ‘fluoro’ functional groups. These molecules contain no hydrogen atoms.

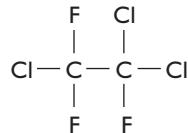
Halons were developed for use in extinguishing fires, particularly in large computer systems and on aeroplanes. Halons are bromofluorocarbons and typically contain at least one ‘bromo’ group as well as ‘fluoro’ functional groups. ‘Chloro’ functional groups may also be present. These molecules contain no hydrogen atoms.

Figure 13.19 shows examples of CFCs and halon molecules.

(a) CFCs



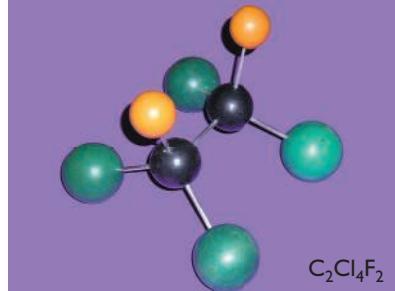
1,1,1-trichloro-2,2,2-trifluoroethane



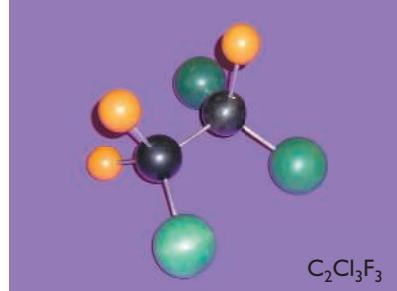
1,1,2-trichloro-1,1,2-trifluoroethane



CCl_3F

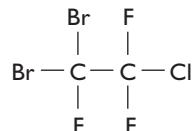


$\text{C}_2\text{Cl}_4\text{F}_2$

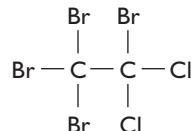


$\text{C}_2\text{Cl}_3\text{F}_3$

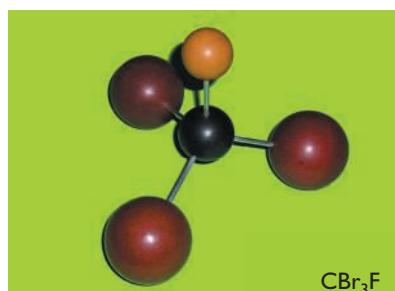
(b) Halons



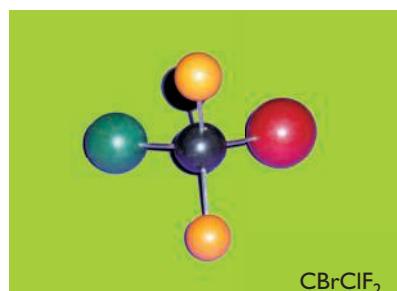
1,1-dibromo-2-chloro-1,2,2-trifluoroethane



1,1,1,2-tetrabromo-2,2-dichloroethane



CBr_3F



CBrClF_2

Figure 13.19

Note the difference in the constituent atoms in (a) CFCs and (b) halons.

Stratospheric ozone depletion

In 1976, the British Antarctic Survey at Halley Bay noted a 10% drop in ozone levels in the stratosphere over Antarctica in the southern spring (August to October). This was unusual, as levels had remained roughly constant since measurements had begun in 1957. These scientists made their measurements using ground-based Dobson UV spectrometers as well as on air samples collected by high-altitude balloons and aircraft. Initially, they considered that either their instruments were malfunctioning or that the apparent seasonal losses were due to natural events such as sunspot activity or volcanic action. They became very concerned in 1983, however, when they observed record losses of ozone that spring.

Measurements

By 1985, atmospheric measurements over Antarctica showed a 50% reduction in ozone concentrations in the stratosphere over the previous decade. This result correlated with independent data recorded by the total ozone mapping spectrometer (TOMS) and a solar backscatter ultraviolet detector orbiting the Earth in the Nimbus-7 satellite. Since then other satellites (including some that use infra-red radiometers) have been used to scan the upper atmosphere to determine ozone levels.

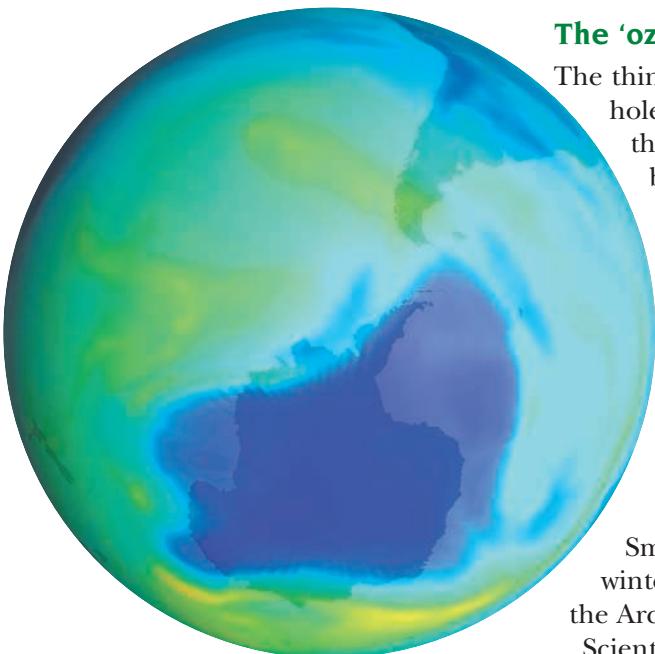
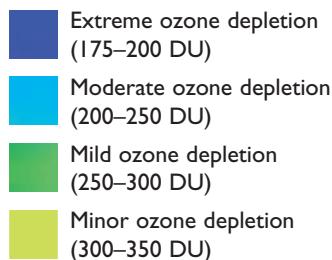
Another technique used to measure ozone levels involves the use of UV lasers. Pulses of different wavelength UV laser light are fired from several lasers at ground level into the stratosphere. The degree of absorption of this light at various levels is measured using UV spectrometers attached to telescopes. From this data the ozone concentration can be calculated. The use of many different methods (including new electrochemical and chemiluminescence techniques) to measure ozone levels has improved the reliability of the collected data and has demonstrated that ozone loss is a real phenomenon.

The 'ozone hole'

The thinning of the ozone layer results in what is often called the 'ozone hole'. In the 1980s the ozone loss worsened, and the area over which the ozone loss occurred became wider. During 1987, the ozone hole broke up, and ozone-depleted air spread over large areas including southern Australia and New Zealand. Over several days in mid-December 1987 the ozone layer had thinned by 12% over Melbourne. Further significant ozone depletions were recorded (by later launches of TOMS instruments) in the southern springs of the 1990s. The largest ozone holes measured so far occurred in 2003, 2000 and 1998. The CSIRO report for September 2005, however, has revealed that the 2005 ozone hole was the fourth largest since 1979. The hole covered an area of 26.4 million square kilometres.

The ozone hole, however, was not confined to the Antarctic. Small decreases in ozone levels were noted above the Arctic in the winters of 1994 and 1995. By 1996 the thinning of the ozone layer over the Arctic had reached 40%.

Scientists became alarmed over the decreasing concentrations of ozone, as this would lead to more UV radiation reaching ground level. The vast numbers of phytoplankton and zooplankton in the surface waters of the ocean would be affected by an increase in UV. As these organisms are vital components of the ocean food chain, a reduction in ozone levels could produce a significant decline in marine organisms. Studies of skin



3 October 1985

Figure 13.20

Ozone maps are produced from data collected by instruments aboard satellites as well as ground-based instruments. (DU = Dobson units)

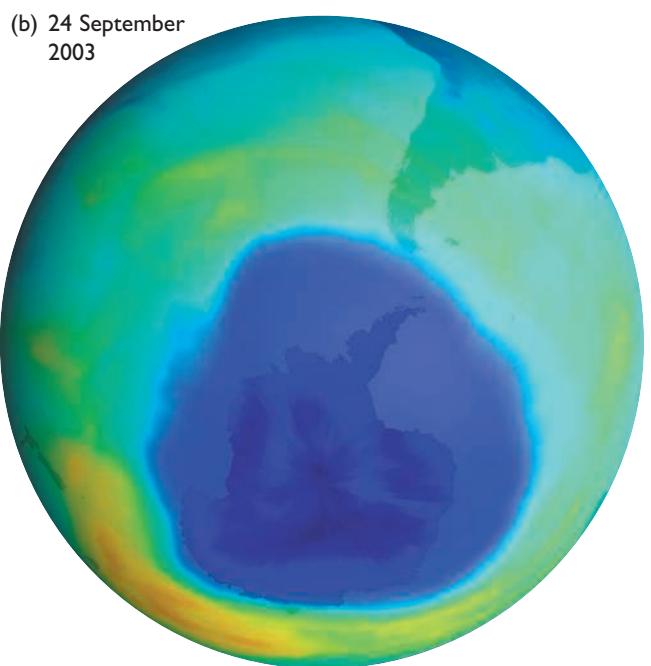
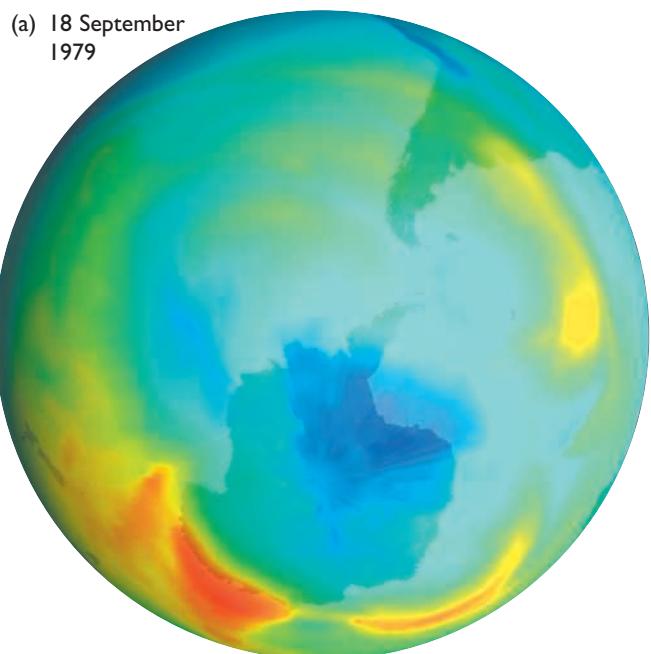
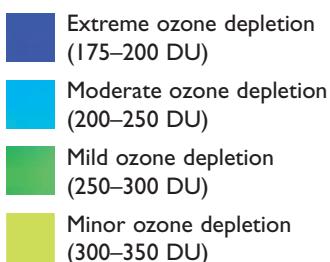
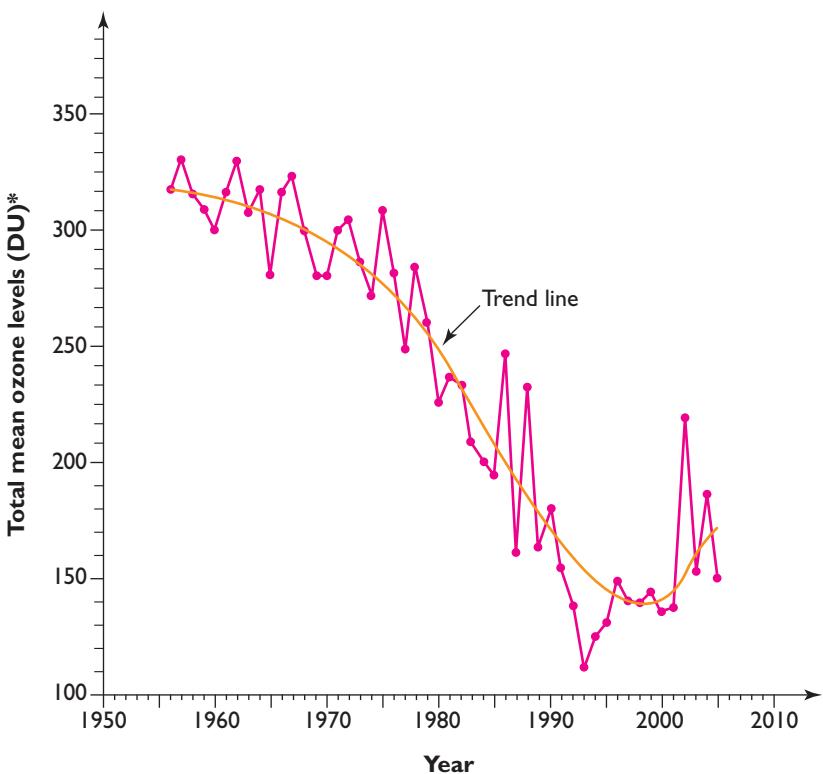
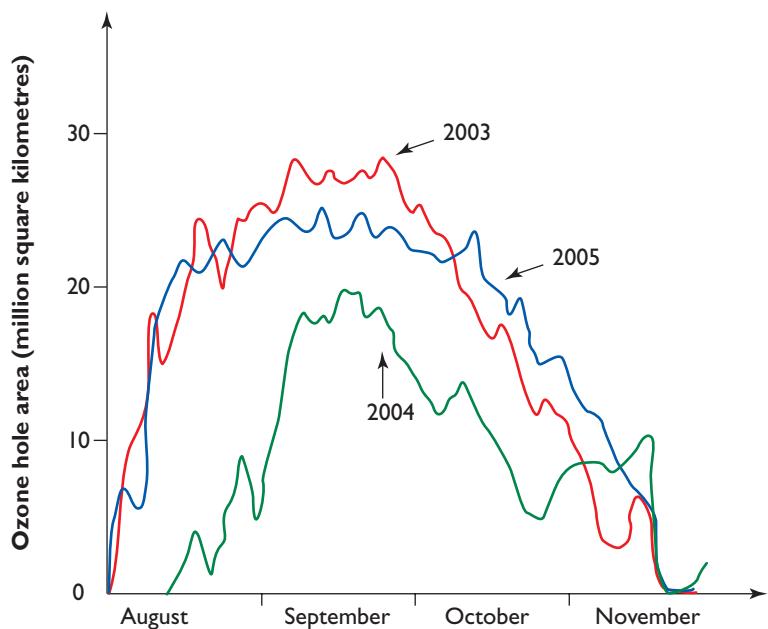


Figure 13.21

The ozone depletion has reached significant levels since the 1980s. Since 1979 (a), and up to 2003 (b), the ozone loss in spring has grown significantly.

cancer and sunburn rates in Punta Arenas, Chile (the southernmost city in the world), in the 14-year period 1987–2000 have shown that there has been an increase of 66% in skin cancers in the second half of this time interval compared with the first half. These results correlate well with the 56% reduction in peak stratospheric ozone recorded over the same period.

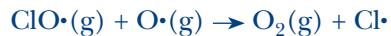


The cause of ozone depletion

Measurements of the levels of chlorine oxide radicals ($\text{ClO}\cdot$) in the stratosphere provided the first piece of evidence that would lead to an explanation of the thinning of the ozone layer. Chlorine oxide is formed when atmospheric chlorine compounds, such as chloromethane (methyl chloride), undergo photodissociation to form methyl radicals and reactive chlorine radicals. Chloromethane is produced by the action of plankton in the oceans and by forest fires. Chloromethane is also industrially synthesised. A small quantity of chloromethane reaches the stratosphere and undergoes photodissociation. The chlorine radicals rapidly attack ozone molecules and produce $\text{ClO}\cdot$.



Chlorine oxide radicals can react with many other species in the stratosphere. For example, the chlorine oxide radicals may react with oxygen free radicals to produce dioxygen and more chlorine radicals.



Another possible reaction pathway is described in the equations below. The $\text{ClO}\cdot$ radical forms a dimer (Cl_2O_2), which ultimately generates more $\text{Cl}\cdot$ radicals to catalyse further ozone decomposition.



Figure 13.22 shows that stratospheric regions with a high $\text{ClO}\cdot$ concentration have a low O_3 concentration.

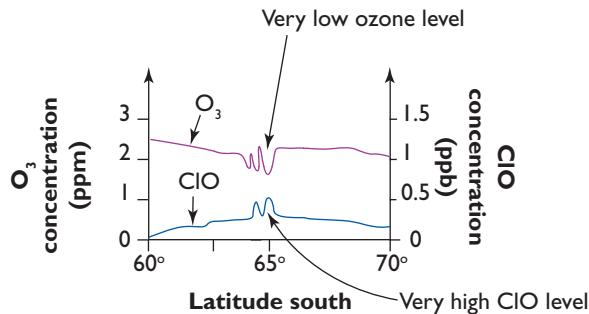


Figure 13.22

The decrease in ozone levels correlates with increases in ClO levels.

Chlorine oxide radicals may also become deactivated by reaction with nitrogen dioxide gas. This reaction produces chlorine nitrate.

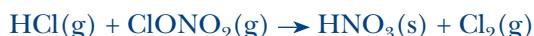


Chlorine free radicals can also become deactivated by reaction with methane to form hydrogen chloride. Both hydrogen chloride and chlorine nitrate are normally inactive with regard to ozone decomposition.



The Antarctic spring

The ozone depletion process reaches its peak in the late Antarctic spring (October) when the sunlight returns to the South Pole following the dark, endless nights of winter. During this long winter a strong circum-polar vortex forms in the middle to lower regions of the stratosphere over Antarctica. This is an ice-cold mass of swirling air in which special icy clouds called *polar stratospheric clouds* are formed at temperatures about -80°C . This vortex isolates the air and the clouds within it. These clouds act as reservoirs for hydrogen chloride and chlorine nitrate, as well as dinitrogen pentoxide and other halogenated species. Chlorine, hypochlorous acid and nitric acid are formed very rapidly by heterogeneous reactions on the surface of these icy crystals.



The presence of nitric acid in the icy crystals slows down the removal of $\text{ClO}\cdot$ radicals by NO_2 in the stratospheric air. Consequently, the presence of nitric acid assists ozone depletion.

As the sunlight returns in spring, there is a rapid rise in UV, which causes photodissociation of chlorine molecules and HOCl molecules to form chlorine radicals as well as hydroxy radicals. These radicals initiate the ozone decomposition process. About 70% of the ozone is destroyed in the lower stratosphere over several weeks.



It has been estimated that one chlorine radical can destroy up to tens of thousands of ozone molecules before it is removed from the stratosphere by other processes. The destruction of ozone molecules by chlorine radicals is much more rapid than the natural decomposition of ozone caused by oxygen radicals. This indicates that the activation energy for the $\text{O}_3/\text{O}\cdot$ reaction is higher than for the $\text{O}_3/\text{Cl}\cdot$ reaction (Figure 13.23).

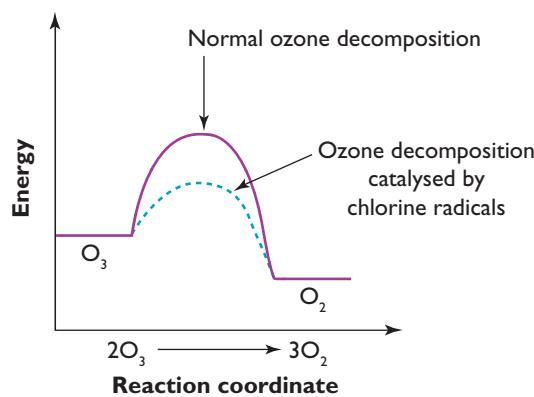


Figure 13.23
Ozone destruction by Cl radicals
is more rapid than that caused
by O radicals.

By the end of spring the ozone destruction process comes to an end due to the exhaustion of the reservoir of molecular chlorine formed during

the previous winter. By December the vortex has broken up. The levels of ozone in the stratosphere over Antarctica return gradually to normal as natural wind currents mix the polar air with air from lower latitudes. This mixing had been prevented during the winter due to the exclusion of outside air by the polar vortex.

CFCs and halons

Chlorinated hydrocarbons and other halogenated hydrocarbons are responsible for the thinning of the ozone layer. Some chlorinated compounds such as CH_3Cl and HCl are natural. They rarely reach the stratosphere in significant amounts as they are oxidised quickly in the troposphere. Other chlorinated compounds are synthetic. These synthetic halogenated hydrocarbons—commonly called chlorofluorocarbons (CFCs) and bromofluorocarbons (halons)—slowly diffuse from the troposphere into the stratosphere. Once in the stratosphere they undergo photodissociation to produce reactive chlorine and bromine radicals that attack and destroy ozone molecules. The work of chemists such as Paul Crutzen, Mario Molina and Sherwood Rowland have led to our understanding of this complex process. In 1995 they were awarded the Nobel Prize in Chemistry for their discoveries about ozone depletion.

The following reactions show the photodissociation reactions involving CFCs and halons. CFC-11 has an atmospheric lifetime of 70 years.

- (a) trichlorofluoromethane (CFC-11) (CFCl_3)

$$\text{CFCl}_3(\text{g}) + \text{UV} \rightarrow \text{CFCl}_2^{\cdot}(\text{g}) + \text{Cl}^{\cdot}(\text{g})$$
- (b) bromotrifluoromethane (Halon 1301) (CF_3Br)

$$\text{CF}_3\text{Br}(\text{g}) + \text{UV} \rightarrow \text{CF}_3^{\cdot}(\text{g}) + \text{Br}^{\cdot}(\text{g})$$

Halons produce bromine radicals that cause greater ozone depletion than chlorine radicals. Halon 1301 has an atmospheric lifetime of 110 years. Halon 1301 has ten times the ozone depleting potential (ODP) of CFC-11. CFC-11 is used as a standard and is assigned an ozone depletion potential of 1.0. Most CFCs have ODP values between 0.01 and 1.0. Halons have ODP values up to 10.



Table 13.2 Ozone depletion potentials (ODP)

Compound	IUPAC name	ODP
CFC-11(standard)	trichlorofluoromethane	1.0
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane	0.8
CFC-115	chloropentafluoroethane	0.6
Halon 1211	bromochlorodifluoromethane	3.0
Halon 1301	bromotrifluoromethane	10.0
CCl_4	tetrachloromethane	1.1
CH_3Br	bromomethane	0.6

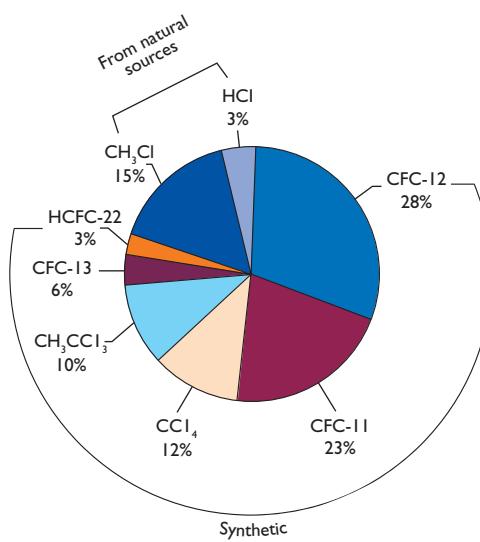


Figure 13.24

The pie graph shows the primary sources of chlorine entering the atmosphere.



CFC DECOMPOSITION OF OZONE

13.2 DATA ANALYSIS

Climate conferences and replacements for CFCs

Tetrachloromethane is commonly called *carbon tetrachloride*. It was once used in dry cleaning but was eventually found to be toxic.

The bromine radicals react with ozone to form bromine oxide radicals. Bromine radicals are then regenerated by reaction with UV light, and the process of ozone decomposition continues.

In the decade from 1988 to 1998, CSIRO atmospheric scientists discovered that the amount of Halon 1211 in the atmosphere at Cape Grim on the west coast of Tasmania had increased by 25%. The atmospheric lifetime of Halon 1211 is 25 years.

SYLLABUS FOCUS

27. CFCS AND ATMOSPHERIC CHEMISTRY

The English physicist Sidney Chapman first proposed a theory in 1930 that explained how sunlight was involved in the formation and decomposition of ozone in the stratosphere. His theory failed to accurately predict the ozone levels at different altitudes. The Belgian scientist Marcel Nicolet later showed that molecular radicals such as $\text{OH}\cdot$ and $\text{HO}_2\cdot$ were responsible for some ozone decomposition.



In 1968–70, Harold Johnston (USA) and Paul Crutzen (Netherlands) showed that nitrogen oxide molecular radicals emitted in the exhaust gases of high-altitude supersonic aircraft could catalytically destroy up to 20% of the ozone in the stratosphere. The $\text{NO}\cdot$ radical is regenerated in this cycle and can go onto to destroy tens of thousands of ozone molecules.



The potential destruction of the ozone layer by Freon®, or chlorofluorocarbons (CFC) gases released during the blowing of plastic foams, as well as the leakages from refrigerant gases in air-conditioners, was described in a paper published by Mario Molina and Sherwood Rowland (USA) in 1974. Despite being chemically inert, these molecules could be transported to the stratosphere and undergo photodissociation to produce reactive chlorine radicals that destroy the ozone.

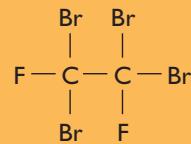


In the early 1980s, restrictions were placed on the use of these ozone-damaging CFCs as propellants and refrigerants. Following the discovery of the thinning ozone layer over Antarctica in the mid 1980s, it was soon realised that halogenated hydrocarbons needed to be phased out completely and alternatives found. Crutzen and other scientists explained the rapid ozone loss in the stratosphere over Antarctica in terms of a catalytic surface process occurring on ice crystals formed in the cold air of the wind vortex over the South Pole. In this vortex, $\text{ClO}\cdot$ and Cl_2 are rapidly formed. A catalytic cycle involving $\text{ClO}\cdot$ leads to extensive ozone destruction.

13.1 Questions

1. The lowest layer of the atmosphere is the
A troposphere.
B stratosphere.
C ionosphere.
D thermosphere.
2. Select the statement that is true about temperature and the layers of the atmosphere.
A Temperature increases with altitude in the thermosphere.
B Temperature increases with altitude in the stratosphere.
C Temperature increases with altitude in the mesosphere.
D Temperature decreases with altitude in the thermosphere.
3. The ozone layer is located in the
A thermosphere.
B mesosphere.
C stratosphere.
D troposphere.
4. Select which of the listed gases has the greatest concentration in the troposphere.
A Hydrogen
B Carbon dioxide
C Ozone
D Argon
5. Select the molecule in which a coordinate bond is present.
A Ozone
B Dioxygen
C Carbon dioxide
D Water
6. Photodissociation of CFCs produces radicals that cause major damage to the ozone layer. Select the radical that is produced by CFC photodissociation.
A Oxygen radical
B Chlorine radical
C Fluorine radical
D Hydrogen radical
7. (Complete Data analysis 13.2 before answering this question.) Select a compound that is currently used as a refrigerant gas replacement for CFCs.
A Carbon dioxide
B Ammonia
C HCFC
D Halons
8. The concentration of nitrogen in sea level tropospheric air is 78.09% (v/v). A 10 litre sample of air is collected at 100 kPa and 0°C.
 - (a) Calculate the concentration, in parts per million, of nitrogen present in the air sample.
 - (b) Determine the volume of pure nitrogen gas that could be extracted from the 10 L sample of air at the same temperature and pressure.
 - (c) Use your answer in (b) to calculate (i) the moles and (ii) the mass of nitrogen extracted.
9. Draw Lewis electron dot diagrams for each of the following molecules and ions.
 - (a) Ozone
 - (b) Nitrogen
 - (c) Hydronium ion
10. (a) Compare the physical properties of diatomic oxygen and ozone.
(b) Explain why oxygen is vital to aerobic organisms.
(c) Explain why ozone is considered to be a tropospheric pollutant and a danger to human health.
11. Write balanced equations for each of the following reactions.
 - (a) The reaction of ozone with oxygen free radicals
 - (b) The photodissociation of 1-chloropropane to produce chlorine radicals
 - (c) The reaction of chlorine radicals with ozone.
12. (a) Explain the danger of the ozone layer thinning.
(b) Describe with the aid of appropriate equations how ozone is naturally formed in the stratosphere.
13. Explain how scientists have collected data on ozone levels in the stratosphere.
14. Figure 13.25 shows structures of two halogenated hydrocarbons.
 - (a) Name each molecule systematically.
 - (b) Classify each molecule as a CFC or a halon.

⊗



⊗



Figure 13.25

15. Tetrachloromethane is also called CFC-10. Draw a structural formula for tetrachloromethane.
16. Draw a structural formula for 1,1,1,2-tetrachloro-2,2-difluoroethane.
17. (Complete Data analysis 13.2 before answering this question.)
(a) Identify the chemical composition of HCFCs and explain why they are important.
(b) HCFC-151 is a molecule with the condensed molecular formula:



- (i) Name this molecule using IUPAC nomenclature.
(ii) Draw a structural formula for, and name, one isomer of HCFC-151.
18. (Complete Data analysis 13.2 before answering this question.)
(a) Explain the relationship between ozone depletion and the Montreal Protocol.
(b) Discuss Australia's compliance with the Montreal Protocol.
(c) Explain why exemptions have been granted for the continued use of methyl bromide by various countries beyond the phase-out dates for brominated hydrocarbons.



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SUMMARY

- The atmosphere consists of layers. These are (in order of increasing altitude) troposphere, stratosphere, mesosphere, thermosphere.
- The atmosphere is a mixture of gases and particulate matter. Nitrogen is the most abundant gas, followed by oxygen, argon and carbon dioxide.
- There are many lower atmospheric pollutants that have been produced by human activity or natural processes. These include carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide, volatile organic compounds and ozone.
- Coordinate covalent bonding occurs when one atom provides both electrons to form the bonding pair. Coordinate bonding occurs in ammonium ions, hydronium ions, carbon monoxide and ozone.
- Oxygen has two allotropic forms: dioxygen and trioxygen (ozone).
- Ozone is more reactive than dioxygen as its bonds are weaker. Oxygen free radicals are more reactive than either dioxygen or ozone.
- The ozone layer in the stratosphere acts as a UV shield.
- The ozone molecules in the stratosphere are constantly decomposing and reforming.
- The presence of CFCs and halons in the upper atmosphere has led to a decrease in ozone levels in spring, particularly over Antarctica. This is caused by catalytic reactions involving chlorine radicals and bromine radicals.
- CFCs and halons are examples of haloalkanes.
- The Montreal Protocol has established phasing out dates for the use of CFCs and halons and their replacement by less-damaging molecules (i.e. that have a lower ozone depleting potential).
- The ozone hole is not expected to recover until 2065.

PRACTICAL ACTIVITIES

13.1



MODELLING HALOALKANES

In this activity, you will use your molecular model kit to construct models of haloalkanes.

Constructing molecular models

1. Use the supplied molecular model kit to construct models of the following haloalkanes.

- (a) $\text{C}_2\text{H}_3\text{Cl}_3$
- (b) $\text{C}_3\text{H}_6\text{FBr}$

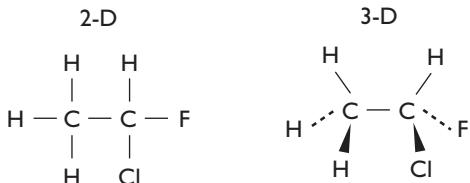
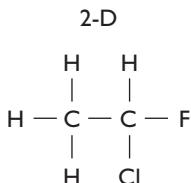
In each case, investigate possible isomers that may be constructed.

2. Use IUPAC rules to name each isomer constructed in question 1.

Drawing 2-D and 3-D diagrams of haloalkanes

Figure 13.26 shows how a 2-D diagram (or structural formula) of a haloalkane can be represented in 3-D.

Example: $\text{C}_2\text{H}_4\text{FCl}$



— In plane
► Out of plane (front)
----- Out of plane (back)

Figure 13.26 Use the information in this diagram to draw 2-D and 3-D diagrams of your haloalkanes.

Using this same technique, construct the following haloalkanes and then draw 2-D and 3-D representations of these molecules.

- (a) CH_2BrCl
- (b) $\text{CH}_2\text{BrCH}_2\text{I}$

Simulations and animations

The internet sites on the CD will allow you to view molecular models of organic molecules including haloalkanes. You may view molecules using ball and stick models or space-filling models. You can also rotate and enlarge these models. (Chime® plug needs to be installed on your computer.)

DATA ANALYSIS

13.2 DATA ANALYSIS

CLIMATE CONFERENCES AND REPLACEMENTS FOR CFCs

Process the following information and answer the questions that follow.

The Montreal Protocol

In 1985, the Vienna Convention examined ways of preventing the destruction of the ozone layer. International cooperation was required for the proposed mechanisms to succeed. As a result of this convention in Vienna, 28 countries signed an international treaty called the *Montreal Protocol* (established under the United Nations Environment Program). By September 1987, 46 countries had signed the Protocol. The treaty came into force two years later. The Montreal Protocol requires the phasing out of ozone-destroying chemicals (such as tetrachloromethane, CFCs and halons) according to a timetable drawn up by the parties to the convention. The treaty also includes trade sanctions to ensure that its goals are achieved. The treaty offers incentives to non-signatory nations to sign this historic agreement. Subsequent meetings in London (1990), Copenhagen (1992), Vienna (1995), Montreal (1997) and Beijing (1999) have produced amendments to the original treaty that aim to speed up the phasing out of CFCs and halons and to establish different phasing-out periods for developed and developing countries. The fourteenth meeting in Montreal in 2002 established a task force to further assist developing countries. The sixteenth meeting was held in Prague in 2004. At that meeting, sixteen exemptions were sought until 2006 for the use of methyl bromide (bromomethane) as an important soil fumigant to control pests.

Timetable

The timetable for implementing the Montreal Protocol is shown below. Australia has met all compliance dates and is ahead of the target for phasing out HCFCs.

Table 13.3 Montreal Protocol control measures

Ozone depleting substances	Developed countries	Australian compliance	Developing countries
CFCs	phased out by end of 1995	phased out	total phase-out by 2010
halons	phased out by end of 1993	phased out	total phase-out by 2010
tetrachloromethane	phased out by end of 1995	phased out	total phase-out by 2010
HCFCs	65% reduction by 2010	2010 target met by 2004	freeze in 2016 at 2015 base levels
	90% reduction by 2015		total phase out by 2040
	phased out by 2020*		

(* Up to 0.5% of base level can be used to 2030.)

By 2004, a total of 189 nations had signed the Montreal Protocol, although many have still not signed the various amendments. Industrialised nations have contributed considerable funds to the program to provide incentives to other nations. Kofi Annan, Secretary-General of the United Nations stated:

Perhaps the single most successful agreement to date has been the Montreal Protocol.

Replacement compounds

As part of the process of phasing out ozone-destroying chemicals, chemists looked for short-term replacement compounds for CFCs and halons.

HCFCs or hydrochlorofluorocarbons are now commonly used in place of CFCs as they are broken down in the troposphere due to the higher reactivity of their C—H bonds. Table 13.4 shows some ozone depletion potential (ODP) values for HCFCs. HCFC-123 (CF_3CHCl_2) is

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used to produce plastic foam. It is oxidised in the troposphere by OH radicals to form CF_3CCl_2 , which in turn is oxidised by oxygen to form carbon dioxide, water and hydrogen halides. CHClF_2 is used to produce plastic foam fast-food containers, as well as the refrigerant in air-conditioners. The long-term toxicity of these HCFCs to humans is yet to be determined. HCFCs are temporary substitutes for CFCs, and are expected to be fully phased out by 2030.

HFCs or hydrofluorocarbons are another promising group of CFC replacements. These molecules contain no bromine or chlorine (ODP = 0) and should not promote ozone destruction even if they are transported into the stratosphere. CF_3CFH_2 (1,1,1,2-tetrafluoroethane) is now being used in place of CFCs in refrigeration units and air-conditioning units.

Table 13.4 Ozone Depletion Potentials for HCFCs

Compound	IUPAC name	ODP
HCFC-22	chlorodifluoromethane	0.055
HCFC-123	2,2-dichloro-1,1,1-trifluoroethane	0.02
HCFC-124	2-chloro-1,1,1,2-tetrafluoroethane	0.02

Despite the efforts being undertaken to ban the use and production of ozone destroying chemicals, the Western world in 2003 was still responsible for half the global emissions of ozone-destroying chemicals.

In 2005, it has been suggested that the continued emissions from Western countries is coming from old appliances such as abandoned refrigerators in waste dumps. Foam goods and aerosol cans manufactured before the mid-1990s are also likely culprits. CFCs are also likely to leak out from appliances when they are crushed during the recycling process. Monitoring at Cape Grim in Tasmania has shown that Australia's rate of emissions of CFCs is now very low.

Questions

- Explain the purpose of the Montreal Protocol.
- Explain why the phasing-out period for bromomethane (methyl bromide) has been extended.
- (a) Identify the chemicals that have been introduced to replace CFCs.
(b) Explain why these molecules were chosen to replace CFCs.
- Explain why HFCs are a promising group to replace CFCs.
- (a) State the systematic name of the molecule with the following condensed structural formula.
 $\text{ClF}_2\text{CCHF}_2$
(b) Classify this molecule as a CFC, HCFC, HFC or halon.
- State one common use of the molecule CF_3CFH_2 .