

LEAVING CERTIFICATE

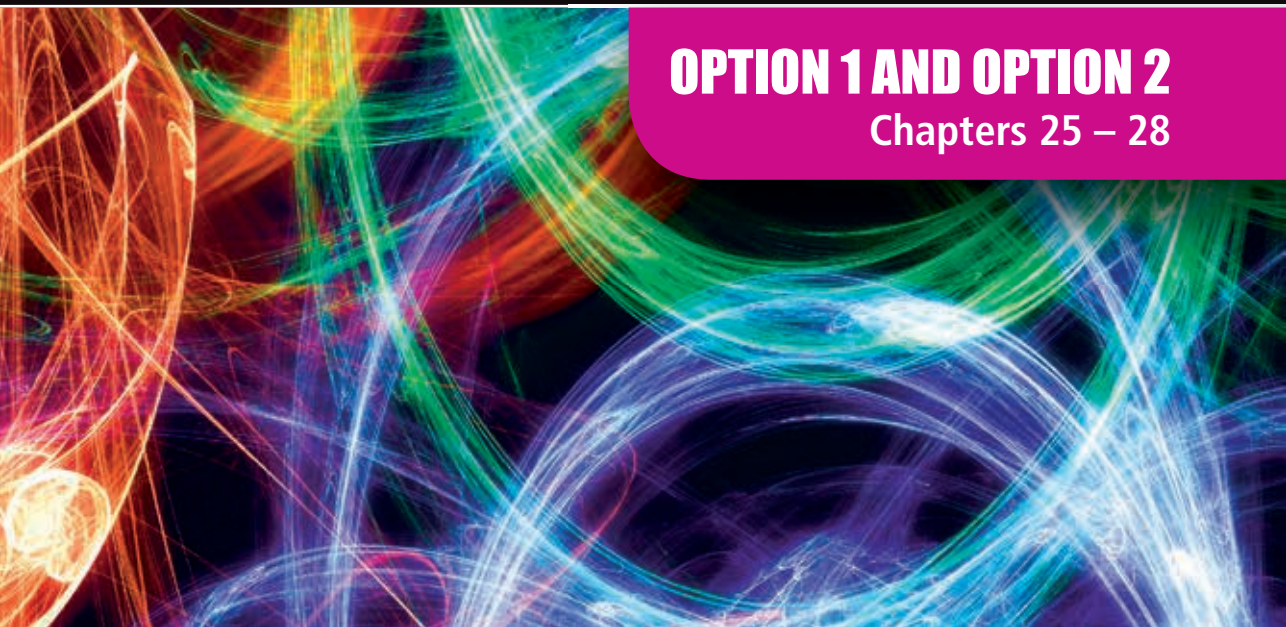
# REVISE

## CHEMISTRY LIVE!

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**OPTION 1 AND OPTION 2**

Chapters 25 – 28



**FOLENS**



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## Option 1

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In this chapter you will revise:

- The contribution of chemistry to society
- General principles of industrial chemistry
- Case Study 1: The manufacture of ammonia and urea by IFI at Cobh
- Case Study 2: The manufacture of nitric acid by IFI at Arklow
- Case Study 3: The manufacture of magnesium oxide by Premier Periclase at Drogheda

For your examination, you need only have a knowledge of one of these three case studies.

## 25.1 The Contribution of Chemistry to Society

Chemistry improves the quality of our lives by:

- providing us with fuels, metals, medicines, enzymes, soaps, detergents, paints, inks, dyes, and water that is fit to drink
- providing us with many important materials such as plastics, synthetic fibres, semi-conductor devices and liquid crystals
- increasing crop yields with the aid of fertilisers, herbicides and pesticides
- providing stable and well-paid employment, as well as contributing thousands of millions of euro to our national economy.

## 25.2 General Principles of Industrial Chemistry

- A product may be manufactured using either a **batch process**, a **continuous process** or a **semi-continuous process**.
- **Batch process** – the raw materials are allowed to react with each other inside a vessel under controlled conditions of temperature and pressure for a given time. The contents of the vessel are then removed. Batch processes are used in the manufacture of pharmaceuticals.
- **Continuous process** – the raw materials are fed in non-stop at one end of the plant and the product is removed non-stop at the other end of the plant, e.g. the manufacture of ammonia. Continuous processes are used in the manufacture of large-scale quantities of materials.
- **Semi-continuous process** – a combination of a batch process and a continuous process. The first stage involves a batch process to make the product. The second

stage involves a continuous process where the product is purified using feed from several batch reactors, e.g. the manufacture of soft drinks.

- All of the three case studies on the Leaving Certificate chemistry syllabus are continuous processes.

The advantages and disadvantages of batch and continuous processes are summarised in Tables 25.1 and 25.2.

	Advantages of Batch Process	Disadvantages of Batch Process
1.	Since small quantities are being made, the capital cost of the plant is not too high.	Filling and emptying the reactor is time-consuming.
2.	The same vessel can be used for a range of products.	Contamination from batch to batch is more likely.
3.	It is easy to cater for slow reactions.	The process may be difficult to control in the case of an exothermic reaction.

**Table 25.1** Some advantages and disadvantages of the batch process.

	Advantages of Continuous Process	Disadvantages of Continuous Process
1.	It is very suitable for large-scale production.	Very high capital costs to build the plant.
2.	Long periods of use are possible before shutdown is needed for maintenance.	The plant is 'tailor made' – less flexibility in terms of products manufactured.
3.	There is low risk of contamination since only one product is being made.	If plant is not run at full capacity, it may not be cost effective to manufacture the product.

**Table 25.2** Some advantages and disadvantages of the continuous process.

In all, there are ten general characteristics of industrial chemical processes.

1. **Feedstock.** The reactants used in the industrial process. Feedstock is produced from raw materials that may have to be treated to ensure that they are sufficiently pure.
2. **Rate.** The best conditions of temperature, pressure and catalyst are selected for the process to occur at the optimum rate.
3. **Yield of product.** The conditions of temperature, pressure and catalyst chosen must be such as to ensure a reasonable yield of product in a reasonable time. When choosing the reaction conditions, there often has to be a compromise between rate and yield.
4. **Co-products.** The other products expected to be formed along with the main product being manufactured. Side reactions may give rise to unwanted products called **by-products**. Co-products and by-products need to be separated from

the main product. They may need to be disposed of or may be useful and sold for extra profit.

5. **Waste disposal and effluent control.** If co-products or by-products are hazardous, they will have to be treated before disposal. Costs are incurred in treating any waste water or gaseous emissions from the plant.
6. **Quality control.** Modern chemical plants have laboratories that continuously monitor the quality of feedstock and products to ensure that these meet the required specifications.
7. **Safety.** Legislation covers all aspects of health and safety in the chemical industry. Many safety features are incorporated in the location and layout of chemical plants. There is frequent on-site training of staff and continuous monitoring of potential hazards.
8. **Costs.** Fixed costs are those costs that have to be paid regardless of the rate of production of the plant, e.g. labour, plant depreciation and repayment of loans. Variable costs depend directly on the rate of production of the plant, e.g. raw materials, costs of effluent treatment and disposal, and distribution costs.  
  
Various ways of reducing costs are employed in chemical plants. These include recycling of unreacted feedstock, using catalysts, selling useful co-products and by-products, and keeping lengths of piping to a minimum. In addition, costs are reduced by using optimum temperatures and pressures for reactions, and by using heat exchangers to transfer heat generated in one part of the plant to another part of the plant where heat is needed.
9. **Location of site.** The location of a chemical industry at a particular site depends on a number of factors. Access by good road or rail connections or deep sea access is essential. The availability of a large supply of cooling water is often an important factor. Other important factors are the availability of a skilled workforce, scope for plant expansion, local availability of raw materials and facilities for disposal and treatment of waste.
10. **Materials used in plant construction.** The construction materials used in a chemical plant are generally unreactive and resistant to corrosion. Materials are chosen that do not react with the feedstock, products, solvents or catalysts used in the production process. Glass-lined vessels and stainless steel components are commonly used.

In order to help you remember the above ten characteristics, use the following mnemonic:  
**For** Revising **Your** Chemistry **Work** **Quite** **Slowly** **Consequently** **Learning** **More**.

## 25.3 Case Study 1: The Manufacture of Ammonia and Urea by IFI at Cobh

- When it was in operation, the IFI plant in Cobh, Co. Cork, used natural gas and air to make ammonia.
- Ammonia,  $\text{NH}_3$ , is used to manufacture nitric acid, nylon and fertiliser constituents such as ammonium sulfate.

- Ammonia is manufactured industrially by the Haber process. This involves passing hydrogen and nitrogen gases over an iron catalyst, resulting in the following reaction taking place:



A flow chart summarising the main stages in the manufacture of ammonia is given in Fig 25.1.

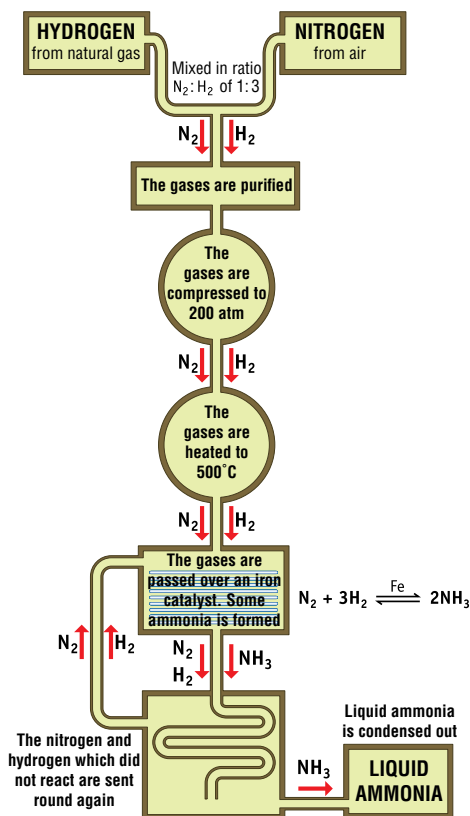
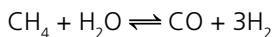
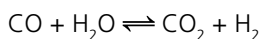


Fig. 25.1 Flow chart summarising the main stages in the manufacture of ammonia.

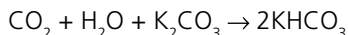
- Feedstock.** Nitrogen and hydrogen are the feedstock for the manufacture of ammonia. The hydrogen comes from natural gas. The nitrogen comes from the air. The hydrogen is obtained from the natural gas in a process called **methane-steam reforming**.



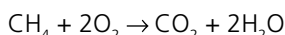
**Shift reaction:**



The carbon dioxide is removed at the secondary reforming stage by reacting it with potassium carbonate ( $K_2CO_3$ ) solution. This forms a solution of potassium hydrogencarbonate:



The nitrogen gas is formed by burning the unreacted methane (from the methane-steam reforming stage) in air that is injected into the reactor. Burning the methane in air forms carbon dioxide and steam.



This reaction is called **secondary reforming**. Thus, the oxygen in the air is removed leaving almost pure nitrogen. This nitrogen is later used to synthesise ammonia.

2. **Rate.** Rate and yield are closely related. Le Chatelier's Principle suggests that low temperature would increase the yield of ammonia by favouring the exothermic reaction. However, low temperature would make the reaction uneconomically slow. Therefore, the reaction is carried out at 500 °C to ensure it takes place at an acceptable rate. An **iron catalyst** is also used to increase the rate.

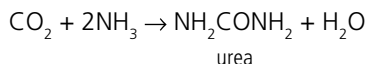
While high pressure would increase the yield of ammonia, very high pressures are expensive to generate and potentially dangerous. In practice, the process is carried out at a pressure of 200 atmospheres to ensure a satisfactory yield.

A high pressure of about 200 atm and a temperature of around 500 °C give a satisfactory rate. Also, by keeping the particle size of the iron catalyst small, the rate of reaction is increased.

3. **Yield of product.** The yield of ammonia in the ammonia synthesis reactor is about 17%. On leaving the reactor, the ammonia is liquefied by refrigeration. The unchanged reactants are re-circulated. The IFI plant at Cobh produced 1500 tonnes of ammonia each day.
4. **Co-products.** Since the Haber process involves the formation of just one product ( $NH_3$ ), there are no co-products. However, in the secondary reforming reaction as shown above, carbon dioxide is formed. This carbon dioxide is a very useful by-product and is used for two purposes: (i) to manufacture urea in another part of the plant and (ii) to put the "fizz" into drinks and it is for this reason that it is sold to the soft drinks and brewing industries.

### Synthesis of urea

Urea was the only fertiliser manufactured by IFI at Cobh. Overall, the formation of urea may be represented as:



5. **Waste disposal and effluent control.** All emissions and effluents from the plant were monitored for the presence of substances such as ammonia or dust from urea. The level of emissions was very low since the substances were recycled back into the cycle of production.
6. **Quality control.** This was carried out at various stages of the production process using gas chromatography and infra-red spectroscopy. In addition, sensors were

used throughout the plant to monitor variables such as temperature, pressure, pH and flow rates of gases. All of these data were monitored from a central control room.

7. **Safety.** All those working in the plant undertook training courses in safety. A fire-fighting team was on standby at all times. All of the normal safety equipment (breathing apparatus, goggles and first aid kits) was available on site.
8. **Costs.** The costs involved in running the plant were: (i) purchase of natural gas, (ii) electricity, (iii) purchase of large quantities of fresh water and (iv) wages for the 200 people who worked at the plant.
9. **Location of site.** The site was chosen for a number of reasons:
  - (i) The Cork–Cobh railway line was very near the plant. This was ideal as ammonia was transported to the IFI plant in Arklow by train.
  - (ii) The site was next to a deep-water harbour for easy export of ammonia and urea by ship.
  - (iii) The site was near the location of natural gas off Kinsale.
  - (iv) There was a good supply of skilled personnel (engineers, chemists and technicians) as the plant was only 20 km from Cork City, which has a university and an Institute of Technology.
10. **Materials for plant construction.** Stainless steel that was specifically designed and custom made was used throughout the plant. This was to ensure that corrosion was kept to a minimum.

The above points are summarised in Table 25.3.

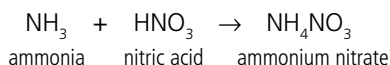
	Characteristic	Haber process to manufacture ammonia
1.	Feedstock	Hydrogen (from natural gas). Nitrogen (from the air).
2.	Rate	A pressure of about 200 atm and a temperature of around 500 °C give a satisfactory rate. Iron catalyst is finely divided to increase rate.
3.	Yield of product	About 17% per cycle.
4.	Co-products	None (but carbon dioxide is a by-product and is used in fizzy drinks and to make urea).
5.	Waste disposal	Emissions monitored for ammonia and urea dust. Recycling reduces waste emissions.
6.	Quality control	Gas chromatography and IR spectrometry.
7.	Safety	Training courses/safety equipment available.
8.	Costs	Labour/Purchase of natural gas, electricity and water.
9.	Location of site	Near rail link/next to harbour/near supply of natural gas.
10.	Materials for plant construction	Stainless steel used to prevent corrosion.

**Table 25.3** Summary of the main characteristics associated with the manufacture of ammonia (Haber process).



## 25.4 Case Study 2: The Manufacture of Nitric Acid by IFI at Arklow

When it was in operation, the IFI plant at Arklow manufactured nitric acid using ammonia (from IFI in Cobh). This nitric acid was then reacted with more ammonia to form ammonium nitrate, an important constituent of fertilisers.



The ammonium nitrate that was formed was mixed with limestone to form a fertiliser called calcium ammonium nitrate (CAN). Ammonium nitrate is also used as an oxidising agent in explosives.

A flow chart summarising the main stages in the manufacture of nitric acid is given in Fig. 25.2.

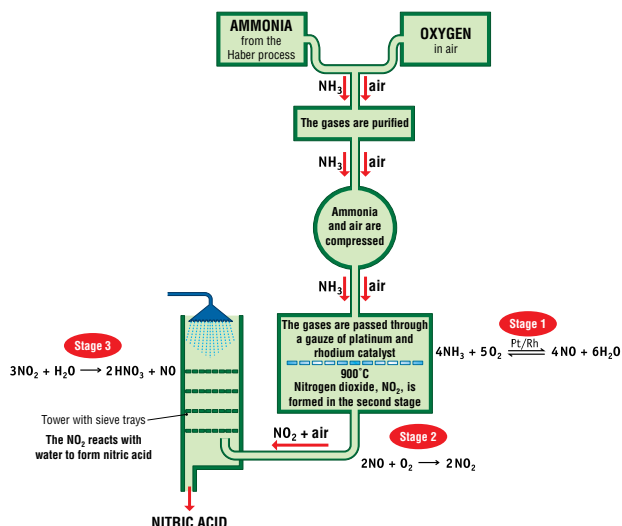
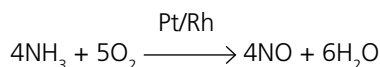


Fig. 25.2 Flow chart summarising the stages in the manufacture of nitric acid.

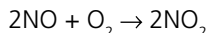
1. **Feedstock.** To manufacture nitric acid, three chemicals are needed, i.e. ammonia, oxygen and water. The ammonia was transported by train to Arklow from the IFI plant in Cobh, Co. Cork. This ammonia was used to manufacture nitric acid.

There are three stages involved in the manufacture of nitric acid.

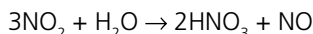
- (i) **The oxidation of ammonia to nitrogen monoxide.** This reaction is carried out by passing the ammonia over a platinum/rhodium catalyst at a temperature of around 900 °C. The following reaction occurs:



- (ii) **The oxidation of nitrogen monoxide to nitrogen dioxide.** This is carried out by introducing more air into the reactor.

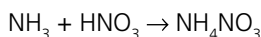


- (iii) **The absorption of nitrogen dioxide in water.** The nitrogen dioxide made in the second step is then absorbed in water to form nitric acid.



Thus, the feedstock for the manufacture of nitric acid consists of ammonia, oxygen and water.

The nitric acid prepared is then reacted with ammonia to make ammonium nitrate.



As can be seen from the above equation, the feedstock for the manufacture of ammonium nitrate consists of ammonia and nitric acid.

2. **Rate.** All reactions proceed at a reasonably fast rate.
3. **Yield of product.** The yields of both nitric acid and ammonium nitrate are very high (around 95%).
4. **Co-products.** There are no co-products formed.
5. **Waste disposal and effluent control.** The main pollutants are the oxides of nitrogen and effluents containing ammonia and nitrates. All effluents from the IFI plant at Arklow were automatically analysed for levels of ammonia and nitric acid. The plant had an Ammonia Recovery Unit installed which recycled the ammonia and the ammonium nitrate back into the process. Thus, the amount of waste generated was kept to an absolute minimum.
6. **Quality control.** The feedstock and products were continually analysed in the laboratory located in the plant. At various stages of the manufacturing process, samples were analysed to ensure that the required specifications were met. This analysis ensured that the nitrogen content of the final fertiliser product was correct. Another important specification was that the fertiliser should flow freely so that it could be easily spread by the farmer.
7. **Safety.** Each member of staff received training in the area of site safety. The company took all precautions to ensure the highest levels of safety. In keeping with the requirements of Health and Safety legislation, IFI produced a detailed document outlining all areas of risk and management of safety.
8. **Costs.** The operating costs of the plant were (i) the cost of ammonia, (ii) the cost of the catalyst, (iii) the cost of limestone, (iv) labour costs, (v) maintenance costs and (vi) the cost of electric power.
9. **Location of site.** The plant was located in Arklow for a number of reasons.
  - (i) The site was close to the Avoca river, which supplied the plant with fresh water for cooling purposes.
  - (ii) The site was near a local harbour for ease of shipping products for export.
  - (iii) The rail link connection to the main Dublin–Rosslare line made delivery of ammonia to the plant and distribution of fertiliser products very easy.

10. **Materials for plant construction.** Most of the material from which the plant was constructed consisted of stainless steel. This was necessary because of the corrosive nature of the reactants and products.

The above points are summarised in Table 25.4.

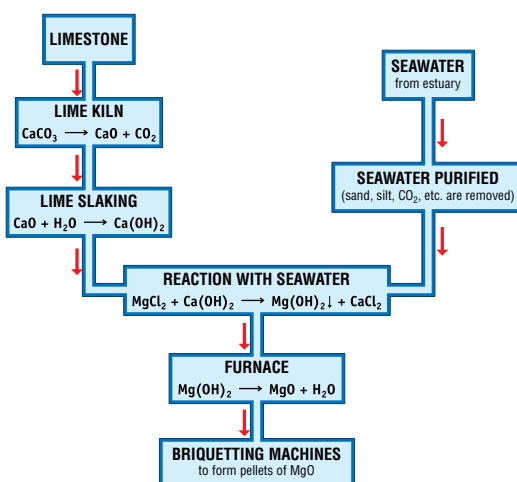
	Characteristic	Nitric Acid Manufacture
1.	Feedstock	Ammonia/oxygen/water.
2.	Rate	All reactions are fast.
3.	Yield of product	About 95%.
4.	Co-products	None.
5.	Waste disposal	Emissions monitored for ammonia, nitrates and oxides of nitrogen. Recycling reduces waste emissions.
6.	Quality control	Fertiliser is analysed for correct nitrogen levels, and for flow characteristics.
7.	Safety	Training courses/safety equipment available.
8.	Costs	Labour/Purchase of ammonia, electricity, limestone and catalyst.
9.	Location of site	Close to river (water for cooling)/near harbour/near rail link.
10.	Materials for plant construction	Stainless steel used to prevent corrosion.

**Table 25.4** A summary of the main characteristics associated with the manufacture of nitric acid.

## 25.5 Case Study 3: The Manufacture of Magnesium Oxide by Premier Periclase at Drogheda

This plant manufactures magnesium oxide from seawater. Magnesium oxide is used as a refractory material in steel-making plants.

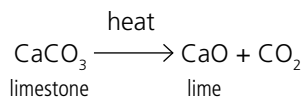
A flow chart summarising the main stages in the manufacture of magnesium oxide is given in Fig. 25.3.



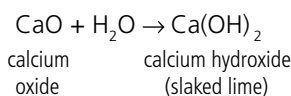
**Fig. 25.3** Flow chart summarising the main stages in the manufacture of magnesium oxide.

The production of magnesium oxide from seawater can be divided into four stages.

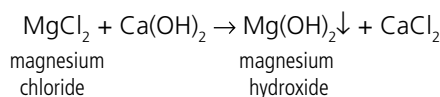
- (i) **The conversion of limestone to lime.** In the first stage, limestone is converted into lime (also known as quicklime) by heating the limestone in a large oven called a kiln.



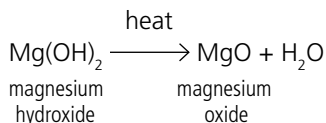
- (ii) **The conversion of lime into slaked lime.** In the second stage, water is added to the lime from the first stage to form a substance commonly called slaked lime (calcium hydroxide).



- (iii) **The reaction of slaked lime with seawater to form magnesium hydroxide.** In the third stage, the calcium hydroxide from step (ii) reacts with seawater. The magnesium chloride found in seawater reacts with the calcium hydroxide to form a precipitate of magnesium hydroxide.



- (iv) **The conversion of magnesium hydroxide to magnesium oxide.** In the fourth stage, magnesium hydroxide from step (iii) is heated in a large furnace to form magnesium oxide. This is then converted into high density pellets by passing it through briquetting machines.



- Feedstock.** The feedstock consists of seawater and limestone. Seawater is taken from the Boyne estuary. Limestone is taken from a local quarry.
- Rate.** The conversion of limestone to lime is a slow reaction. The other three reactions proceed at a fast rate.
- Yield of product.** A litre of seawater yields only about 2 g of magnesium oxide. Hence, the company needs to have large quantities of seawater available.
- Co-products.** No co-products are produced.
- Waste disposal and effluent control.** All emissions from the plant are carefully monitored for the presence of dust. Particles of dust in chimney stacks are removed by electrostatic precipitators. In addition, the effluents from the plant are analysed with regard to the concentration of suspended solids and pH levels. The seawater that has been used in the plant is treated to bring its pH and suspended solid level in line with normal seawater. It is then pumped out to sea 1500 m from the shore.

6. **Quality control.** The quality control laboratory carries out a detailed chemical analysis of all reactants and products at every stage of the production process. Techniques commonly used are acid-base titrations and X-ray analysis.
7. **Safety.** The company pays great attention to safety regulations. Training in the area of health and safety is provided to all employees working on the site. A health and safety team operates throughout the plant. Safety clothing is provided to all employees. As excessive noise can damage hearing, ear protection is provided to employees working in areas that have high noise levels.
8. **Costs.** The main costs involved in running the plant are (i) energy for operating kilns, furnaces and pumps, (ii) labour costs, (iii) maintenance costs, (iv) purchase of limestone, (v) administration.
9. **Location of site.** The location at Drogheda is ideal for a number of reasons.
  - (i) The site is close to a plentiful supply of seawater.
  - (ii) The site is close to a limestone quarry.
  - (iii) The plant is built next to the river Boyne for easy export of the product.
  - (iv) There is a good road network to allow easy transport of limestone to the plant.
10. **Materials for plant construction.** Many of the buildings on the site are made from steel with cladding on the outside. Lime is stored in large concrete silos. The seawater and calcium hydroxide are reacted together in a large concrete reactor. The kiln used to convert limestone to lime is made of steel on the outside and refractory bricks on the inside to withstand the high temperature. Similarly, refractory bricks are used in the furnaces where the magnesium hydroxide is converted into magnesium oxide.

The above points are summarised in Table 25.5.

	Characteristic	Magnesium oxide manufacture
1.	Feedstock	Seawater/limestone.
2.	Rate	Limestone $\rightarrow$ lime is slow/other reactions are fast.
3.	Yield of product	Low $\Rightarrow$ large quantities of seawater needed.
4.	Co-products	None.
5.	Waste disposal	Dust particles removed by electrostatic precipitation (from gases) and filtration (from waste water)/pH of waste water adjusted.
6.	Quality control	Titration and X-ray analysis.
7.	Safety	Training courses/safety equipment available/hearing protection.
8.	Costs	Labour/Purchase of energy for kilns, electricity and limestone.
9.	Location of site	Close to supply of seawater and limestone/next to river and road network.
10.	Materials for plant construction	Steel/concrete/refractory bricks.

**Table 25.5** A summary of the main characteristics associated with the manufacture of magnesium oxide.

# 26

## Atmospheric Chemistry

In this chapter you will study:

- Oxygen – the reactive gas
- Nitrogen – the unreactive gas
- Inorganic carbon compounds
- The carbon cycle
- The greenhouse effect
- Atmospheric pollution
- The ozone layer
- CFCs
- CFC substitutes

### 26.1 Introduction

The atmosphere is a layer of gas that extends about 100 km above the surface of the Earth. The composition (by volume) of dry, unpolluted air is shown in Table 26.1.

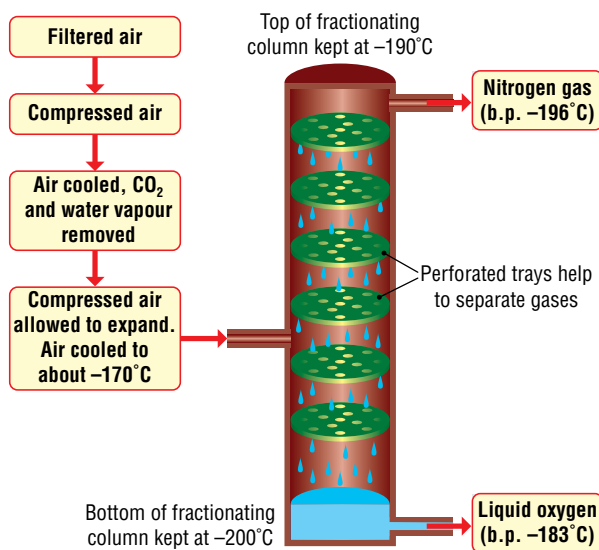
Name of Gas	Composition (by Volume)
Oxygen	21%
Nitrogen	78%
Other gases (e.g. noble gases, carbon dioxide)	1%

**Table 26.1** The composition of dry, unpolluted air.

### 26.2 Oxygen – The Reactive Gas

- Oxygen is the most reactive gas in the air.
- Oxygen is used in hospitals for people who have difficulty in breathing, and in the steel industry to remove impurities from iron. It is also used in the purification of river water, in rocket fuels and in oxyacetylene welding and cutting.
- Oxygen is prepared in the laboratory by decomposing hydrogen peroxide. Industrially, it is manufactured by **liquefaction** followed by **fractional**

**distillation** of the air. Air is first turned into a liquid and the different gases are then allowed to boil off at different temperatures, Fig. 26.1.



**Fig. 26.1** Oxygen and nitrogen may be separated from the air by liquefaction of the air, followed by fractional distillation.

## 26.3 Nitrogen – The Unreactive Gas

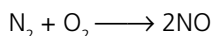
- Nitrogen is the most abundant gas (78%) present in the air.
- Nitrogen is a colourless, odourless, tasteless gas and is unreactive. Nitrogen is so unreactive because of the large amount of energy needed to break the triple bond in the nitrogen molecule.
- Due to its inertness, nitrogen gas is used to keep food fresh by preventing oxidation by air, e.g. in bags of crisps and to flush dangerous vapours out from empty oil tankers. It is also used in the manufacture of ammonia.
- Liquid nitrogen ( $-196^{\circ}\text{C}$ ) is used for quick-freezing of food, for storage of semen, and in medicine to remove warts.
- Nitrogen is essential for plant growth as nitrogen is needed to manufacture proteins. Since it is so unreactive, it cannot be used directly by plants.

**Nitrogen fixation** is the conversion of atmospheric nitrogen to compounds which can be used by plants.

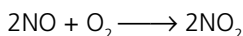
There are two methods of fixing nitrogen in nature. These processes come under the heading of *natural fixation*. The two methods of natural fixation are:

### 1. During thunderstorms

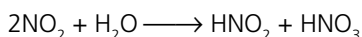
- The discharge of electricity that takes place during thunderstorms provides enough energy for the nitrogen and oxygen in the air to react together. A substance called nitrogen monoxide, NO, is formed.



The nitrogen monoxide then reacts with oxygen from the air to form nitrogen dioxide.



The nitrogen dioxide then dissolves in rainwater to form nitrous acid,  $\text{HNO}_2$ , and nitric acid,  $\text{HNO}_3$ .



The nitric acid falls to earth in rainwater and forms nitrate ( $\text{NO}_3^-$ ) compounds in the soil. These are absorbed by plants through their roots and become incorporated into the plant's tissues in the form of proteins.

### 2. Nitrogen-fixing bacteria

- A second method of fixing nitrogen involves nitrogen-fixing bacteria. Certain plants called legumes (e.g. peas, beans and clover) have tiny root swellings that contain *rhizobium* bacteria which can fix nitrogen.
- The bacteria are present in nodules on the roots of the plant, Fig. 26.2.
- Not enough nitrogen is fixed by natural processes to provide for our needs.
- Soils for growing crops must therefore have fertiliser added to them. Most of this fertiliser is produced by **artificial fixation** (for example using the Haber process).
- Nitrogen must be recycled throughout an ecosystem and returned to the atmosphere. Bacteria, called **nitrifying** and **denitrifying bacteria**, are necessary in this process of recycling. The nitrogen cycle is summarised in Fig. 26.3.



**Fig. 26.2** Some plants called legumes have nodules (swellings) on their roots. These nodules contain bacteria that convert nitrogen from the air into nitrogen compounds, which can be used by the plant to grow.



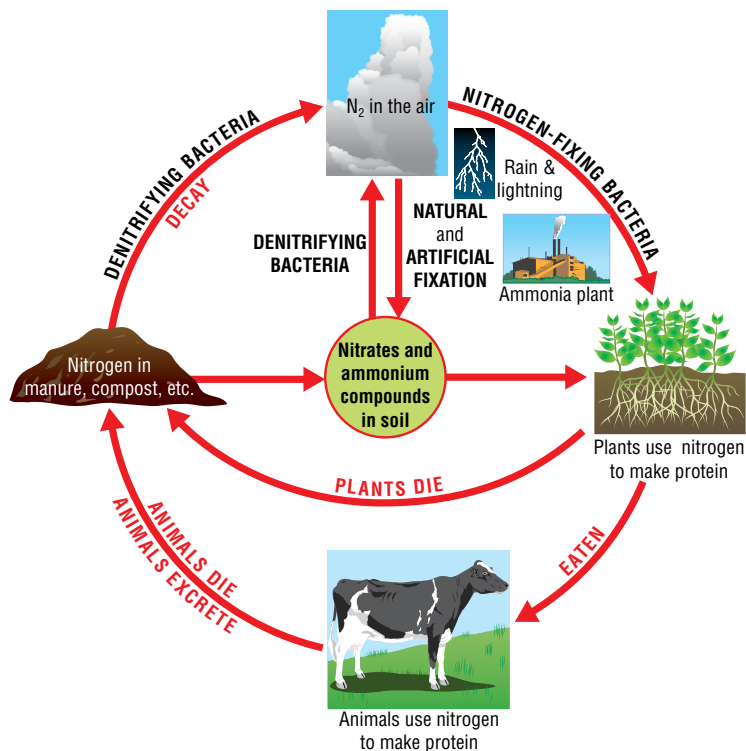
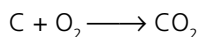


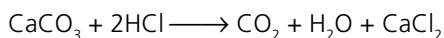
Fig. 26.3 The nitrogen cycle.

## 26.4 Inorganic Carbon Compounds

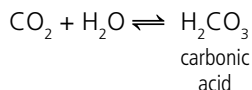
- The compounds of carbon that are classified as **inorganic** are carbon dioxide, carbon monoxide (CO), carbonate compounds, hydrogencarbonate compounds and carbides.
- Carbon dioxide is used to put the “fizz” in drinks. It is also used in fire extinguishers and in the form of “dry ice” which is used to refrigerate certain items that are being transported. Solid carbon dioxide is also used to create a “mist” effect on stage.
- Powdered carbon can be burned in air producing carbon dioxide.



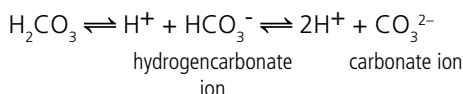
- As discussed in Chapter 6, carbon dioxide is released when an acid is added to calcium carbonate.



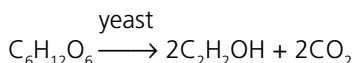
- Carbon dioxide will dissolve in water to produce carbonic acid.



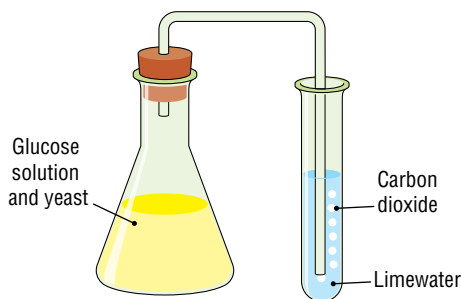
- The dissociation of carbonic acid in water leads to the presence of carbonate and hydrogencarbonate ions in water.



- These ions result in the formation of compounds such as calcium carbonate, sodium hydrogencarbonate, etc.
- Carbon dioxide is an acidic oxide. Bubbling it through some universal indicator solution causes the solution to turn from green to red as the carbon dioxide dissolves to form carbonic acid.
- Carbon dioxide is also produced during a process called **fermentation**.

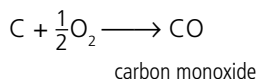


The process of fermentation is shown in Fig. 26.4.



**Fig. 26.4** Carbon dioxide is given off when fermentation takes place. The carbon dioxide turns the limewater milky.

- If carbon is burned in a limited supply of oxygen, carbon monoxide (CO) is formed instead of carbon dioxide. For example, this occurs in car engines and in cigarette smoke.



- Carbon monoxide is a colourless gas which has no smell, is highly poisonous, does not dissolve in water, and does not react with either acids or bases. For this reason it is said to be a **neutral oxide**.

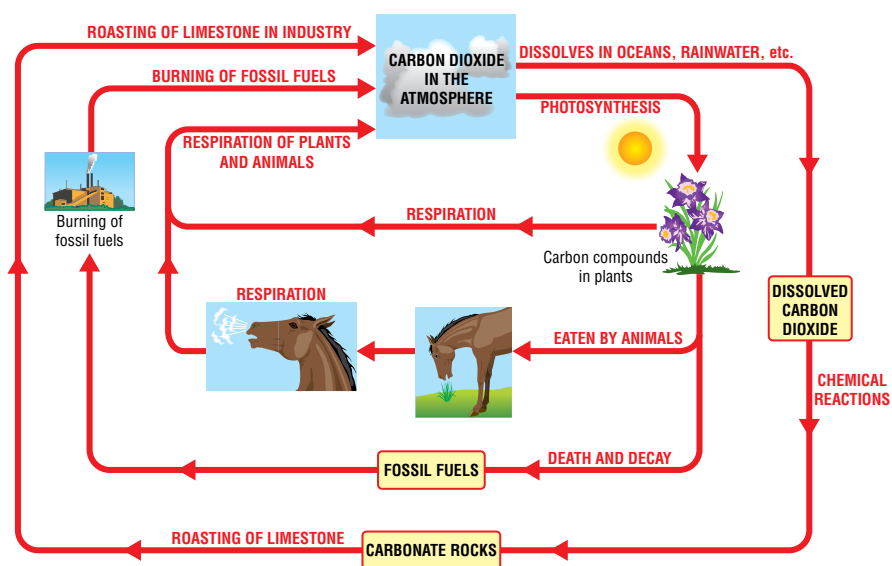
## 26.5 The Carbon Cycle

- The percentage of carbon dioxide in the atmosphere is fairly constant at 0.03%. This is because, as some processes remove  $\text{CO}_2$  from the air, other processes return  $\text{CO}_2$  to the air, Table 26.2.

Processes that remove $\text{CO}_2$ from the air	<ul style="list-style-type: none"> <li>Photosynthesis  <math display="block">6\text{CO}_2 + 6\text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2</math>                     (over millions of years, some of the carbon becomes incorporated into fossil fuels)                 </li> <li>Dissolving in rainwater, rivers, oceans (some of the <math>\text{CO}_2</math> becomes incorporated into limestone)</li> </ul>
Processes that return $\text{CO}_2$ to the air	Respiration by living things $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \longrightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$ <ul style="list-style-type: none"> <li>Burning of fossil fuels</li> <li>Roasting of limestone</li> </ul>

**Table 26.2** Some processes remove  $\text{CO}_2$  from the air and others return it.

- These processes give rise to the **carbon cycle**, Fig. 26.5.

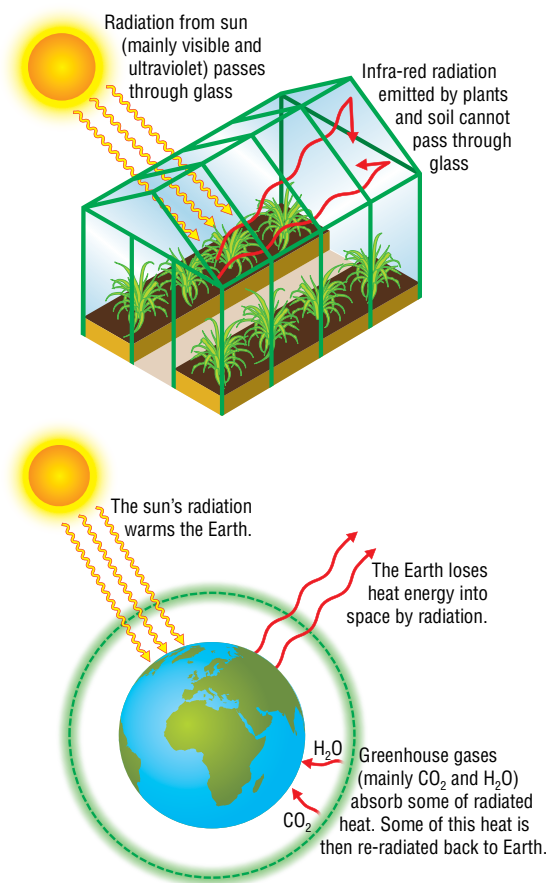


**Fig. 26.5** The carbon cycle.

## 26.6 The Greenhouse Effect

- When sunlight strikes the surface of the Earth, some of the radiation is reflected back out into space. Certain frequencies of this radiation (particularly in the

infra-red range) are unable to penetrate some of the gases in the Earth's atmosphere. These gases, known as **greenhouse gases**, include carbon dioxide and water vapour, Fig. 26.6.



**Fig. 26.6** The Earth's atmosphere acts like a greenhouse. Some of the gases in the Earth's atmosphere trap some of the heat being lost from the Earth as it cools down.

- This phenomenon is known as the **greenhouse effect** and results in heat being trapped near the Earth's surface. Without this greenhouse effect, the Earth would be too cold to sustain life as we know it.
- The ability of a gas to behave as a greenhouse gas is measured by its **greenhouse factor**, which compares the heat-absorbing properties of each gas with those of carbon dioxide.

The **greenhouse factor** is a measure of the greenhouse effect caused by a particular gas, relative to the same amount of carbon dioxide which is taken as the standard and is assigned a value of 1.

- Table 26.3 gives the greenhouse factor for each of the main greenhouse gases in the atmosphere. Note that neither oxygen nor nitrogen is a greenhouse gas.

Gas	Greenhouse Factor
Water vapour	0.1
Carbon dioxide	1
Methane	30
N <sub>2</sub> O	160
CFCs	21,000–25,000

**Table 26.3** The main greenhouse gases and their corresponding greenhouse factors.

- Several human activities are leading to an increase in the concentration of these greenhouse gases in the air. In particular, the level of CO<sub>2</sub> is giving cause for concern.
- The burning of fossil fuels results in large amounts of CO<sub>2</sub> being added to the air.
- The increase in the rate at which CO<sub>2</sub> is released into the air is not matched by the rate at which it is removed by photosynthesis or by its dissolving in the oceans etc. The “**residence time**” of CO<sub>2</sub> in the air is about 100 years, i.e. a molecule of CO<sub>2</sub> will remain in the air for this length of time.
- Other greenhouse gases are also being added to the air as a result of human activity. These are summarised in Table 26.4.

Gas	Activity that is increasing its concentration	Residence time
Methane	<ul style="list-style-type: none"> <li>Increasing size of cattle herds – these animals release a large amount of CH<sub>4</sub> from their intestines</li> <li>Growing of rice in paddy fields</li> <li>Anaerobic breakdown of organic material in rubbish dumps</li> </ul>	10 years
CFCs (chlorofluorocarbons)	<ul style="list-style-type: none"> <li>Propellant gas in aerosol sprays</li> <li>Discarded fridges</li> </ul>	100 years
Dinitrogen oxide, N <sub>2</sub> O	Car exhaust fumes	100 years

**Table 26.4** The residence times of some greenhouse gases in the air.

- Increasing concentrations of these greenhouse gases in the atmosphere may be leading to an “**enhanced**” greenhouse effect. This may in turn bring about an increase in the temperature of the surface of the planet, an effect that is referred to as **global warming**.

Potential implications of global warming include:

- **Climate change:** More extreme weather conditions will develop, e.g. severe storms, drought in some areas but flooding in others.
- **Rise in sea level:** The extra heat may lead to melting of the Polar ice caps. This will add to climate change and also cause a rise in sea level. However, the greatest increase in the volume of water in the sea will be as a direct result of the extra heat. This will lead to the water in the oceans expanding, which may lead to the flooding of low-lying areas of the planet.
- One of the possible benefits of an enhanced greenhouse effect is an increase in the rate of photosynthesis in plants. This would come about due to the increase in carbon dioxide levels in the air.
- Strategies for bringing about a reversal of the increase in CO<sub>2</sub> levels include (a) developing alternative energy sources other than fossil fuels and (b) growing many more trees worldwide.

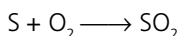
## 26.7 Atmospheric Pollution

- As the size of the human population increases, more and more polluting gases are being added to the atmosphere.

**Air pollution** is a situation that exists when a constituent in the air is present to the extent that there is a significant hazard to present or future health or to the environment.

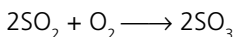
- Gases released into the air spread throughout the atmosphere by diffusion. This means that pollutant gases generated in one part of the world can become an issue in other parts.
- Normal rainwater is slightly acidic due to the presence of carbonic acid. This can lead to unpolluted rain having a pH of about 5.6. However, some gases present in the atmosphere can lead to rainwater becoming quite acidic, with a pH as low as 2.
- **Sulfur dioxide**, SO<sub>2</sub>, and **nitrogen dioxide**, NO<sub>2</sub>, are the main pollutants that give rise to **acid rain** – this is the term used to describe rain that is acidic as a result of atmospheric pollution.
- Some of the SO<sub>2</sub> in the air is naturally present due to volcanic activity and rotting vegetation.
- However, most of the sulfur dioxide in the air is as a result of the burning of fossil fuels. These fuels contain a small amount of sulfur. When the fuel is burned, the sulfur combines with oxygen to form sulfur dioxide.

sulfur + oxygen → sulfur dioxide



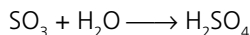
- The SO<sub>2</sub> reacts with oxygen in the air to form sulfur trioxide, SO<sub>3</sub>.

sulfur dioxide + oxygen → sulfur trioxide



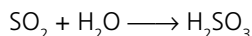
- The sulfur trioxide then dissolves in rainwater to form sulfuric acid.

sulfur trioxide + water  $\longrightarrow$  sulfuric acid



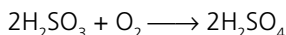
- Sulfur dioxide can also combine directly with water to form sulfurous acid,  $\text{H}_2\text{SO}_3$ .

sulfur dioxide + water  $\longrightarrow$  sulfurous acid



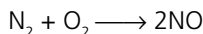
- This sulfurous acid can then become oxidised by oxygen in the air to form sulfuric acid.

sulfurous acid + oxygen  $\longrightarrow$  sulfuric acid



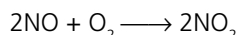
- The oxides of nitrogen also lead to acid rain. These oxides are produced in power stations and at the high temperature created at the spark plug in car engines. This high temperature provides enough energy to cause nitrogen gas to combine with oxygen gas.

nitrogen + oxygen  $\longrightarrow$  nitrogen monoxide



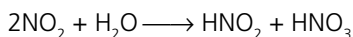
- The nitrogen monoxide then combines with oxygen in the air to form nitrogen dioxide.

nitrogen monoxide + oxygen  $\longrightarrow$  nitrogen dioxide

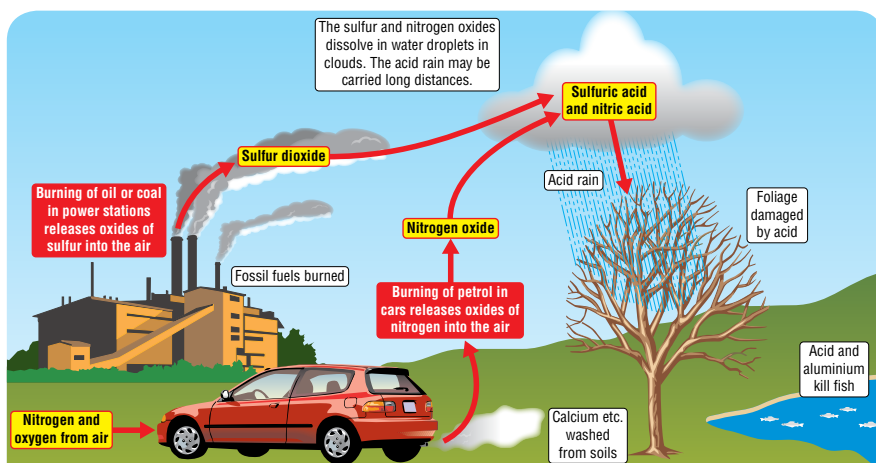


- The nitrogen dioxide then dissolves in rainwater to form a mixture of nitrous acid and nitric acid.

nitrogen dioxide + water  $\longrightarrow$  nitrous acid + nitric acid



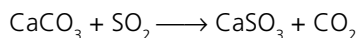
- These acids, along with sulfuric acid, fall to the ground in rain, Fig. 26.7.



**Fig. 26.7** Acid rain is formed when sulfur dioxide and oxides of nitrogen dissolve in water. Acid rain contains sulfuric acid and nitric acid.

- Some of the harmful effects of acid rain include foliage damage to trees, leaching of metal ions, e.g. aluminium, out of soil into lakes. This aluminium can interfere with the gill mechanism of fish, killing them. Buildings and statues that are made of limestone are eroded by the action of acid rain.
- The use of scrubbing systems in the chimneys of power stations has decreased the incidence of acid rain caused by sulfur dioxide. The  $\text{SO}_2$  is made to combine with limestone to form calcium sulfite,  $\text{CaSO}_3$ .

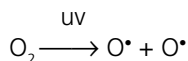
limestone + sulfur dioxide  $\longrightarrow$  calcium sulfite + carbon dioxide



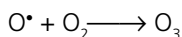
- The calcium sulfite reacts with oxygen to form calcium sulfate,  $\text{CaSO}_4$ , which is called gypsum and can be used to make plaster.
- The use of catalytic converters in car exhausts has substantially decreased the incidence of acid rain caused by oxides of nitrogen.

## 26.8 The Ozone Layer

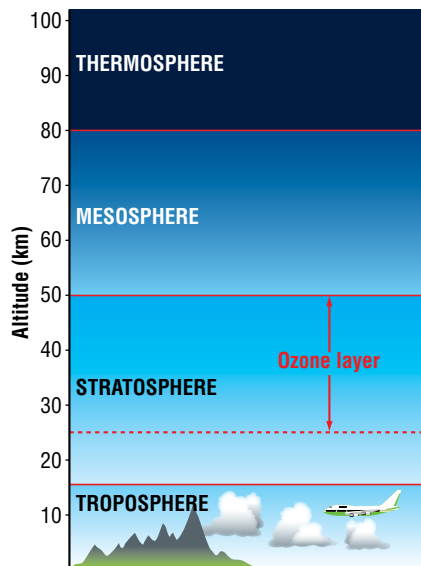
- Trioxxygen,  $\text{O}_3$ , is a form of oxygen more commonly known as ozone. There is a layer of ozone surrounding the Earth about 25 km above the Earth's surface, Fig. 26.8.
- Ozone is formed in the stratosphere by the reaction between an oxygen atom and an oxygen molecule. The oxygen atoms are formed when ultraviolet light of particularly high energy breaks the oxygen molecule into oxygen atoms.



- This is an example of **photodissociation**, i.e. the breaking of a bond using radiation. Oxygen atoms are very reactive since they have an unpaired electron. (They are often referred to as oxygen **free radicals** and are represented by  $\bullet$  written after – or before in some cases – the symbol. This dot represents the unpaired electron.) As soon as the oxygen atoms are formed, they react with the oxygen molecules in the atmosphere to form ozone.



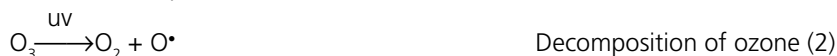
Production of ozone (1)



**Fig. 26.8** The ozone layer is in the stratosphere and absorbs much of the harmful ultraviolet radiation from the Sun.



- When the ozone formed in the above reaction absorbs ultraviolet radiation, **photodissociation of the ozone** occurs, i.e. the above reaction is reversed and the ozone is decomposed:



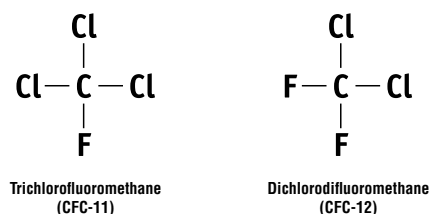
- Reaction (2) is responsible for the very important screening effect of ozone since it absorbs much of the harmful ultraviolet radiation. Excessive exposure to ultraviolet light causes skin cancer.
- Some of the oxygen atoms produced in reaction (2) destroy ozone molecules by converting them to oxygen molecules:



- The oxygen molecules in (2) and (3) are broken down by ultraviolet light to form oxygen atoms (free radicals) which lead to the production of ozone as in (1) above.
- Ozone can also be formed by the electric discharge that takes place during lightning storms and in photocopiers and electric motors.
- Thus, as can be seen from reactions (1)–(3) above, ozone is being made and destroyed continuously. Therefore, the concentration of ozone would be expected to remain constant.
- In 1984 a “hole” in the ozone layer was discovered over the Antarctic. It is now known that there is a general depletion of ozone in other areas around the globe.
- Chlorine atoms are mainly responsible for destroying the ozone layer.
- Substances called chlorofluorocarbons (CFCs) are responsible for producing chlorine atoms in the atmosphere and causing much of the damage to the ozone layer.

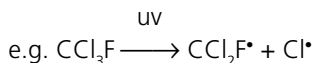
## 26.9 CFCs

- Chlorofluorocarbons (CFCs) are compounds of chlorine, fluorine and carbon. Two examples are shown in Fig. 26.9.
- CFCs have low boiling points, low toxicity, low flammability and are very unreactive. Their uses were based on these properties. Some of these uses were:
  - propellant gases in aerosol sprays
  - a foaming agent in making expanded polystyrene
  - as a cooling agent in fridges and air-conditioning systems.
- It is this lack of reactivity that has led to CFCs being responsible for the depletion of ozone in the stratosphere.



**Fig. 26.9** Two examples of CFCs. Each CFC is given a number to identify it and to avoid the need to write the full name.

- CFCs can travel unchanged as far as the stratosphere. However, in the stratosphere CFCs are broken down by the high level of ultraviolet radiation present.



- These chlorine atoms then attack ozone to form oxygen and chlorine oxide.

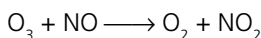


- The chlorine oxide is very reactive (it is a radical) and attacks an oxygen atom.



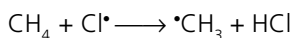
- Reaction (ii) releases more chlorine atoms to attack further ozone molecules as in reaction (i) above. Thus, the cycle continues and a chain reaction occurs.
- The chlorine atom used up in reaction (i) is regenerated in reaction (ii). Every time reaction (i) occurs, an ozone molecule is destroyed. It has been estimated that one single chlorine atom can destroy tens of thousands of molecules of ozone.
- Nitrogen monoxide also reacts with ozone in the stratosphere and destroys the ozone.

ozone + nitrogen monoxide  $\longrightarrow$  oxygen + nitrogen dioxide



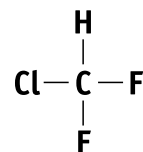
- Although methane causes problems as a greenhouse gas, it is of benefit when helping to prevent damage to the ozone layer. Methane reacts with Cl atoms and prevents the concentration of chlorine atoms building up. This helps to slow down the rate at which ozone is being destroyed.

methane + chlorine atom  $\longrightarrow$  methyl radical + hydrogen chloride



## 26.10 CFC Substitutes

- Replacement compounds for CFCs are called **hydrochlorofluorocarbons (HCFCs)** since they contain hydrogen, chlorine, fluorine and carbon.
- The presence of the C-H bond means that these molecules are broken down by radicals naturally present in the lower atmosphere (troposphere). Hence these molecules do not reach the ozone in the stratosphere.
- An example of a HCFC molecule is chlorodifluoromethane,  $\text{CHClF}_2$ , Fig. 26.10.
- HCFCs do destroy some ozone since they contain some chlorine but they destroy a lot less ozone than CFCs do.
- Considerable research is taking place to develop CFC and HCFC substitutes which have no chlorine in their molecules. Such compounds are called **hydrofluorocarbons, HFCs**. These are hydrogen-containing fluoroalkanes, e.g.  $\text{CH}_2\text{FCF}_3$ .



Chlorodifluoromethane  
(HCFC-22)

**Fig. 26.10** This compound is one of the replacements for CFCs. It is an example of a hydrochlorofluorocarbon (HCFC).

# Materials: Crystals, Metals and Addition Polymers

27

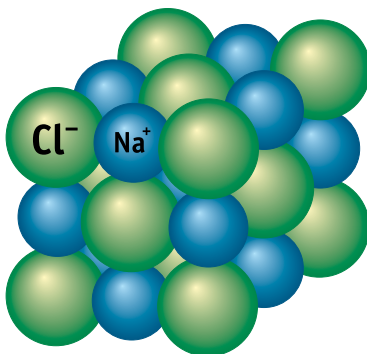
In this chapter you will revise:

- Crystals
- Metals and non-metals
- Addition polymers
- Recycling of plastics

## 27.1 Crystals

A **crystal** is a solid particle with a regular shape consisting of faces intersecting at definite angles. There is an ordered arrangement of particles within the crystal.

- William Bragg and his son Lawrence used X-ray crystallography to determine the arrangement of particles within crystals.
- This technique involves passing X-rays through a crystal of the substance and studying the diffraction pattern formed.
- The arrangement of particles inside a crystal is referred to as the **crystal lattice**.
- The crystal lattice always consists of a structure that repeats throughout the crystal. This repeating structure is called the **unit cell**.
- Sodium chloride consists of an arrangement of sodium ions and chloride ions in which the repeating structure (unit cell) is the cube shown in Fig. 27.1.



**Fig. 27.1** The unit cell of the sodium chloride crystal lattice is a cube consisting of  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

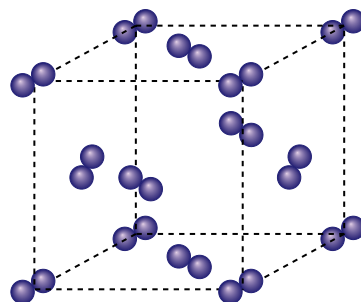
- The points occupied by the sodium ions and chloride ions are called **lattice points**.
- Dorothy Hodgkin was awarded the Nobel Prize for Chemistry in 1964 for determining the structure of vitamin B<sub>12</sub> using X-ray crystallography. She also determined the structure of penicillin.
- Crystalline solids are classified into four groups – ionic crystals, molecular crystals, covalent macromolecular crystals and metallic crystals.

## (a) Ionic Crystals

- Units present and binding forces.** Examples of ionic crystals are NaCl, KI and MgO. In ionic crystals the lattice points are occupied by ions as shown in Fig. 27.1. The binding force is the electrostatic attraction between the positive and negative ions.
- Melting points.** They tend to have high melting points in order to overcome the electrostatic attraction.
- Hardness.** Ionic crystals tend to be hard due to strong electrostatic attraction between the ions, and brittle due to repulsion when a force is applied to the crystal.
- Electrical conductivity.** Ionic crystals cannot conduct electricity in the solid state since the ions occupy fixed regions in the crystal lattice. Dissolving or melting the crystal enables the ions to conduct electricity since the ions are now free to move.
- Solubility.** Most ionic crystals dissolve in water since there is an attraction between the positive and negative ions and the polar water molecules. However, ionic crystals are usually insoluble in non-polar solvents since there is no force of attraction between the ions and the solvent molecules.

## (b) Molecular Crystals

- Units present and binding forces.** Examples of molecular crystals are iodine, solid carbon dioxide, naphthalene, sulfur (S<sub>8</sub>), solid HCl and ice. In a molecular crystal, the lattice points of the crystal lattice are occupied by molecules, Fig. 27.2. The binding forces between the iodine molecules are weak van der Waals forces. In the case of polar molecules such as HCl, the binding forces are dipole–dipole interactions. In the case of ice, the binding forces are hydrogen bonds.
- Melting points.** The melting points of molecular crystals are low due to the weak intermolecular (van der Waals, dipole–dipole, etc.) forces between the molecules.
- Hardness.** Molecular crystals are usually quite soft due to the weak intermolecular (van der Waals, dipole–dipole, etc.) forces between the units in the crystal lattice.



**Fig. 27.2** Iodine is an example of a molecular crystal. The lattice points are occupied by I<sub>2</sub> molecules. There is an I<sub>2</sub> molecule at each corner of the cube and an I<sub>2</sub> molecule in the centre of each face.

- (iv) **Electrical conductivity.** Since there are no ions or free electrons present, molecular crystals do not conduct electricity.
- (v) **Solubility.** The solubility depends on the nature of the molecules at the lattice points. For example, crystals of iodine are insoluble in water since they are non-polar and there is no attraction between the non-polar iodine molecules and the polar water molecules. However, iodine is soluble in non-polar solvents such as hexane. Crystals of HCl will dissolve in water due to the polar nature of the HCl molecule.

## (c) Covalent Macromolecular Crystals

### (i) Units present and binding forces.

Examples of covalent macromolecular crystals are diamond and quartz (silicon dioxide,  $\text{SiO}_2$ ). In these structures, covalent bonds join the atoms together to form a giant interlocking network. For example, diamond consists entirely of carbon atoms and each tetrahedral carbon atom is joined to four other carbon atoms by single covalent bonds, Fig. 27.3.

- (ii) **Melting points.** The melting points of covalent macromolecular crystals are high due to the strong covalent bonding within the crystal.

- (iii) **Hardness.** Covalent macromolecular crystals are generally very hard because of the giant, interlocking structures described above. Diamond is the hardest naturally-occurring substance known to man.

- (iv) **Electrical conductivity.** Since there are no ions or free electrons present, covalent macromolecular crystals do not conduct electricity.

- (v) **Solubility.** Since the lattice is held so strongly together by the network of covalent bonds, covalent macromolecular crystals do not dissolve in water or in non-polar solvents.

- Diamond is an **allotrope** of carbon.



**Fig. 27.3** The model shows that the crystal structure of diamond consists of a network of carbon atoms. Each carbon atom is joined to four other carbon atoms by single covalent bonds.

**Allotropes** are different physical forms of the same element.

- Carbon exists in three different physical forms – diamond, graphite and buckminsterfullerene.
- Graphite consists of flat sheets or layers of covalently-bonded carbon atoms arranged in hexagons. These layers are held in place by weak van der Waals forces, which explain the use of graphite as a lubricant and in pencil “lead”.

- Graphite is the only non-metal that conducts electricity.
- Carbon atoms can link together to form a molecule that looks like a football. This molecule has 60 carbon atoms and is called buckminsterfullerene. This name was given to it because it resembled the structures designed by Buckminster Fuller, an American architect.

## (d) Metallic Crystals

- (i) **Units present and binding forces.** Most metals are composed of spheres packed as close together as possible. In most cases each sphere is in contact with six other spheres.

Metals are made up of positive metal ions formed when metal atoms lose one or more outer electrons. These outer electrons become delocalised all over the positive metal ions and form a sea of electrons. The attraction between the positive metal ions and the sea of electrons forms the metallic bond.

- (ii) **Melting points.** The melting points of metals vary enormously because the strength of the metallic bond varies from metal to metal. Melting point depends on factors such as the size of the ion and the amount of charge on the ion.
- (iii) **Hardness.** It is difficult to generalise as this depends on the strength of the metallic bond.
- (iv) **Electrical conductivity.** Since the electrons are delocalised over the entire crystal lattice, metallic crystals are excellent conductors of electricity, i.e. the electrons in the electric current can easily pass through the “sea of electrons” in the metal.
- (v) **Solubility.** Metals do not tend to be soluble as the metallic bond is sufficiently strong to hold the metal ions together in the crystal lattice.

## 27.2 Metals and Non-metals

- Some general properties of metals and non-metals are summarised in Table 27.1.

	Property	Metals	Non-Metals
1.	Hardness	Usually hard. Most are solid at room temperature.	Usually soft. Most are liquids or gases at room temperature.
2.	Lustre	Usually shiny.	Usually dull.
3.	Malleability	Can be hammered into different shapes.	Tend to be brittle and soft when solid.
4.	Ductility	Can be drawn into thin wires.	Cannot be drawn into thin wires.
5.	Heat and electrical conductivity	Very good conductors of heat and electricity.	Poor conductors of heat and electricity.

**Table 27.1** Comparing some general properties of metals and non-metals.

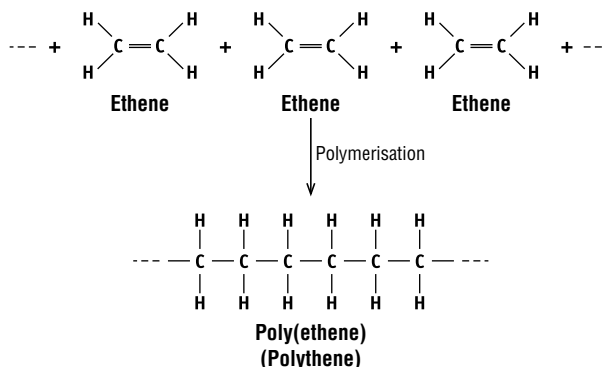
- Metals can be mixed with another element to form an **alloy**. For example, brass is an alloy of copper and zinc. Similarly, bronze is an alloy of copper and tin.
- Alloys can be more useful than the pure metals as the alloy has properties of both metals in the mixture. Steel is an alloy of iron with the non-metal carbon. Steel contains about 0.15% carbon. The carbon makes the steel harder and tougher than pure iron.

## 27.3 Addition Polymers

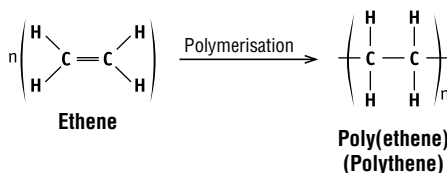
- A **polymer** is a long-chain molecule made by joining together many small molecules.
- The small molecules from which the polymer is made are called **monomers**.
- Ethene is the monomer used in the manufacture of the polymer polythene.
- Polythene is referred to as an addition polymer because it is manufactured using addition reactions.
- There are five addition polymers on our course: poly(ethene), poly(chloroethene), poly(propene), poly(phenylethene) and poly(tetrafluoroethene).

### (a) Poly(ethene) or polythene

- It was discovered in 1933 by Eric Fawcett and Reg Gibson at the ICI plant in Cheshire when ethene was heated under high pressure, Fig. 27.4.



This may also be written as:

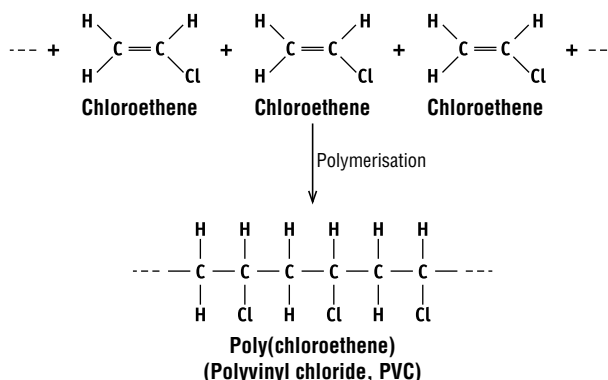


**Fig. 27.4** Molecules of ethene undergo addition reactions among themselves to form the addition polymer polythene.

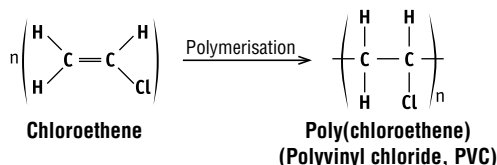
- Tests on this material showed that it had good electrical insulating properties and so it was used for insulating underwater electric cables.
- This type of polythene is commonly called **low-density polythene** due to the long chains of carbon atoms becoming branched, coiling around each other, and leaving a lot of empty space.
- Today low-density polythene is used for wrapping film and shopping bags.
- In 1953 Karl Ziegler carried out further research at ICI to polymerise ethene at a lower pressure using special types of catalysts. These catalysts consisted of metals bonded to organic groups. His work led to the discovery of **high-density polythene**.
- High-density polythene has very little branching along the chains, allowing the chains to pack more closely, thus increasing the density of the polythene.
- High-density polythene is harder and stiffer than low-density polythene and has a much higher melting point. It is used to make food storage containers, buckets and crates for bottles.

## (b) Poly(chloroethene) or polyvinyl chloride (PVC)

- Chloroethene undergoes polymerisation to form **poly(chloroethene)** or **polyvinyl chloride**, Fig. 27.5.



This may also be written as:



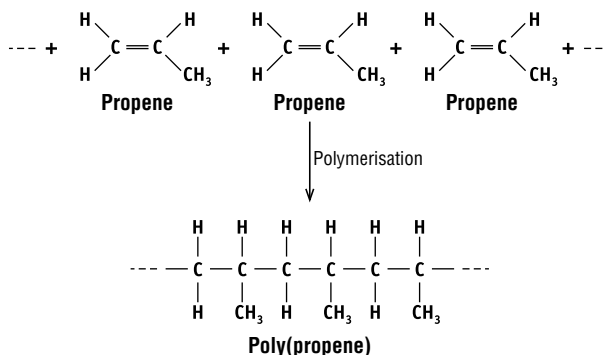
**Fig. 27.5** Chloroethene undergoes polymerisation to form poly(chloroethene). The old name for chloroethene was vinyl chloride. Hence poly(chloroethene) is also known as polyvinyl chloride or PVC.



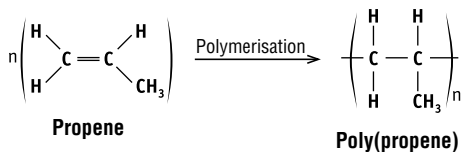
- PVC is a strong, rigid plastic and is used to manufacture window frames, gutters and drain pipes.
- Addition of plasticiser makes PVC into a softer and more flexible plastic used for raincoats, shower curtains and wellington boots.

### (c) Poly(propene) or polypropylene

- Poly(propene) is made by the polymerisation of propene using Ziegler catalysts, Fig. 27.6.



This may also be written as:

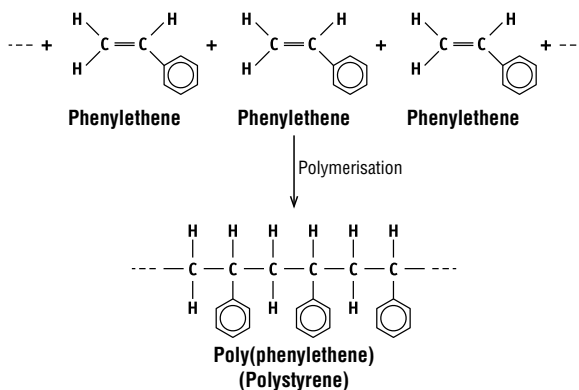


**Fig. 27.6** Poly(propene) is made by polymerising propene. Poly(propene) is commonly called polypropylene.

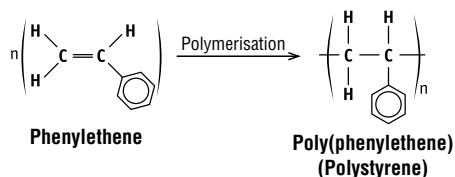
- The polymer chains pack closely together in poly(propene) and this gives it similar properties to high-density polythene. Poly(propene) is used for making chairs, laboratory beakers, toys and water pipes for plumbing.
- Fibres of polypropylene are used to make ropes, carpets and fishing nets.

### (d) Poly(phenylethene) or polystyrene

- Poly(phenylethene) or polystyrene is made by polymerising phenylethene, Fig. 27.7.



This may also be written as:



**Fig. 27.7** Poly(phenylethene) is made by polymerising phenylethene. Poly(phenylethene) is commonly called polystyrene.

- The polymer chains are quite rigid and hence polystyrene tends to be brittle.
- Rigid polystyrene is used for making yoghurt containers and disposable drinking cups.
- Expanded polystyrene is made by adding hexane to the polystyrene beads and heating the polymer.
- Expanded polystyrene is used as packing for fragile objects, for ceiling tiles and for insulation.



In this chapter you will learn about:

- The electrochemical series and corrosion
- Electrolysis of molten lead bromide
- Extraction of sodium from molten sodium chloride
- Extraction of aluminium from bauxite
- Manufacture of iron and steel

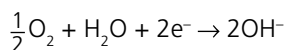
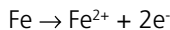
## 28.1 The Electrochemical Series and Corrosion

- Different combinations of metals produce different voltages in a simple cell.
- Galvani discovered that the muscles in a dissected frog's leg twitched when touched by two different metals.
- Volta invented the first battery using plates of copper and zinc separated by cardboard that was soaked in salt solution.
- Elements near the top of the electrochemical series have a great tendency to lose electrons and form positive ions. These metals tend to be very reactive.
- Elements near the bottom of the electrochemical series have a small tendency to lose electrons. These metals tend to be very unreactive.

**Corrosion** is any undesired process whereby a metal is converted to one of its compounds.

- Since metals near the top of the electrochemical series tend to lose electrons readily, these metals corrode easily.
- Metals near the bottom of the electrochemical series are very unreactive and do not corrode easily.
- Aluminium is quite high in the electrochemical series but does not corrode to the same extent as iron. This is because the oxide of aluminium ( $\text{Al}_2\text{O}_3$ ), formed when it reacts with air, sticks firmly to the metal surface and prevents further corrosion.
- Stainless steel is an alloy of steel with chromium. The chromium in the steel reacts with air to form a layer of chromium oxide that protects the steel from corrosion.

- Corrosion is an electrochemical process in which electrons are transferred from iron to oxygen.



The  $\text{Fe}^{2+}$  ions and the  $\text{OH}^{-}$  ions then come together to form iron(II) hydroxide,  $\text{Fe}(\text{OH})_2$ . This is then oxidised in air to form rust,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

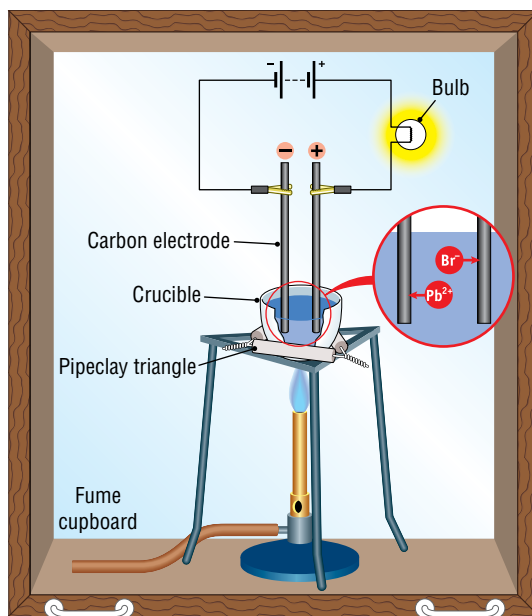
- There are a number of ways of preventing corrosion: (i) painting and greasing, (ii) galvanising, (iii) coating of surface with another metal, (iv) alloying with another metal and (v) using sacrificial anodes.
- In the sacrificial anode method of preventing corrosion, the iron is placed in contact with a metal that is more easily oxidised, e.g. a block of zinc is bolted to the iron on a ship's hull. In this case, the zinc corrodes rather than the iron.

## 28.2 Electrolysis of Molten Lead Bromide

- Electrolysis is the use of electricity to bring about a chemical reaction.
- Electrolysis was used by Humphry Davy to isolate a number of elements.
- Michael Faraday introduced the term electrolysis into chemistry and made many discoveries in the area of electrolysis (e.g. Faraday's Laws of Electrolysis).
- Electrolysis is used to extract strongly electropositive metals from their compounds.
- Lead metal may be extracted from molten lead bromide by electrolysis, Fig. 28.1.
- The following are the reactions that occur during the electrolysis of lead bromide:

**Negative electrode:**  $\text{Pb}^{2+} + 2\text{e}^{-} \rightarrow \text{Pb}$

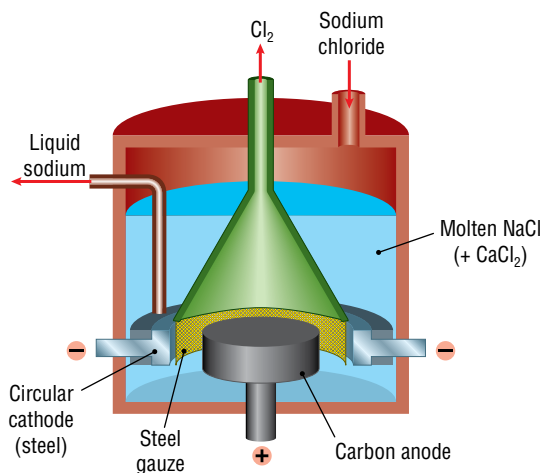
**Positive electrode:**  $2\text{Br}^{-} \rightarrow \text{Br}_2 + 2\text{e}^{-}$



**Fig. 28.1** When molten lead bromide is electrolysed, lead metal is formed at the negative electrode and bromine vapour is formed at the positive electrode. Lead metal has been extracted from the lead bromide salt.

## 28.3 Extraction of Sodium from Molten Sodium Chloride

- Sodium metal is produced on an industrial scale by carrying out electrolysis in a special type of cell called the Downs cell, Fig. 28.2.



**Fig. 28.2** The Downs cell is used to extract sodium from sodium chloride. The sodium metal is formed at the negative electrode.

- A mixture of solid sodium chloride and calcium chloride is placed in the Downs cell. The presence of the calcium chloride lowers the melting point of the sodium chloride.
- A large electric current is passed through the cell and this melts the mixture.
- The following reactions occur:

**Negative electrode:**  $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

**Positive electrode:**  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

- Chlorine gas is a useful by-product of the process.
- The negative electrode is made of steel as steel is a very good conductor. The positive electrode is made of graphite. If the positive electrode were made of steel, the chlorine formed at the electrode would react with the iron in the steel.

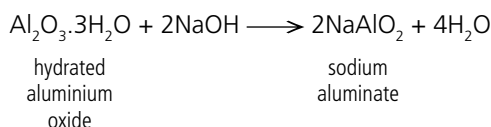
## 28.4 Extraction of Aluminium from Bauxite

- Bauxite is the ore from which aluminium metal is extracted. Bauxite contains about 50% aluminium oxide,  $\text{Al}_2\text{O}_3$ .
- There are two stages involved in obtaining aluminium metal from bauxite.
  - Pure aluminium oxide is obtained from the bauxite.
  - The pure aluminium oxide is electrolysed to extract aluminium metal from it.

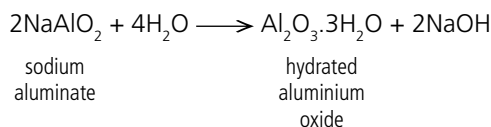
### (i) Obtaining Aluminium Oxide from Bauxite

Aughinish Alumina, on the Shannon estuary, converts bauxite into pure aluminium oxide. There are five stages involved in this process.

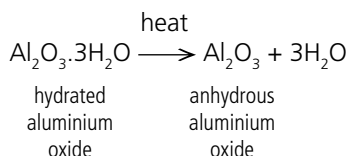
1. **Crushing and mixing.** The bauxite is crushed to a fine powder (to ensure complete reaction) and mixed with hot sodium hydroxide solution.
2. **Digestion.** The mixture of ground bauxite and sodium hydroxide is heated.



3. **Clarification (removal of impurities).** Flour is added to help the insoluble impurities in the bauxite to stick together and precipitate out. These impurities are then filtered off and pumped to the waste storage area. The waste is commonly referred to as "red mud".
4. **Precipitation of aluminium oxide.** The sodium aluminate solution is pumped to precipitation tanks. The solution is cooled and tiny "seed" crystals of  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  are added to help the formation of more crystals of this substance.



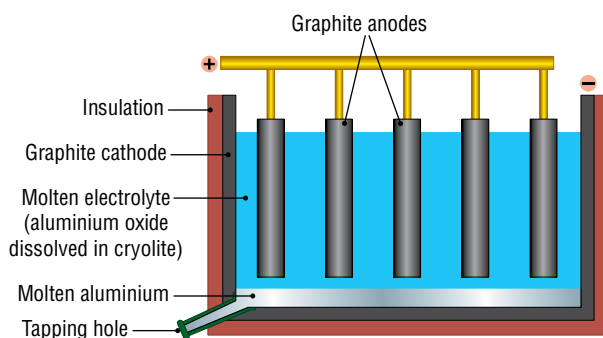
5. **Removal of water of crystallisation.** The water of crystallisation is removed by heating the hydrated aluminium oxide in a large kiln.



- The pure aluminium oxide formed consists of a fine white powder.
- To avoid any damage to the environment, all waste is treated within the plant and the local environment is continually monitored.

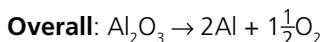
## (ii) Extraction of Aluminium Metal from Aluminium Oxide by Electrolysis

- The aluminium oxide undergoes electrolysis in smelters abroad to give aluminium metal, Fig. 28.3.



**Fig. 28.3** This electrolysis cell is used to extract aluminium metal from aluminium oxide.

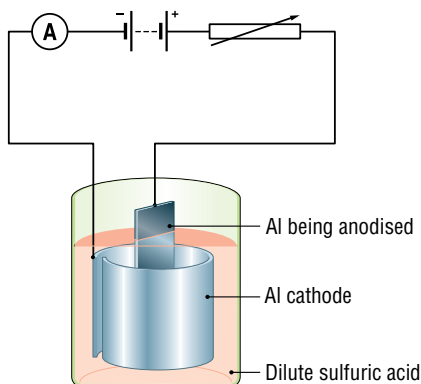
- The aluminium oxide is dissolved in a molten substance called cryolite,  $\text{Na}_3\text{AlF}_6$ , as the presence of cryolite lowers the melting point of the pure aluminium oxide.
- The following are the reactions that occur:



- The electrolysis is carried out at a temperature of about  $1000^\circ\text{C}$ .
- The molten aluminium is tapped off periodically at the bottom of the cell.
- The oxygen given off at the positive electrode reacts with the large graphite anodes to form carbon dioxide, i.e. the anodes are burned away and have to be replaced from time to time. This is of benefit to the extraction process as the oxygen formed is thus removed from the system. Otherwise, the molten aluminium could possibly recombine with the oxygen to form aluminium oxide. In addition, the heat given out by the reaction between the graphite and the oxygen helps to keep the electrolyte molten.
- Smelters consume vast quantities of electricity and are usually built in countries that have cheap hydroelectric power.
- More emphasis must be placed on the recycling of aluminium both from an economic and an environmental point of view.
- When the natural oxide coating on the surface of a piece of aluminium has been made thicker, the aluminium is said to be **anodised**. Anodised aluminium is more resistant to corrosion than ordinary aluminium.



- A piece of aluminium may be anodised using the apparatus shown in Fig. 28.4.



**Fig. 28.4** The piece of aluminium to be anodised is made the anode of the cell, i.e. it is connected to the positive electrode of the battery.

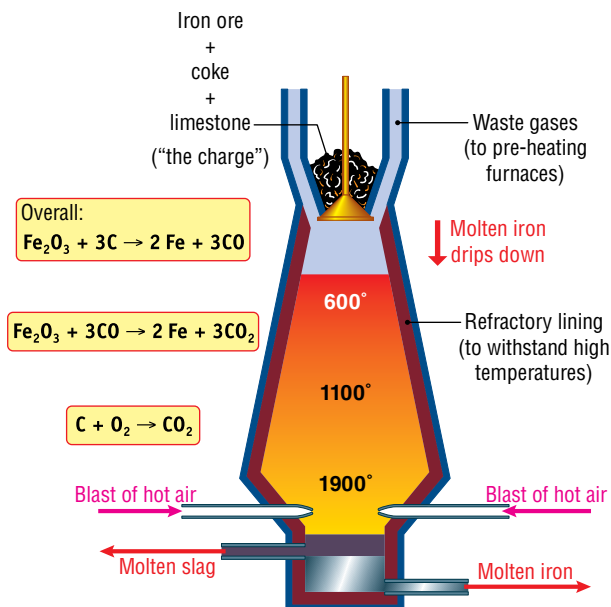
- The following are the reactions that occur:  
**Positive electrode (anode):**  $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^-$   
**Negative electrode (cathode):**  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
- The oxide layer of anodised aluminium has a porous nature that allows it to be dyed.

## 28.5 Manufacture of Iron and Steel

- Since iron is located farther down the electrochemical series than aluminium, it may be extracted using **chemical reduction**.
- Iron is needed for various uses, e.g. construction of buildings, manufacture of machines, tools, car bodies and railways.
- Iron is extracted from iron ore using chemical reduction in a blast furnace.
- Iron (in the form of steel) may also be manufactured using the electric arc process.

### (i) The Blast Furnace

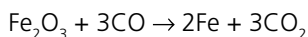
- Haematite,  $\text{Fe}_2\text{O}_3$ , is the main ore of iron from which iron metal is commonly extracted.
- A mixture of iron ore, coke and limestone is added through the top of the furnace, Fig. 28.5.



**Fig. 28.5** A blast furnace is used to extract iron metal from iron ore by chemical reduction using carbon (in the form of coke).

- Blasts of hot air are blown in at the bottom of the furnace.
- The overall reaction that takes place in the furnace is:  

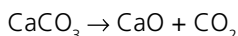
$$\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$$
- The carbon (coke) acts as the reducing agent and causes the iron ore to be reduced to iron metal.
- The coke acts as a fuel to provide heat for the blast furnace. The coke burns in the hot air to form carbon monoxide and carbon dioxide and this helps to maintain the temperature of the blast furnace.
- The coke provides a physical support for the materials in the furnace. Coke is a porous material and it allows the hot gases to move upwards through the furnace, as well as allowing the hot molten iron to trickle down to the bottom of the furnace.
- Carbon monoxide is also formed and is, in fact, the *main* reducing agent to convert the iron ore to iron metal.



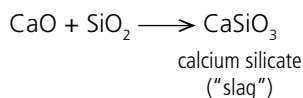
- Any carbon monoxide that remains unreacted is collected with the other waste gases and burned in special stoves to heat the blast of incoming air at the bottom of the furnace.
- The ore is normally added in the form of pellets rather than in powdered form – the pellets leave spaces to enable the carbon monoxide to move through the ore and bring about reduction. In addition, the gaps between the pellets allow the

molten metal to pass down towards the bottom of the blast furnace. Also, if the ore were in powdered form, it is possible that some of it would be carried away by the hot waste gases.

- The purpose of adding the limestone is to remove impurities in the ore. When the limestone is added, it decomposes into lime and carbon dioxide.



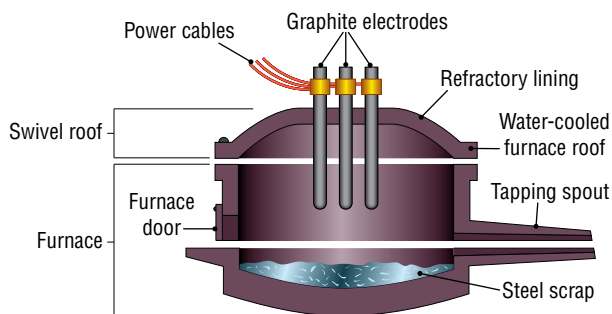
- The main impurity in the haematite is sand,  $\text{SiO}_2$ . The lime reacts with the sand to form a substance commonly referred to as **slag**.



- The slag runs down to the bottom of the furnace. Since the slag is less dense than the molten iron, it floats on top of the iron. The slag is removed at intervals and becomes a solid on cooling. Slag is usually used for road building and cement making.
- A blast furnace produces molten iron – commonly called **pig iron** or **cast iron**. It is quite brittle and is used for making items such as manhole covers and car-engine blocks.
- Most of the iron is converted into steel since there is a far greater demand for steel than for pig iron.
- The steel is manufactured in two stages: (i) Pure oxygen is blown on to the surface of the molten iron. This removes various impurities such as carbon and sulfur by burning them off as the gases carbon dioxide and sulfur dioxide. (ii) Different elements (e.g. manganese, chromium and tungsten) are then added to the molten iron to give steel of a particular specification, e.g. hardness and resistance to corrosion.
- **Environmental considerations:** (i) Industries are obliged to restore the landscape to an acceptable state after quarrying. (ii) The sulfur dioxide formed by burning is removed by a "scrubbing" process in chimneys. (iii) Dust is kept to a minimum and is removed electrostatically.

## (ii) Electric Arc Process

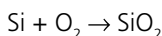
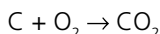
Steel may also be manufactured in an Electric Arc Furnace which is used to melt the scrap metal, Fig. 28.6.



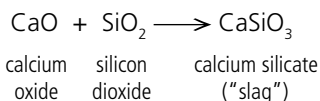
**Fig. 28.6** Steel can be manufactured using the electric arc furnace.

There are 5 steps involved in the manufacture of steel using the electric arc furnace.

1. **Charging.** The lid of the Electric Arc Furnace is swung back and the steel scrap is placed in the furnace using an overhead crane. The scrap metal is commonly called the "charge" and filling the furnace with the scrap metal is called "charging".
2. **Melting.** Three large graphite electrodes are lowered down into the furnace close to the scrap. A huge electric current is passed between the electrodes and the high temperature produced by the arc melts the scrap metal.
3. **Sampling and refining.** A sample of molten steel is taken from the furnace and sent to the laboratory for analysis. Oxygen is then blown into the molten steel using an oxygen lance. The main purpose of the oxygen is to remove excess carbon in the form of carbon dioxide. Other impurities like silicon are oxidised to silicon dioxide.



Calcium oxide (lime) is then added to remove impurities like silicon dioxide as slag.



The slag is less dense than the liquid steel and floats on top of the steel. The furnace is tilted backwards and the molten slag is poured off.

4. **Tapping.** The furnace is then tilted forward and the molten steel is transferred to a ladle. Various other elements (manganese, chromium and vanadium) are added to the molten steel in the ladle to alter the properties of the steel as required by the customer.
  5. **Casting.** The molten steel is then poured into the top of a casting machine where the steel solidifies to produce a slab of red hot steel. This is then cut into various lengths to give steel products required by the construction industry, e.g. beams, columns and channels.
- **Environmental considerations:** All emissions are strictly controlled to ensure that they meet the statutory requirements. Fumes from the furnace are collected by ducts and fans and filtered to remove particles of dust. Strict control is also maintained on water quality used in the process. Large amounts of water are used for cooling and re-circulated in a closed-loop system so that there is no discharge from the plant.