

Carbon chemistry

1.1 Naming of carbon compounds

The systematic naming of carbon compounds is in two parts:

(a) Stem

A stem to show the number of carbon atoms,

C_1	meth-	C_6	hex-
C_2	eth-	C_7	hept-
C_3	prop-	C_8	oct-
C_4	but-	C_9	non-
C_5	pent-	C_{10}	dec-

(b) Ending

An **ending** to show the grouping of atoms or functional group.

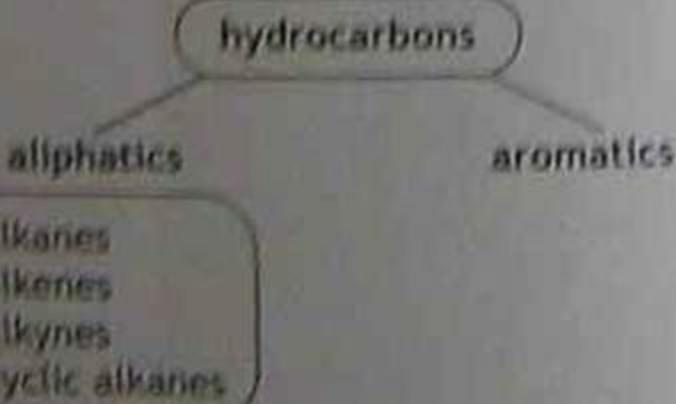
For hydrocarbons with

single bonds -ane

a double bond -ene

a triple bond -yne

Hydrocarbons are compounds which are made up of hydrogen atoms and carbon atoms only.



Alkanes

- 1. Saturated hydrocarbons.
- 2. Same homologous series.
- 3. General molecular formula C_nH_{2n+2} .
- 4. Found in natural gases (C_1-C_4) and liquid petroleum (C_5-C_{17}).
- 5. Functional group is alkyl group.
- 6. Contain single C-C bonds only.

Branched-chain hydrocarbons

Alkyl groups are alkane chains minus a hydrogen atom. The -ane of the parent hydrocarbon is dropped and the -yl is added.

Table 1.1 Alkyl groups

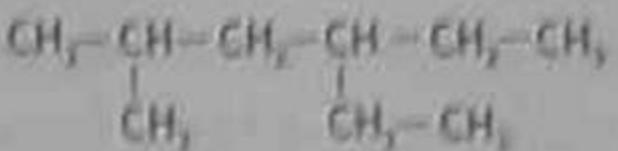
No. of carbon atoms	Structural formula		Alkyl group name
	Full	Condensed	
One	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}- \\ \\ \text{H} \end{array}$	CH_3-	methyl
Two	$\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array}$	CH_3CH_2-	ethyl

Rules for naming branched-chain alkanes

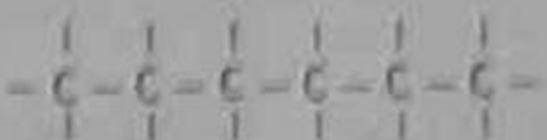
1. Find the longest chain of carbon atoms in the molecule.
2. Name any branch (side) chains as the alkyl groups.
3. Number the side chains from the end of the parent chain which will give them the lowest number.
4. When there is more than one side chain, they are listed alphabetically.
5. If the same side chain occurs more than once, prefixes di-, tri-, tetra- are used.

Example 1

To name the compound drawn below:



Step 1. Draw the longest carbon chain.



Step 2. Use the chain like a surname.

..... hexane

Step 3. Name side chain in alphabetical order.

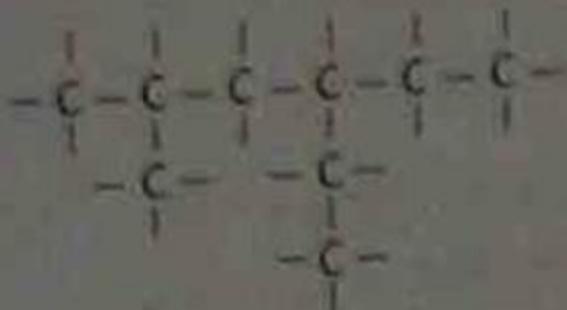
ethyl-methyl

Step 4. Number from the end of the skeleton to give the lowest number for side chains.
Naming of branches is alphabetical before numerical.

Table 1.2 The alkanes (first 3 members)

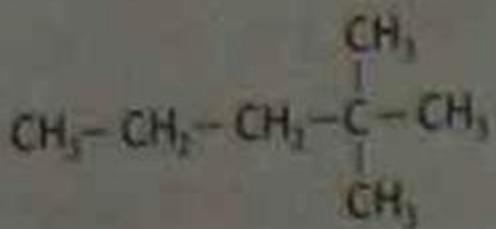
Name	Molecular formula	Structural formula	State (SLC*)	Uses as fuels
Methane	CH_4	$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array} $	gas	natural gas (78%)
Ethane	C_2H_6	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	gas	natural gas (small %)
Propane	C_3H_8	$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	gas	LPG (butane and propane)

* SLC – standard laboratory conditions (25°C/100 kPa)



(Answer: 4-ethyl-2-methylhexane)

Example 2



When same-name side chains are involved, use prefixes, di-, tri-... The compound above is called 2, 2-dimethylpentane.

Isomerism in alkanes

Isomers are compounds which have the same molecular, but different structural, formula.

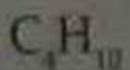
Structural Isomerism

chain
e.g. butane

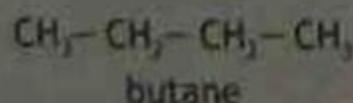
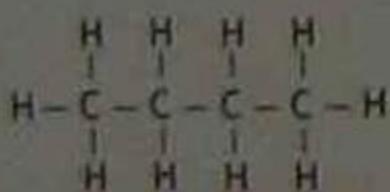
position
e.g. butene

Isomers of butane

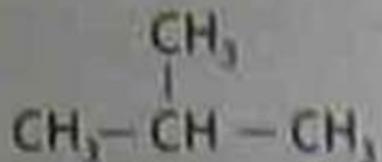
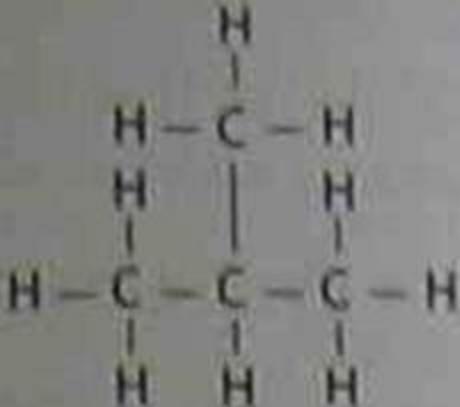
Molecular formula



Straight chain



Branched chain



2-methylpropane

Alkenes

Unsaturated hydrocarbons.

General molecular formula C_nH_{2n} .

Functional group $\text{C} = \text{C}$.

Models

Model kits should be used regularly to show that carbon-carbon covalent bonds may be

single: C - C

double: C = C

or triple: C ≡ C

Other elements can join these structures, the commonest being hydrogen, oxygen, nitrogen, sulfur and the halogens.

After propene, different isomers are possible by shifting the position of the double bond, so the double bond must be numbered.

1-butene

C_4H_8

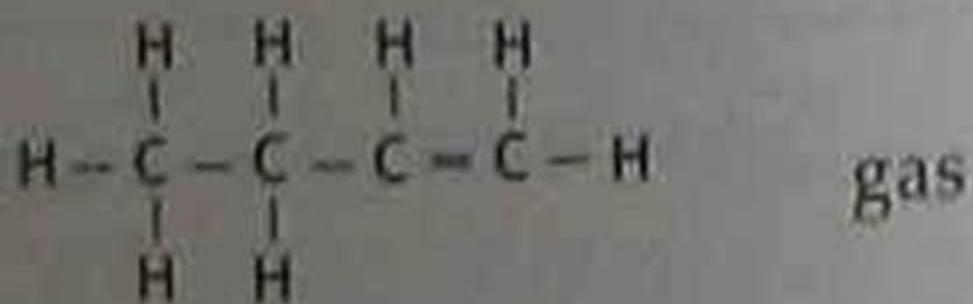
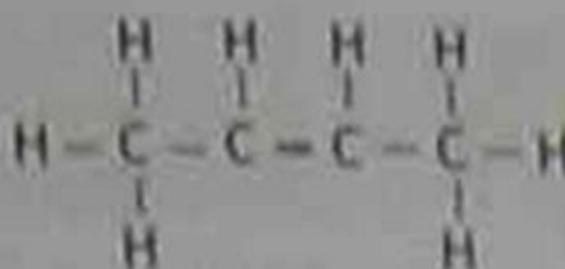


Table 1.3 The alkenes

Name	Molecular formula	Structural formula	State (SLC) 25 °C/100 kPa	Uses
Ethene	C ₂ H ₄	<pre> H H C = C H H </pre>	gas	making plastics (e.g. polyethylene), alcohol, antifreeze (ethylene glycol)
Propene	C ₃ H ₆	<pre> H H H H - C - C = C - H H </pre>	gas	making plastics (e.g. polypropylene)

2-butene

C₄H₈



gas

Position isomers

Same homologous series,

Different position of functional group, e.g. alkenes C = C bond. Owing to isomerism, additional naming rules are needed.

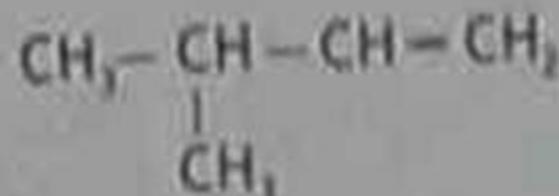
Rules for naming alkenes

1. Choose the longest consecutive chain of carbon atoms that includes the double bond, and name it as the parent alkene.
2. Number the chain from the end that gives the double bond its smaller number.
3. Name and number the alkyl groups as with the alkanes.

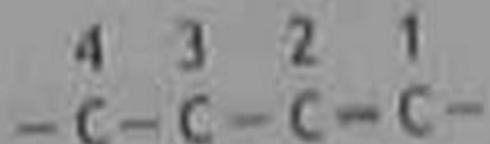
Example

When side chains are present.

Name the compound drawn below:



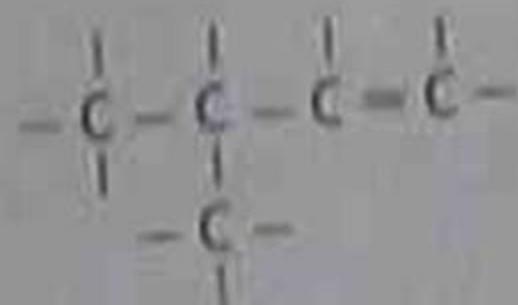
Step 1. Draw the longest carbon chain that contains the double bond.



Step 2. Use the chain as a surname. Number the chain.

.....1-butene

Step 3. Name and number any side chains, using the same numbering system as for the double bond.



3-methyl-1-butene

Haloalkanes

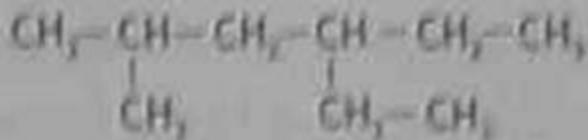
Compounds in which one or more hydrogen atoms of alkanes have been replaced by halogen atoms (F, Cl, Br, I) are called haloalkanes.

Rules for naming branched-chain alkanes

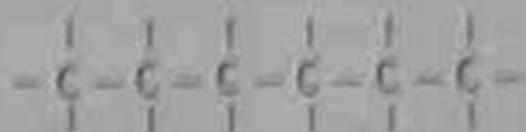
1. Find the longest chain of carbon atoms in the molecule.
2. Name any branch (side) chains as the alkyl groups.
3. Number the side chains from the end of the parent chain which will give them the lowest number.
4. When there is more than one side chain, they are listed alphabetically.
5. If the same side chain occurs more than once, prefixes di-, tri-, tetra- are used.

Example 1

To name the compound drawn below:



Step 1. Draw the longest carbon chain.



Step 2. Use the chain like a surname.

..... hexane

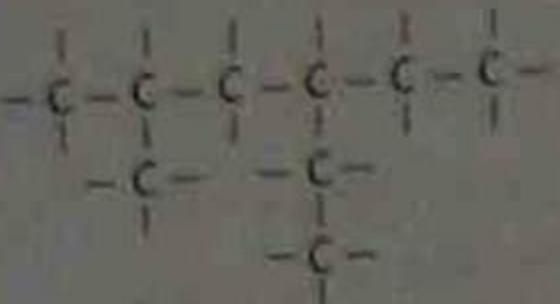
Step 3. Name side chain in alphabetical order.

ethyl-methyl

Step 4. Number from the end of the skeleton to give the lowest number for side chains.
Naming of branches is alphabetical before numerical.

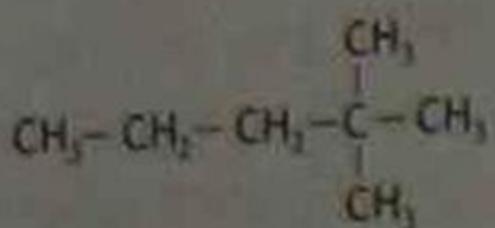
Table 1.2 The alkanes (first 3 members)

Name	Molecular formula	Structural formula	State (SLC*)	Uses as fuels
Methane	CH ₄	<pre> H H—C—H H </pre>	gas	natural gas (78%)
Ethane	C ₂ H ₆	<pre> H H H—C—C—H H H </pre>	gas	natural gas (small %)
Propane	C ₃ H ₈	<pre> H H H H—C—C—C—H H H </pre>	gas	LPG (butane and propane)



(Answer: 4-ethyl-2-methylhexane)

Example 2



When same-name side chains are involved, use prefixes, di-, tri-... The compound above is called 2, 2-dimethylpentane.

Isomerism in alkanes

Isomers are compounds which have the same molecular, but different structural, formula.

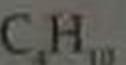
Structural Isomerism

chain
e.g. butane

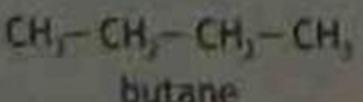
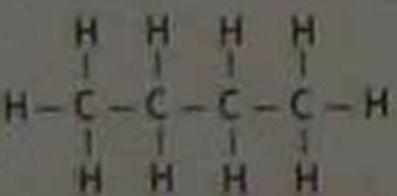
position
e.g. butene

Isomers of butane

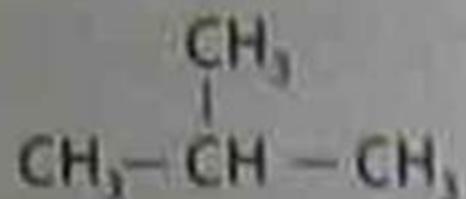
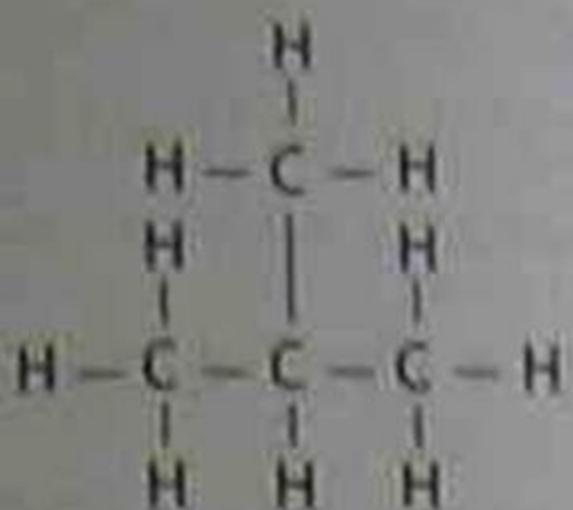
Molecular formula



Straight chain



Branched chain



2-methylpropane

Alkenes

Unsaturated hydrocarbons.

General molecular formula C_nH_{2n} .

Functional group $C=C$.

Models

Model kits should be used regularly to show that carbon-carbon covalent bonds may be

single: $C - C$

double: $C = C$

or triple: $C \equiv C$

Other elements can join these structures, the commonest being hydrogen, oxygen, nitrogen, sulfur and the halogens.

After propene, different isomers are possible by shifting the position of the double bond, so the double bond must be numbered.

1-butene

C_4H_8

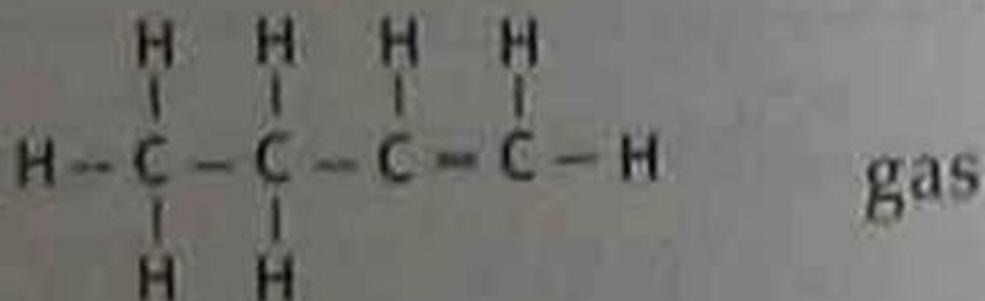
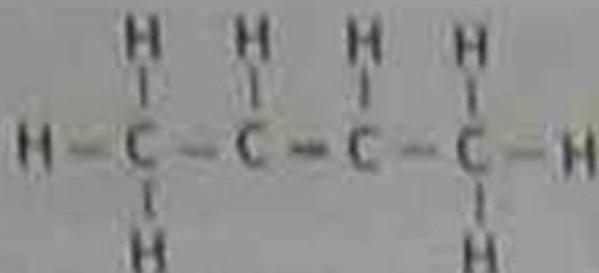


Table 1.3 The alkenes

Name	Molecular formula	Structural formula	State (SLC) 25 °C/100 kPa	Uses
Ethene	C ₂ H ₄	<pre> H H C = C H H </pre>	gas	making plastics (e.g. polyethylene), alcohol, antifreeze (ethylene glycol)
Propene	C ₃ H ₆	<pre> H H H H - C - C = C - H H </pre>	gas	making plastics (e.g. polypropylene)

2-butene

C₄H₈



gas

Position isomers

Same homologous series.

Different position of functional group, e.g. alkenes C=C bond. Owing to isomerism, additional naming rules are needed.



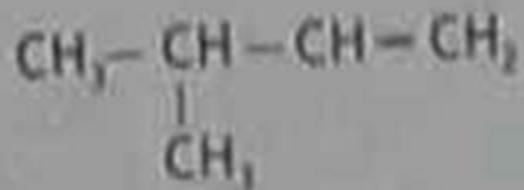
Rules for naming alkenes

1. Choose the longest consecutive chain of carbon atoms that includes the double bond, and name it as the parent alkene.
2. Number the chain from the end that gives the double bond its smaller number.
3. Name and number the alkyl groups as with the alkanes.

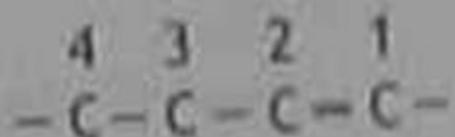
Example

When side chains are present.

Name the compound drawn below:

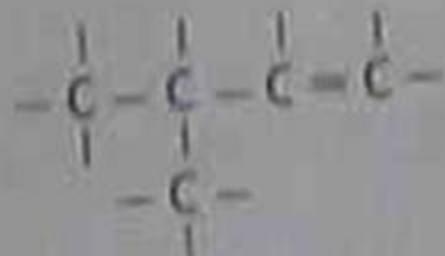


Step 1. Draw the longest carbon chain that contains the double bond.



Step 2. Use the chain as a surname. Number the chain.

Step 3. Name and number any side chains, using the same numbering system as for the double bond.



3-methyl-1-butene

Haloalkanes

Compounds in which one or more hydrogen atoms of alkanes have been replaced by halogen atoms (F, Cl, Br, I) are called haloalkanes.

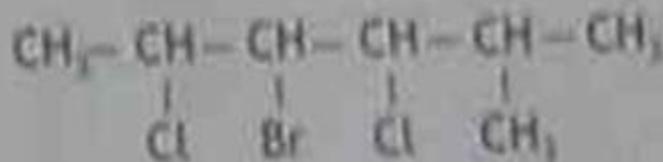


Rules for naming haloalkanes

1. Prefixes bromo-, chloro-, fluoro- and iodo- are used with the parent hydrocarbon.
2. The carbon chain is numbered so that the halogen atom has the smallest possible number.
3. In the case of polyhalogen compounds:
 - (a) If only one type of halogen atom is present, each is numbered, and di-, tri-, etc are used.
 - (b) If more than one type of halogen atom is present, they are listed alphabetically as in 1.
4. Since the halogen atoms are functional groups, they are numbered in preference to any side chains.

Example

To name the compound below.



Step 1. Find the longest straight carbon chain.

.....hexane

Step 2. Number from the end that will make the halogens the lower.

Step 3. Arrange halo atoms in alphabetical order.

Step 4. Name and number any side chains present.

The name of the compound is
3-bromo-2,4-dichloro-5-methylhexane.

1.2

Classification of organic reactions

Substitution

This is the replacement of one atom or group by another:



Substitution reactions occur with the chlorination of alkanes in the presence of ultraviolet light. A mixture of CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 can be formed.

Addition

It is possible to add atoms or groups of atoms to alkenes or alkynes. The reaction occurs at a double bond or at a triple bond.



Here one bond breaks and the reagent adds onto the molecule.

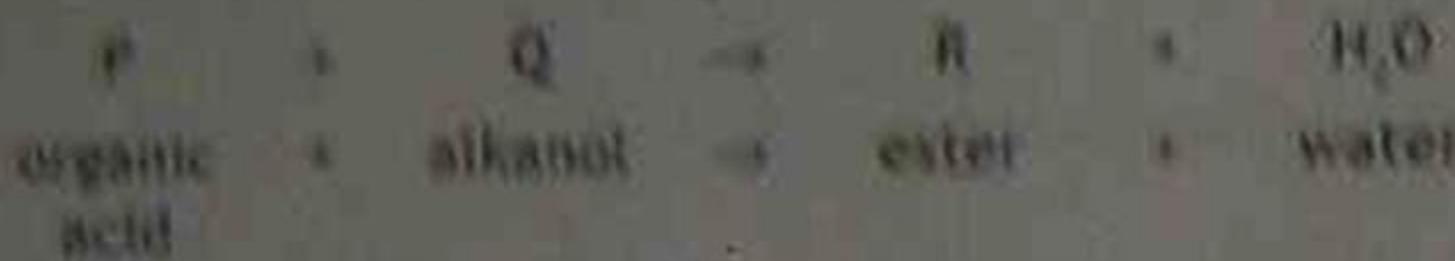
Elimination

This is the reverse of addition. A small molecule breaks off and a double bond is formed.



Condensation

Two molecules react, forming a new compound and a small molecule, usually water.



Hydrolysis

This is the opposite of condensation. The action of water on a molecule results in two new products:



The equilibrium can be shifted by adding acids or bases.

Polymerisation

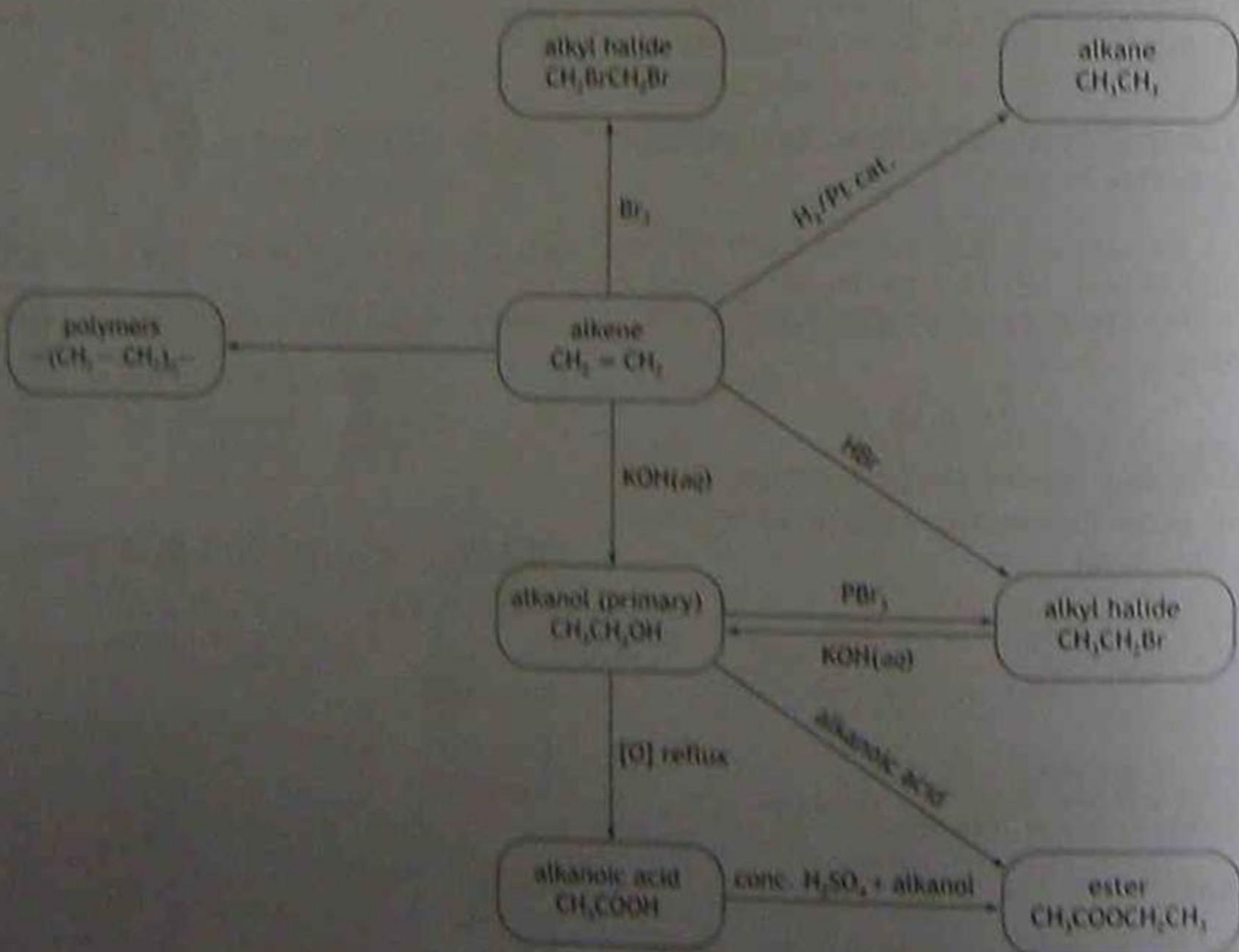
Polymerisation, to form a long-chain molecule or polymer from monomers, can be

- (i) addition, e.g. in alkenes, or
- (ii) condensation, when a small molecule is eliminated, e.g. nylon-66.

E3

Common aliphatic reactions involving ethylene

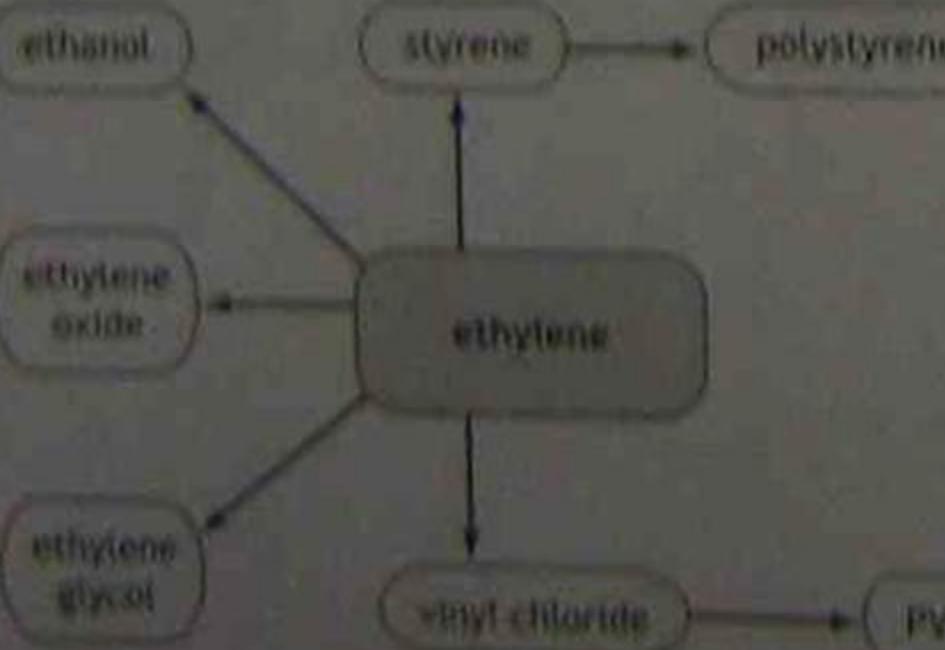
Ethylene, because of the high reactivity of its double bond, is readily transformed into many useful products as seen in the flowchart below:



1.4 | The industrial source of ethylene



Because of the reactivity of its double bond, ethylene is used in the manufacture of polyethylene and many key intermediate products.

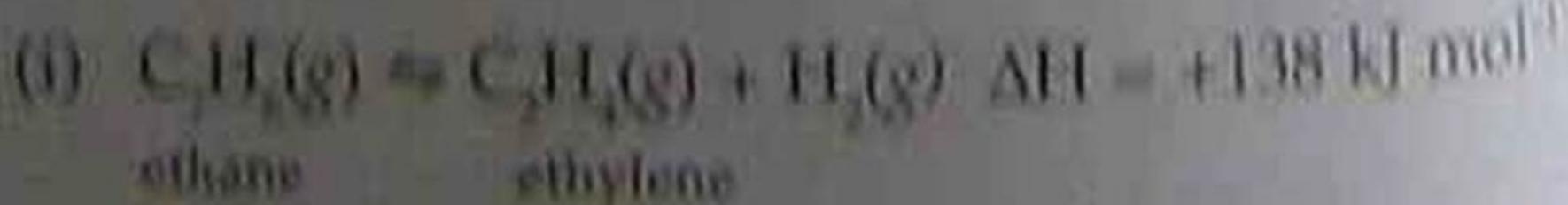


Ethylene is produced either from natural gas or crude oil, which are mixtures of hydrocarbons (mostly alkanes); petroleum refineries use both chemical and physical changes to produce ethylene.

Thermal cracking

The main method used to produce unsaturated hydrocarbons such as ethene (ethylene) is by the thermal cracking of suitable feedstock. Typical feedstocks are:

- (a) Ethane and propane from natural gas.
- (b) Ethene can also be produced from the fractional distillation of crude oil using naphtha or gas oil fractions. The type of feedstock used determines and alters the plant conditions needed to yield the desired product. Examples of chemical reactions which occur during the thermal cracking process are as follows:



Hydrogen is a useful by-product that is used to manufacture fertiliser and harden margarine.

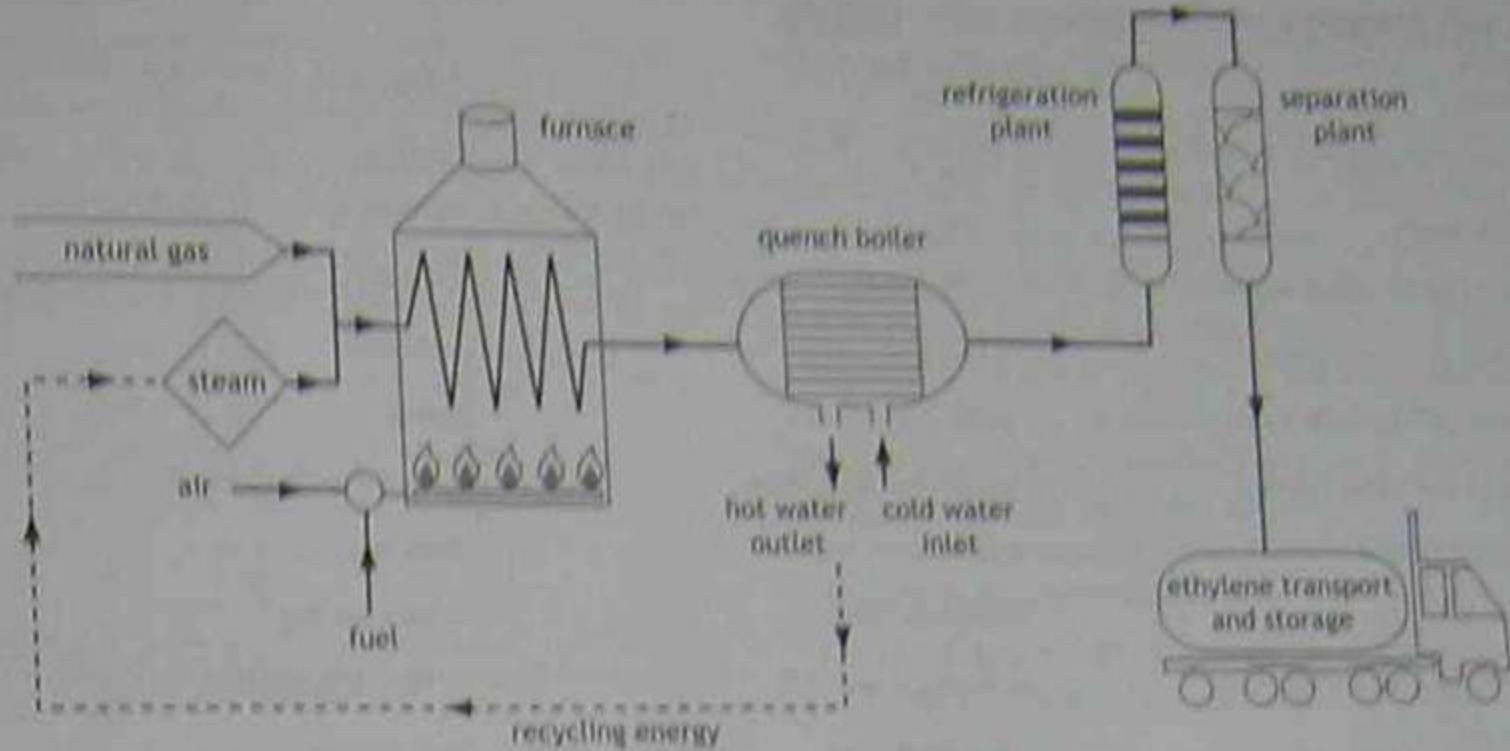
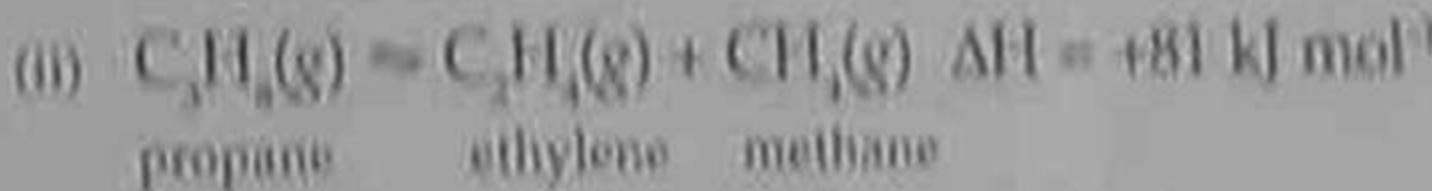


Figure 1.6 Thermal cracking flow chart



Any methane produced is mixed with natural gas.

Since both reactions are endothermic, high temperatures (reduced by the use of catalysts) will result in a high equilibrium yield of ethene.

Ethylene is used as a starting point in the production of synthetic organic compounds including insecticides, refrigerants, explosives and pharmaceuticals, as well as the products shown in Figure 1.5.

The cracking of alkanes to produce lighter fractions is now carried out by the *catalytic cracking* process. By using *zeolite catalysts*, cracking can be carried out at 400–500°C. Zeolites are a naturally occurring group of substances containing a mixture of aluminium and silicon oxides.

15.1 Differences between alkanes and alkenes

The alkanes comprise most of the compounds in crude oil.

Their general molecular formula is C_nH_{2n+2} . The formula of each successive member of the series increases by a $-CH_2$ group, so its overall mass increases by 14. The alkanes form a *homologous series* with similar chemical properties and physical

properties that change gradually with increasing molar mass. Carbon forms no more than four bonds in any of its compounds, so the alkanes which bond to four other atoms from each carbon atom are called saturated hydrocarbons.

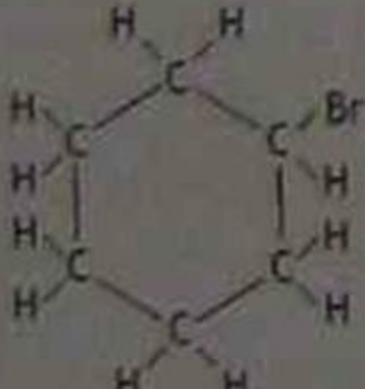
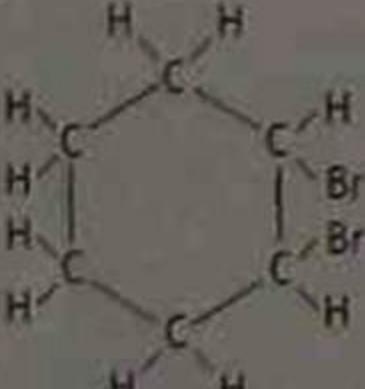
Note: Both alkanes and alkenes show their non-polar nature by being insoluble in the polar solvent water since the forces between water molecules are relatively strong. Alkanes and alkenes will dissolve in other hydrocarbons and similar compounds since they all have dispersion forces as their sole intermolecular force. The size of the intermolecular force depends on the size of the molecule and thus increases with increasing molecular size.

A simple distinguishing test

A simple test to distinguish between an alkene and the corresponding alkane depends on the greater reactivity of alkenes. The test is usually demonstrated in the laboratory using cyclohexane and cyclohexene, since they are both liquids at room temperature and pressure (RTF).

Table 1.5 Properties of alkanes and alkenes

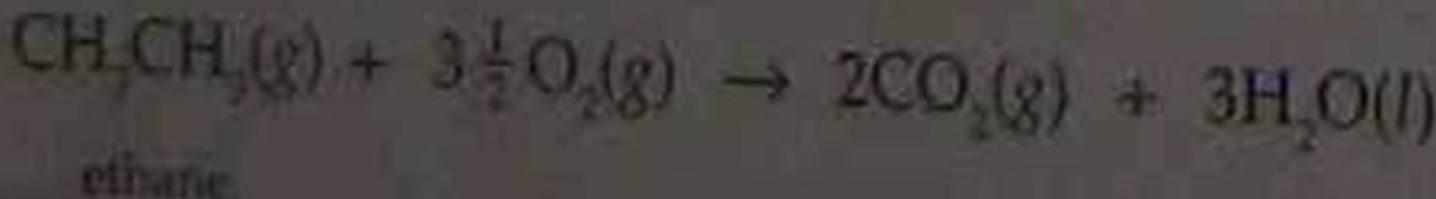
Property	Alkanes	Alkenes
General formula	C_nH_{2n+2}	C_nH_{2n}
Family name	-ane	-ene
Melting point (1st member)	-183°C	-169°C
Boiling point (1st member)	-162°C	-104°C
State at RTP (members 1-4)	gases	gases
State at RTP (remainder)	low BP liquids or solids	low BP liquids or solids
Solubility in water	insoluble	insoluble
Organic solvents	mainly soluble	mainly soluble
Combustion with excess O_2	to form CO_2 and H_2O	to form CO_2 and H_2O
Reactivity	fairly unreactive	very reactive
Characteristic reaction	substitution	addition
First member	CH_4	$CH_2 = CH_2$
Name	methane	ethylene
Bonding	single C – C bonds	one double C = C bond at least

Reagent	Cyclohexane C_6H_{12}	Cyclohexene C_6H_{10}
Bromine water	brown colour of Br_2 remains with slow fading in ultraviolet light.	brown colour of Br_2 is decolourised instantly
Type of reaction	substitution	addition
	 <p>bromocyclohexane</p>	 <p>1,2-dibromocyclohexane</p>
Equation		
	$CH_3CH_3(g) + Br_2(l) \rightarrow$ ethane $CH_3BrCH_3(l) + HBr(g)$ bromoethane	$H_2C=CH_2(g) + Br_2(l) \rightarrow$ ethene $CH_2BrCH_2Br(l)$ 1,2-dibromoethane

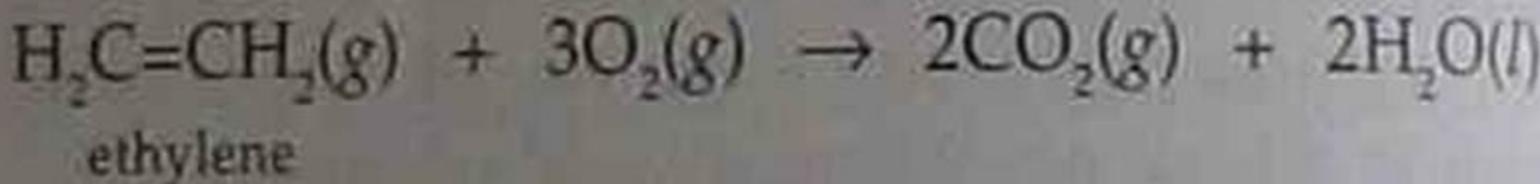
Combustion of alkanes and alkenes

When sufficient oxygen is present, the products of combustion are carbon dioxide and water. Reactions are exothermic.

Example 1



Example 2



Classification of plastics

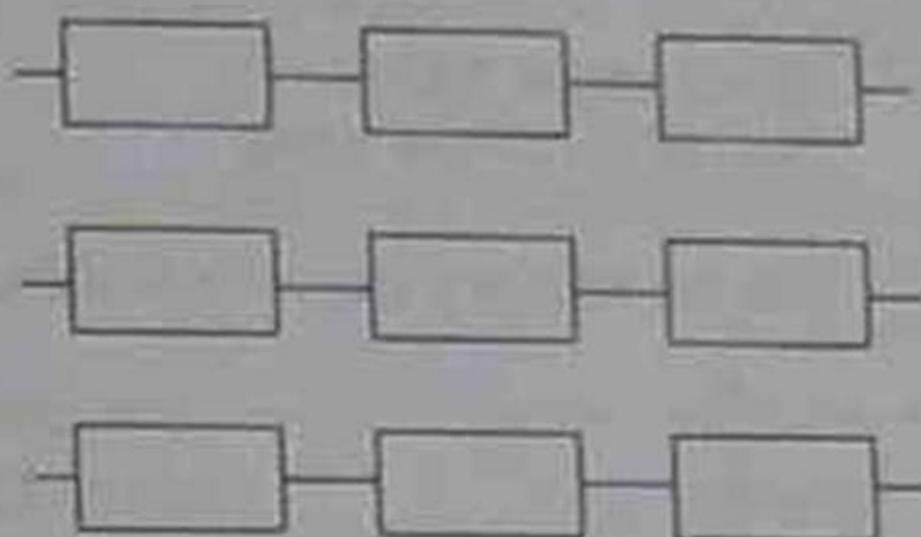
Plastics are manufactured materials that may contain some or all combinations of carbon with oxygen, hydrogen, nitrogen and other organic and inorganic elements. These combinations, although solid in the finished state, are fluid at some stage of manufacture and are capable of being formed into various shapes by the application of heat and pressure, or both. Although they form large and varied groups, plastics can be defined under two major classifications:

(a) Thermosets

These are set into a permanent shape when heat and pressure are applied to them. Reheating will not soften these materials. The simple building block on which synthetic plastics are based is called a single unit or 'monomer'. When monomers are combined into long chain-like structures, the new structures are called 'polymers'. If the polymer strands are cross-linked, then the material is described as thermosetting plastic, e.g. bakelite.

(b) Thermoplastics

Thermoplastics become soft when exposed to sufficient heat and harden on cooling. These properties are retained, no matter how often the process is repeated. If the polymer chains remain unlinked, then the material is said to be thermoplastic, e.g. polyethylene.



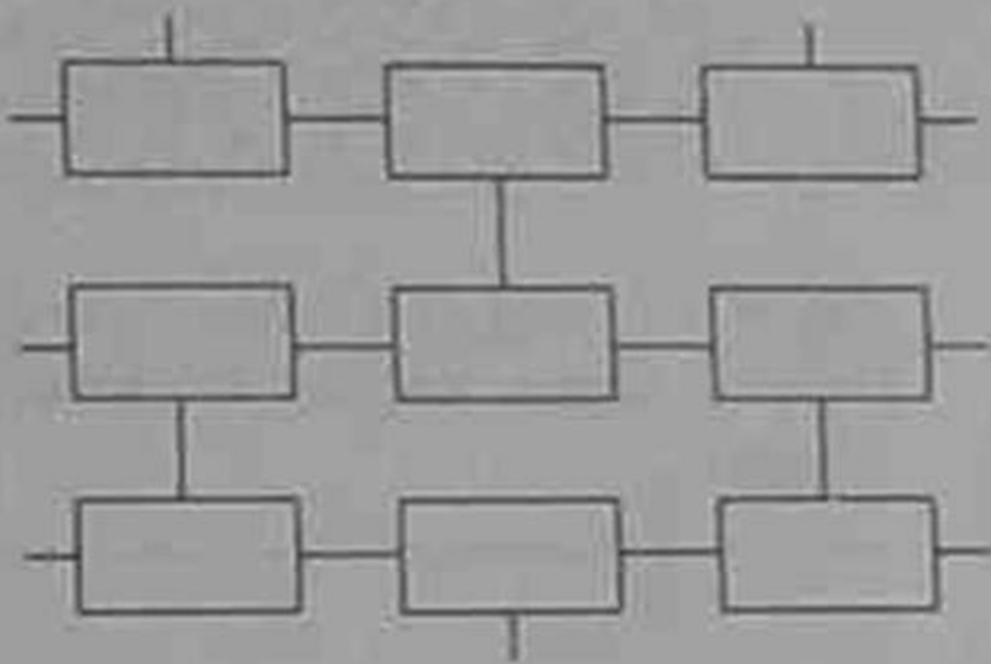


Figure 1.8 Thermosetting network. Chains are cross-linked by covalent bonds.

Polymerisation is the process by which the many small molecules join together. Different processes involving changeable conditions of temperature, pressure and a variety of catalysts are used to produce different polymers. The reaction can occur simply by adding many monomer units to each other and is called 'addition polymerisation', e.g. the thermoplastics polyethene, polystyrene, polyvinyl chloride and polyacrylonitrile.

Differences between plastics depends on the following:

- The monomer used.
- How many molecules are joined together (molecular weight).
- Whether the polymer molecule has a straight or branched chain.
- If other molecules are in the chain (copolymer).
- What additives are present.
- The degree of crystallinity in solid polymers.

1.7

The commercial preparation of polyethylene

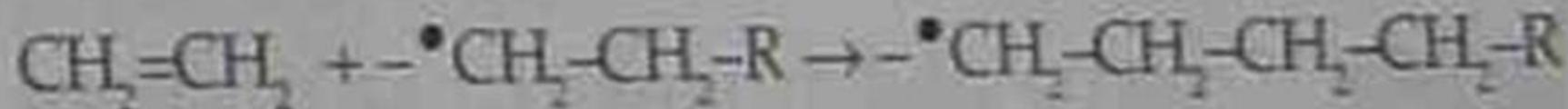
Chain growth polymerisation is started by adding an 'initiator' to the monomer. The most common type of initiator is a substance which, when added in small quantities, is decomposed by heat or light to produce a free radical (symbol R^{\bullet}). Free radicals are formed when a covalent bond is broken and a bonding electron is left on each part of the broken molecule. Free radicals are easily formed in peroxides since the O-O bond is weak. Dibutyl peroxide is commonly used as an initiator in chain-growth polymerisation.

Note: The molecular weight distribution of a polymer affects its properties and also the way in which it behaves during processing.

Ethylene feedstocks are used by a petrochemical complex to produce two main types of polyethylene:

(a) Low density polyethylene production (LDPE)

Production requires a temperature range of 100–300°C and a very high pressure of 1500–3000 atmospheres. An organic peroxide or oxygen is used as the initiator for the reaction.



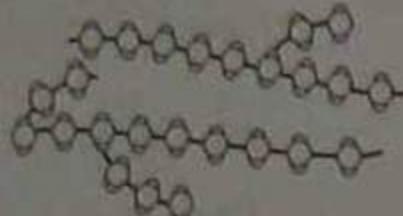
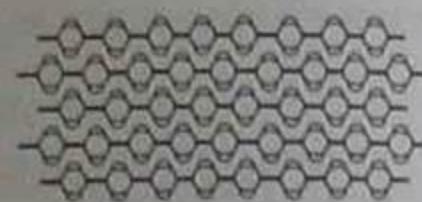
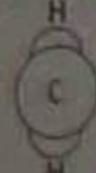
The product of this reaction is polyethylene $-[-\text{CH}_2-\text{CH}_2-]_n$. Low density polyethylene has molecular chains which can have many short branches (2–4C). These disrupt the close regular packing of the linear chains and also results in fewer of the long linear chains in the molecule. Low density polyethylene is a tough, flexible, translucent semicrystalline plastic. A high purity product is obtained.

(b) High density polyethylene (HDPE)

The polymerisation is carried out using special aluminium-based metal oxide catalysts, called *metallocene catalysts*, at atmospheric pressure and a temperature of about 300°C. The molecules have fewer side chains, so the long chains are almost linear and the molecules can pack closer on cooling to produce a more dense and crystalline material. Crystalline regions provide strength to the polymer. Some impurities are present (due to the catalyst).

Table 1.7 is an example of two polymers made from the same monomer, but having different properties due to the configuration of their molecules.

Table 1.7 Properties of two polymers prepared from ethene

Property	LDPE	HDPE
Flexibility	more flexible used for sandwich bags, cling wrap, motor vehicle covers	more rigid used for freezer bags
Strength	not as strong (irregular packing)	strong (regular packing) suitable for water pipes
Heat resistance		useful above 100°C can use for water pipes
Transparency	good (more amorphous, i.e. non-crystalline regions)	less transparent (more crystalline)
Density	low, so lighter	higher
Schematic of chains		
Key:		
	chains with short branches (2 – 4C) in amorphous regions. Packing is irregular and non-crystalline.	chains are long and linear in crystalline regions. Closer packing is therefore possible.

Source and domestic use of some commercially significant polymers

To extend the range of plastics, additives are used to alter properties of polymers, e.g. to decrease flammability, as indicated below:

- (a) Plasticisers which render the finished material more flexible by weakening the attractions between the polymer chains. These additives stop polyvinyl chloride (PVC) from becoming brittle over time.

- (b) Fillers which are added to modify a particular property, e.g. as a reinforcing agent to improve strength, such as fibre glass. Fillers also add bulk and reduce cost.
- (c) Dyes and pigments which are used as decoration.

(d) Stabilisers which are incorporated to reduce damage to plastic from exposure to the environment, e.g. ultraviolet stabilisers which absorb sunlight and prevent long chains from being broken. A number of plastics, e.g. polystyrene, react with oxygen in the air, so antioxidants are added to stop the chain breaking.

Copolymers

To extend the range of polymers produced by chain growth, more than one monomer may be incorporated. This is called *copolymerisation*.

Example 1

The monomers styrene, butadiene and acrylonitrile may be incorporated to form an ABS copolymer. This is used to make telephone cases.

Example 2

About 60% of the world's rubber is made by the copolymerisation of butadiene and styrene.

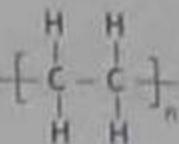
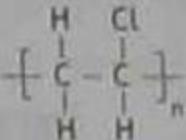
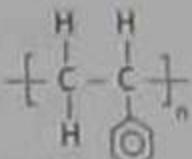
Reinforced plastics

The addition of fibres to most polymer materials results in greatly increased stiffness and strength to the plastic, e.g. glass, carbon and 'Kevlar', which is a brand name for a polyamide containing aromatic rings. Carbon is widely used in the manufacture of tennis racquet handles and golf club shafts. 'Fibre-glass' is added to the styrene-polyester polymers used to make canoes, boats and surf skis.

Shaping Plastics

Once polymers are synthesised they can be processed in different ways to provide a wide range of shapes and structures.

Table 1.8 Commercially significant polymers

Name	Monomer	Polymer	Properties
Ethylene	$\text{CH}_2 = \text{CH}_2$		LDPE light, flexible, translucent HDPE strong, stiffer, high resistance to chemicals and corrosion
		polyethylene	
Chloroethylene (c.n. vinyl chloride)	$\text{CH}_2 = \overset{\text{H}}{\underset{\text{H}}{\text{C}}} - \text{Cl}$		since PVC is not weather-resistant, it is only used as electrical conduit indoors or as underground water pipes
Styrene (c.n. vinyl benzene) accepted systematic name	$\text{CH}_2 = \overset{\text{H}}{\underset{\text{H}}{\text{C}}} - \text{C}_6\text{H}_5$		easily formed to produce good thermal, sound and insulation properties, transparent sheets and pipes

Fibres

- (a) **Cold drawing** is the process which produces fibres by stretching a liquid polymer into a long, thin filament. The polymer chains form a more crystalline structure which leads to increased strength, e.g. nylon fibres.
- (b) **Extrusion**, in which small granules of polymer are melted and then forced through a nozzle to produce a continuous length of fibre, e.g. terylene fibre.

Sheets, tubes and pipes

These can also be produced by *extrusion*. In this process, thermoplastic raw material in powdered or granulated form is fed into a heated cylinder. A plunger or screw mechanism compacts the plastic mass in the cylinder where it melts and is then shaped by being forced through a die.

To make hollow objects such as bottles by extrusion, *blow moulding* is used.

Injection moulding

An injection unit forces the material into a mould, to produce a wide variety of shapes with great accuracy.

Calendering

A molten mass of polymer is passed through *heated rollers* to form a *sheet* that is used to produce semi-

finished goods such as coverings, flooring and plastic wrappings.

Foam

Many polymers, e.g. polystyrene, polyethylene and polyvinyl chloride are foamed to reduce their density. In the foaming process, a gas is introduced into the polymer, either by mixing compressed air or gas into the melted polymer mass, or by adding a 'blowing agent', e.g. sodium hydrogen carbonate (NaHCO_3), to the plastic raw material. When the hot melt is formed, NaHCO_3 decomposes to produce CO_2 , which forms bubbles in the foam. Expanded polymers such as this can be used for foam insulation, drinking cups and egg boxes.

1.9

Reactions of some condensation polymers

Condensation polymerisation

This process involves a reaction between two functional groups where a small molecule, usually water, is eliminated and the two functional groups are linked together. An example of a condensation copolymer is the formation of 'terylene', which is a polyester polymer which makes useful textile fibres.

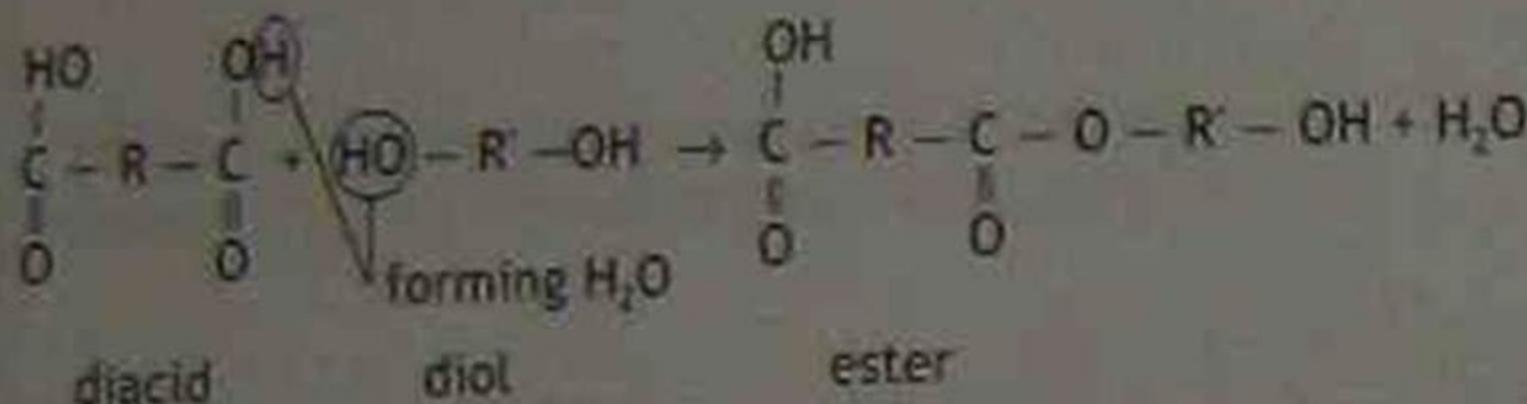
Table 1.9 Source and domestic uses of some polymers

Source	Raw materials	Monomer	Polymer	Uses
Crude oil	ethylene	ethylene	polyethylene	LDPE: cling wrap, sandwich bags, motor vehicle cover HDPE: milk bottles, garbage cans, kitchenware
Crude oil salt	ethene chlorine	vinyl chloride	polyvinyl chloride (PVC)	plastic plumbing features, toys, upholstery, floor tiles, rainwear
Crude oil	propene ammonia	acrylonitrile	polyacrylonitrile	Orlon fibre, carpet, acrylic sweaters
Crude oil	ethene benzene	styrene	polystyrene easily formed	surf boards, wall tiles, foam insulation, most of fridge cabinets and insulation

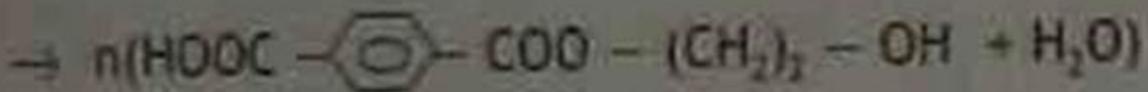
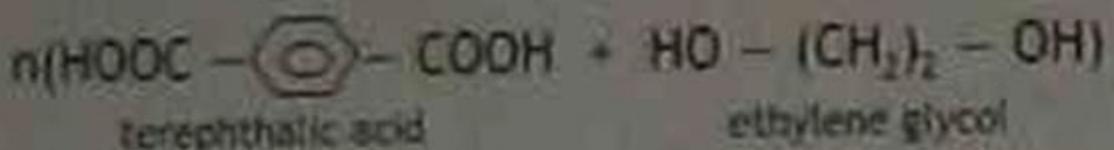
The structure of the

Example 1

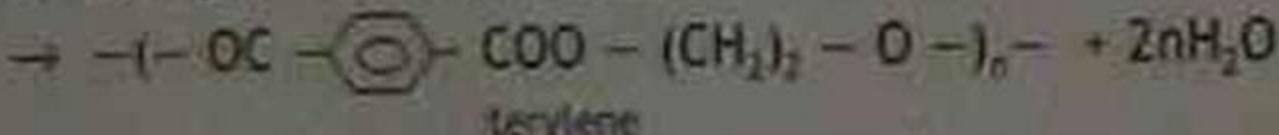
General reaction between a dicarboxylic acid and a diol



Formation of terylene

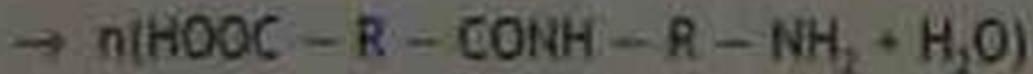
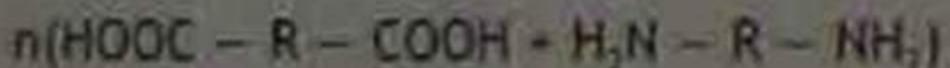


by step growth polymerisation

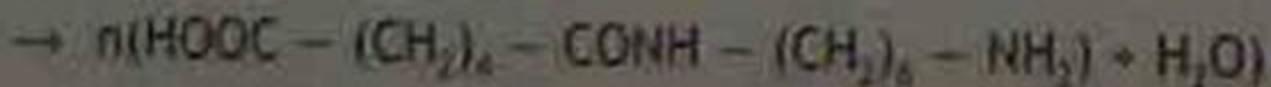
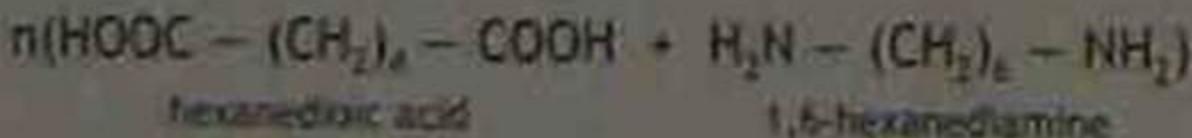


Example 2

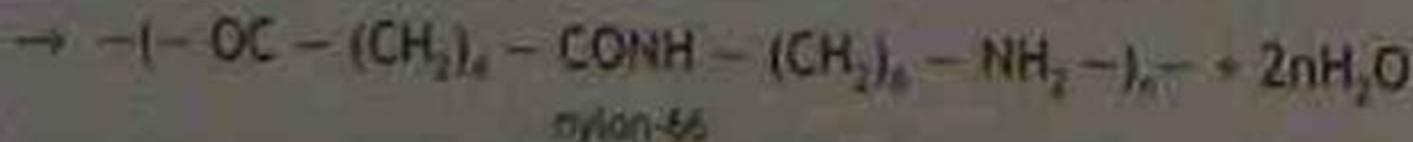
General reaction between a dicarboxylic acid and a diamine



Formation of nylon-66



by step growth polymerisation



Example 3

Example 3

Biopolymers of the monomer glucose (starch and cellulose) are also examples of condensation polymers where two -OH functional groups from the two glucose monomers are linked and a molecule of water is eliminated.

Note: In Examples 1 and 2, the functional groups are different. In Example 3, the functional groups are the same.

1.10 The structure of the biopolymers starch and cellulose

Starch

Starches are polymers of glucose, that is, starch molecules consist of many hundreds of glucose molecules joined together.

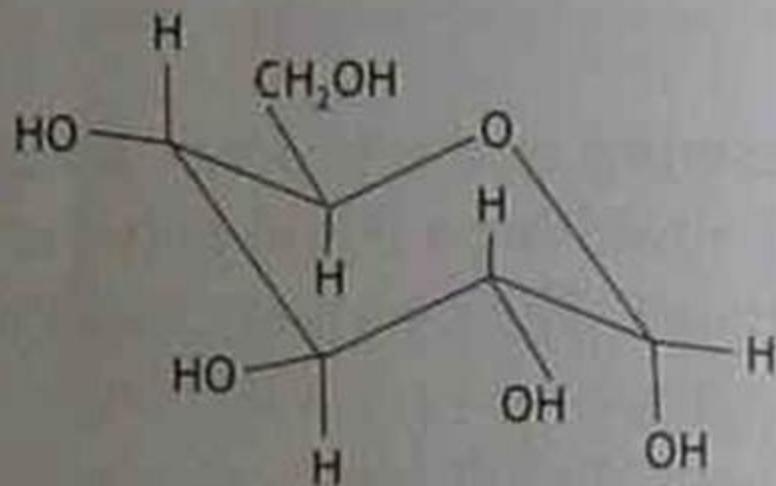


Figure 1.9 Glucose

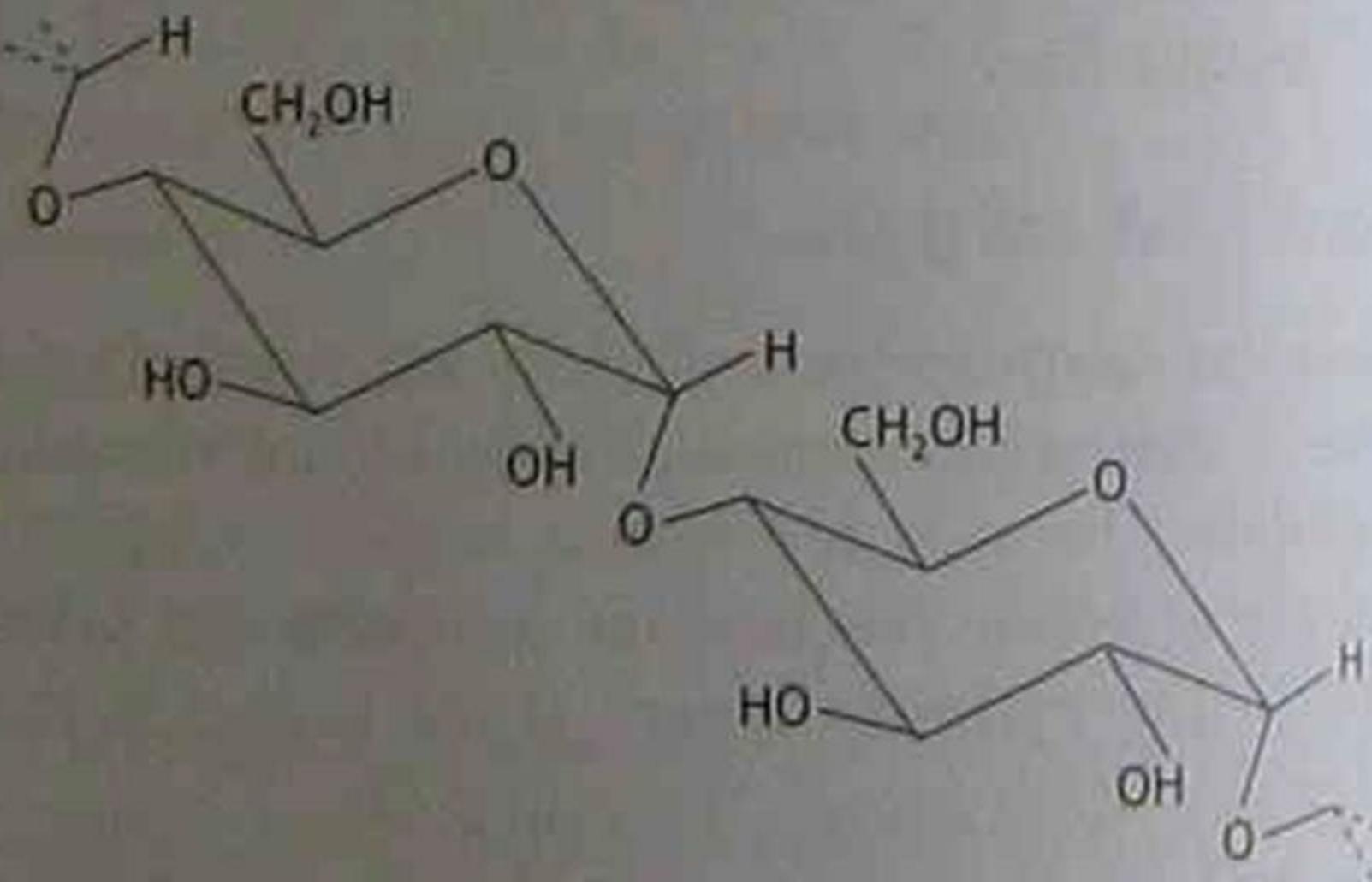


Figure 1.10 Amylose. A type of starch

Electrochemistry

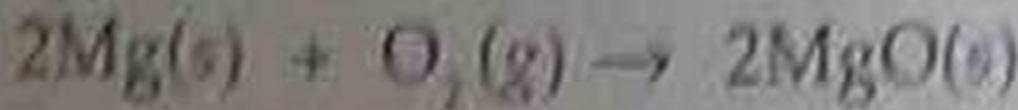
13.1 Reactions involving metals

Electrochemical cells are important sources of energy. Another important use of electrochemistry is the electro-refining and electroplating of metals to produce or enhance useful materials. These processes involve reactions between metals and non-metals.

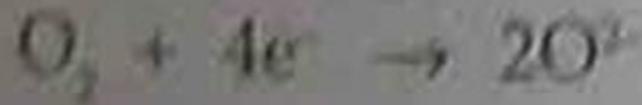
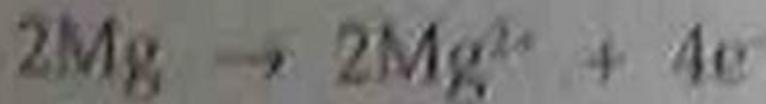
Reactions between metals and non-metals

At the beginning of the twentieth century when the theory of atomic structure and bonding was developed, the changes that occur within atoms also investigated.

Consider the oxidation of magnesium to magnesium oxide and the changes in the electron configurations that occur:



It is easier to understand the electron transfers that take place if the equations are written as half-equations



Many other non-metals were found to be capable of removing electrons from magnesium atoms.

Example

- (a) $Mg(s) + Cl_2(g) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$
(b) $Mg(s) + S(l) \rightarrow Mg^{2+}(aq) + S^-(aq)$

This led to an extension of reduction-oxidation or redox reactions to include reactions with substances other than oxygen.

- Oxidation is defined as the loss of electrons from a substance. Reduction is defined as the gain of electrons by a substance. An oxidising agent or oxidant is defined as an electron acceptor and a reducing agent or reductant as an electron donor. The oxidation number of an element in a

molecule is the charge that the atom would have if the molecule were completely ionic. The oxidation number of an element is a zero.



Redox reactions are reactions where electrons are transferred. The reaction is made up of two half-reactions, one for oxidation and one for reduction.

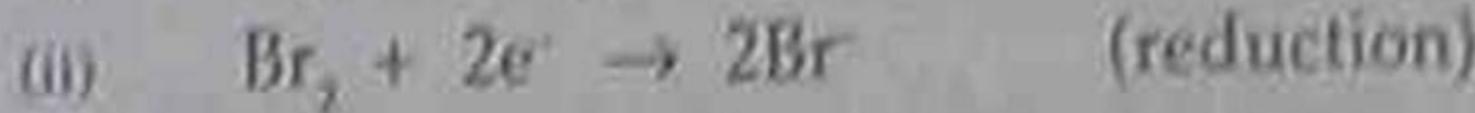
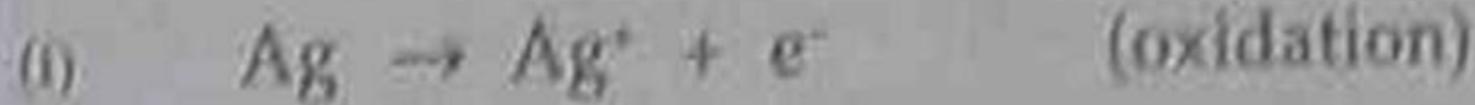
Table 1.12 Characteristics of redox reactions

Process	No. of electrons	Oxidation no.
Oxidation	decreases	increases
Reduction	increases	decreases
Oxidant	increases	decreases
Reducant	decreases	increases

In the following example, the metal will be the electron donor, so it will be a reductant. The non-metal will be the electron acceptor so it will be an oxidant. The reductant (reducing agent) is itself oxidised. The oxidant (oxidising agent) is itself reduced.

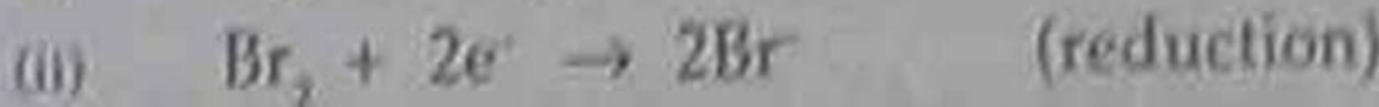
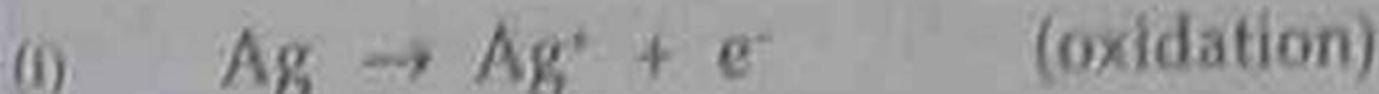
Example

The reaction with the metal silver and the non-metal bromine is:



Example

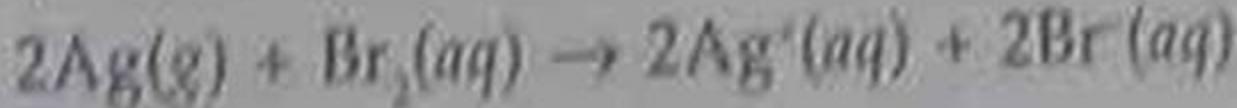
The reaction with the metal silver and the non-metal bromine is:



To balance the electrons, we must multiply the half-reaction (i) by 2:



Add (ii) and (iii):



In this reaction, Ag is the reductant and Br₂ the oxidant.

Note:

Ionic equations must be balanced both atomically and electrically.

1. Write the half-equations including the electrons.
2. Adjust equations if needed so that the electrons are balanced.
3. Add the half-equations. The electrons should then cancel.

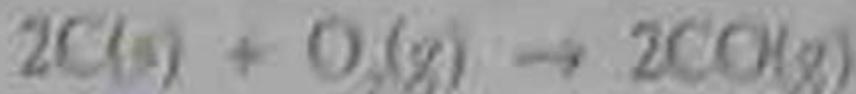
Reactions to extract metals from ores

Industry uses a number of reactions to extract metals from their ores. Most ores consist of the sulfides or oxides of metals.

Example

The extraction of iron in a blast furnace. At first, coke is converted to carbon monoxide, which is used to convert the iron oxide (haematite), Fe_2O_3 , to iron.

Formation of carbon monoxide:



In this reaction, carbon is the reductant.



In this reaction the metal oxide is reduced to the metal, so Fe_2O_3 is the oxidant and carbon monoxide is the reductant.

Summary of major points in reactions of metals

Table 1.13 The activity series

	Reductant	Oxidant
K	$E^\circ = -2.9$	$K^+ + e^-$
Ba	$E^\circ = -0.9$	$Ba^{2+} + 2e^-$
Ca	$E^\circ = -0.4$	$Ca^{2+} + 2e^-$
Na	$E^\circ = -0.9$	$Na^+ + e^-$
Mg	$E^\circ = -0.9$	$Mg^{2+} + 2e^-$
Al	$E^\circ = -0.9$	$Al^{3+} + 3e^-$
Zn	$E^\circ = -0.9$	$Zn^{2+} + 2e^-$

as reductants

Increasing strength

Increasing strength	ED				Decreasing ED
Fe	ag		$\text{Fe}^{2+} + 2\text{e}^-$		
Sn	ag		$\text{Sn}^{2+} + 2\text{e}^-$		
Pb	ag		$\text{Pb}^{2+} + 2\text{e}^-$		
$(\text{H}_2)^{**}$	ag		$2\text{H}^+ + 2\text{e}^-$		
Cu	ag		$\text{Cu}^{2+} + 2\text{e}^-$		
Ag	ag		$\text{Ag}^+ + \text{e}^-$		
Hg	ag		$\text{Hg}^{2+} + 2\text{e}^-$		

Note 1. Because of its thin protective skin of aluminium oxide, aluminium is often difficult to dissolve in replacement acids. In laboratories that analyse aluminium and aluminium alloys, a small amount of hydrogen peroxide is added to hydrochloric acid to facilitate the reaction.

Note 2. Replacement acids are acids in which the hydrogen ion can oxidise reactive metals. These are the inorganic acids, hydrochloric acid and dilute sulfuric acid, and some organic acids such as ethanoic acid.

Note 3. Hydrogen is included in Table 1.13 because metals above it in the series can reduce the H^+ ions of replacement acids, liberating $H_2(g)$, whereas those metals below it do not react with replacement acids.

1. The higher a metal is in the activity series, the more powerful it is as a reductant. It follows that the most powerful reductant, potassium, will be the metal most readily oxidised to form potassium ions.

2. Conversely, the lower a metal is in the activity series, the more difficult it is to oxidise.
3. Any metal in the activity series will displace any metal below it from a solution of its salts. The further apart the metals are, the more vigorous will be the reaction.

Example

If zinc is placed in copper sulfate solution, zinc sulfate is formed and copper is deposited.

Displacement of a metal from a solution of its salt by another metal

From Table 1.13 we can see that the reducing strength of metals decreases as we go from K → Hg. Hence, any metal in the table will reduce the ion of any metal below it. Using the activity series we can predict whether reactions will occur.



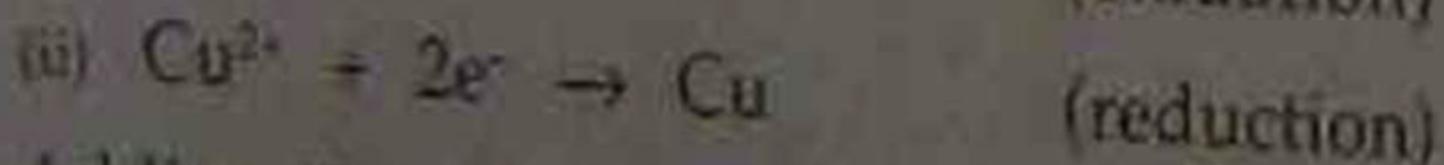
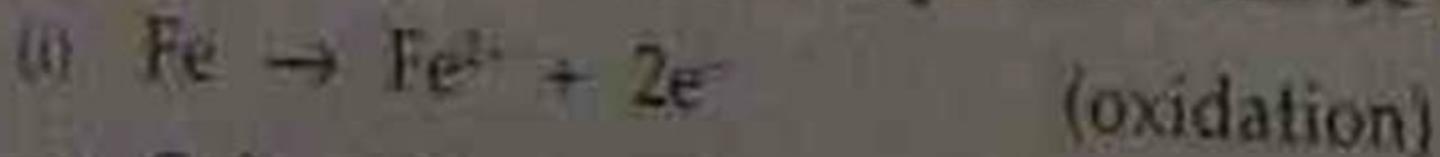
Practical work

The reactions of selected metals with ions of other metals in solution should be observed.

Example

If a piece of iron wire is dipped into a solution of copper sulfate, will a reaction take place?

Since iron is higher than copper in the activity series, the following half-equations can be written:



Adding (i) and (ii):



$\text{Fe(s)} + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu(s)}$

If such a reaction were left overnight, the blue colour of the copper sulfate would disappear and copper would be deposited. Iron is the reductant and copper the oxidant.

This simple reaction is used for copper recovery in mining processes.

119

Reactions where metal atoms show different oxidation states

Oxidation number is very useful in dealing with elements whose compounds show a variety of oxidation states (e.g. transition metals).

The oxidation number is the charge, real or imaginary, that an atom would have if it occurred as an ion in a compound.

Iron is a typical transition metal, showing more than one oxidation state. Another example is titanium which has oxidation states of +2, +3 and +4.

Other metals, which are not transition metals, may occur in more than one oxidation state, for example, tin (+2 and +4).

Rules for assigning oxidation numbers

1. In uncombined elements, each atom has an oxidation number (O.N.) of zero.
For example, Na and Cl₂ have an oxidation number of 0.
2. The oxidation number of a monatomic ion is equal to the charge on that ion.
For example, Na⁺ (O.N. = +1), Fe³⁺ (O.N. +3), S²⁻ (O.N. = -2) and Cl⁻ (O.N. = -1).

3. Oxygen has an oxidation number of -2 in compounds.

[Peroxides and superoxides are the exceptions.

For example, H_2O_2 (O.N. = -1) and KO_2 (containing O_2^- ion).]

4. Hydrogen has an oxidation number of +1 in compounds.

[Ionic hydrides are the exception where the O.N. = -1. For example, NaH (O.N. = -1).]

5. The sum of the oxidation numbers of all atoms
- (a) in a neutral molecule is zero, and
 - (b) in a polyatomic ion,
is equal to the charge on the ion.

Example 1

In the compound FeCl_3 , the O.N. for iron is +3.
In the compound FeCl_2 , the O.N. for iron is +2.

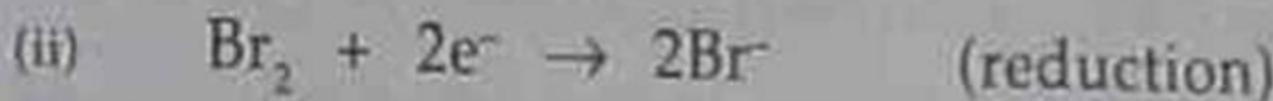
Example 2

Find the O.N. for manganese in the following compounds:

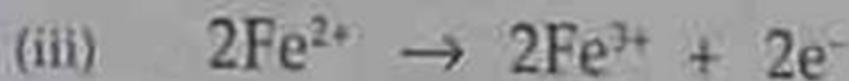
- | | | |
|-------|-----------------|--------------------|
| (i) | MnCl_2 | +2 |
| (ii) | MnCl_3 | +3 |
| (iii) | KMnO_4 | +7 [1 + Mn + (-8)] |

Example 3

Write half-equations for the reaction which takes place when iron (II) nitrate has bromine added to it. Write the balanced equation for the reaction and state the oxidant and the reductant.



Multiply (i) by 2:



Add (ii) and (iii):



Br_2 is the oxidant; Fe^{2+} is the reductant.

1.20

The use of redox reactions to generate electricity

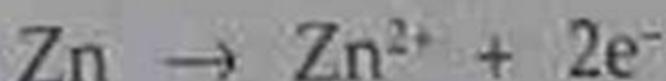
The Daniell Cell

Professor John Daniell produced the first practical depolarising cell in 1836 to overcome a polarising effect observed in existing primary cells that drastically reduced current. He adopted a two-fluid (or two-cell) approach that was taken up and improved on by later researchers.

The Daniell cell is divided into two half-cells:

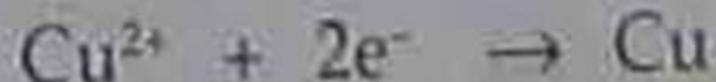
- (a) The electron donor half-cell, where loss of electrons (oxidation) occurs, which is called the anode.

Anode half-cell reaction:



- (b) The electron acceptor half-cell, where electrons are gained (reduction), which is called the cathode.

Cathode half-cell reaction:



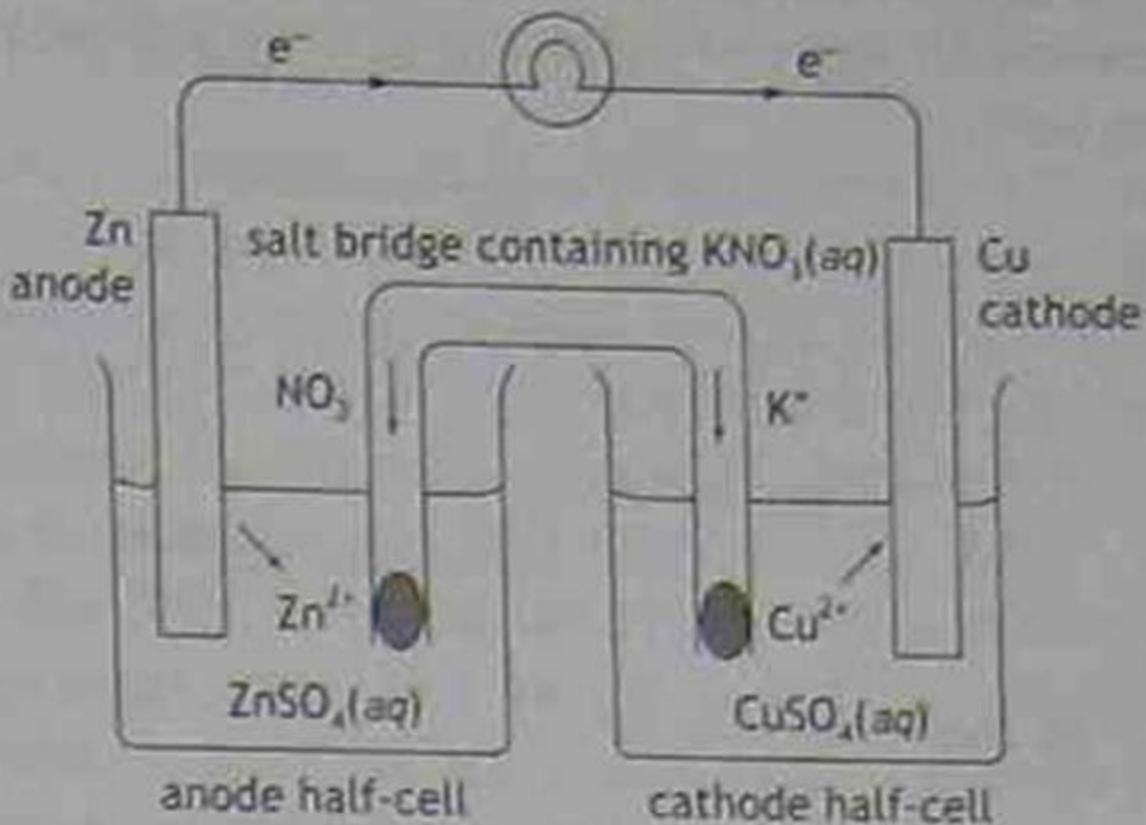


Figure 1.20 The Daniell cell

The half-cells are connected by an external wire which forces electrons, released by the anode, to travel by an external circuit to the cathode rather than through the solution.

A salt bridge, usually filled with KNO_3 , between the two half-cells, completes the circuit and enables ions to move. The salt bridge may be an inverted U-tube of KNO_3 with cotton wool plugs at the ends, or strips of filter paper soaked in the salt. The movement of ions through the salt bridge balances the charges due to the electron flow in the external circuit.

The overall cell reaction is obtained by adding the anode and cathode half-cell reactions. The electrons must be balanced.



The potential difference or electromotive force (emf) of a galvanic cell depends on the nature of the electrodes and the electrolyte. It does not depend on the size of the cell.

Electrode potentials

In electrochemical cells, also called galvanic or voltaic cells, chemicals interact spontaneously to produce an electric current.

Every half-reaction has its own redox potential as shown in Table 1.14. These have been obtained by measurement of the potential difference produced when the half-cell, under stated conditions, is coupled with a hydrogen reference electrode (Figure 1.21). By convention, the redox potentials are listed

in the table as standard reduction potentials and the standard hydrogen electrode is given a potential of zero volts.

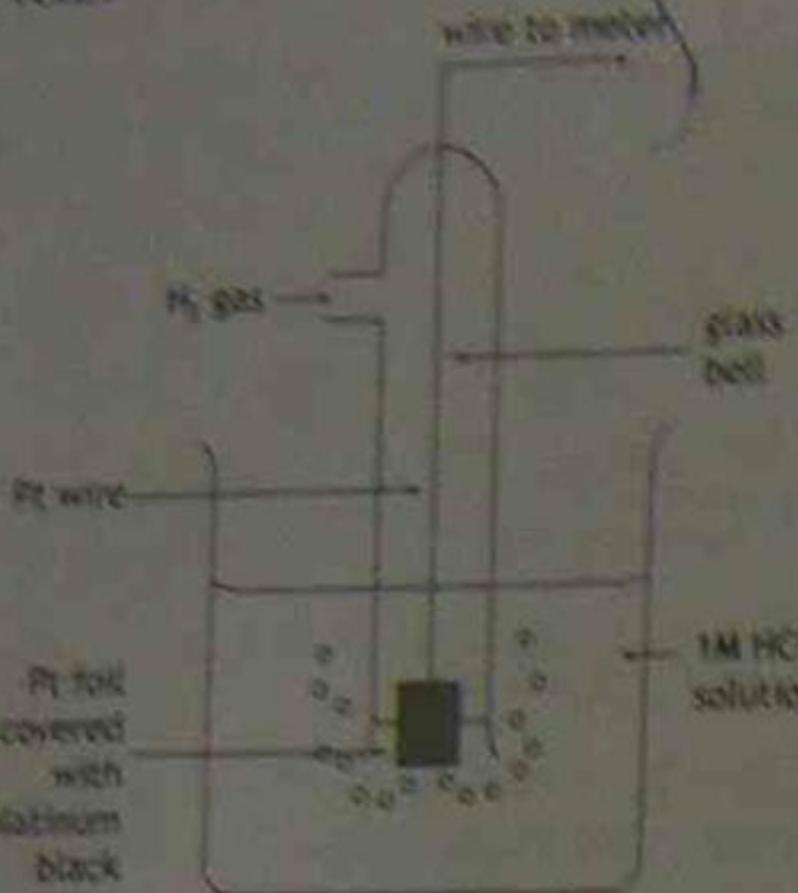


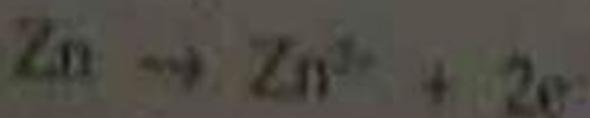
Figure 1.21 Standard hydrogen electrode. The reference electrode consists of a platinum electrode in a solution which contains 1M (H^+) ions through which hydrogen gas is bubbled at a pressure of 101.3 kPa and a temperature of 298 K.

Note: Standard state conditions for operating a voltaic cell include 1M concentrations for reactants and products that are in solution and 101.3 kPa pressure for those that are gases. The temperature of the cell would be taken as 298 K (25°C). For the Daniell cell (Figure 1.20), Zn/Zn²⁺//Cu²⁺/Cu if the cell is operating under standard state conditions then the emf of the cell is called the standard emf, E° volts. If the cell is not operating under standard state conditions then it has an emf of E volts.

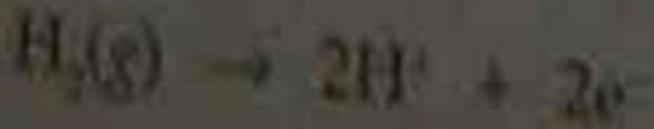
When coupled with another half-cell, the total potential across the cell will be due to the electrode of the other half-cell.

Case 1

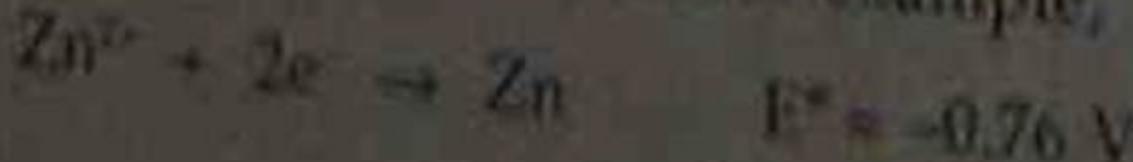
If the metal in Figure 1.22 is zinc, the potential difference will be 0.76 V. This means that the reaction



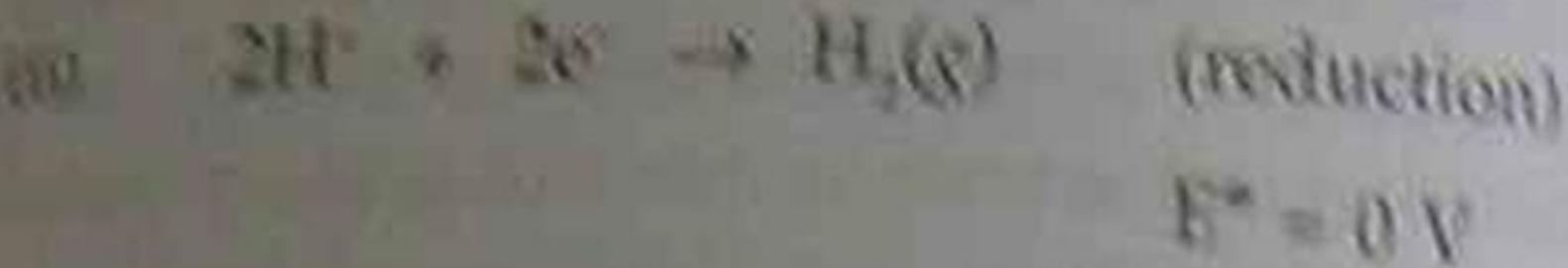
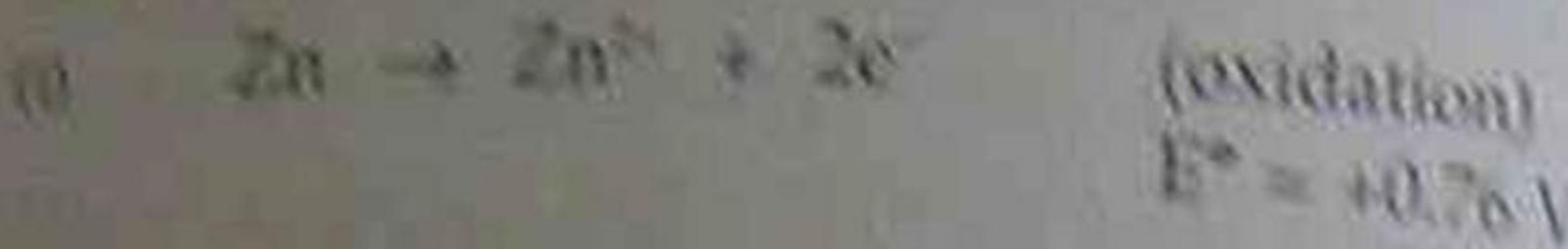
has a greater tendency to occur than the reaction



By convention, the redox potentials in the table are listed as reduction potentials, for example,



Since oxidation is the reverse of reduction, we can reverse the equation and also the sign of the E° value. We then have two half-equations:



Cell reaction

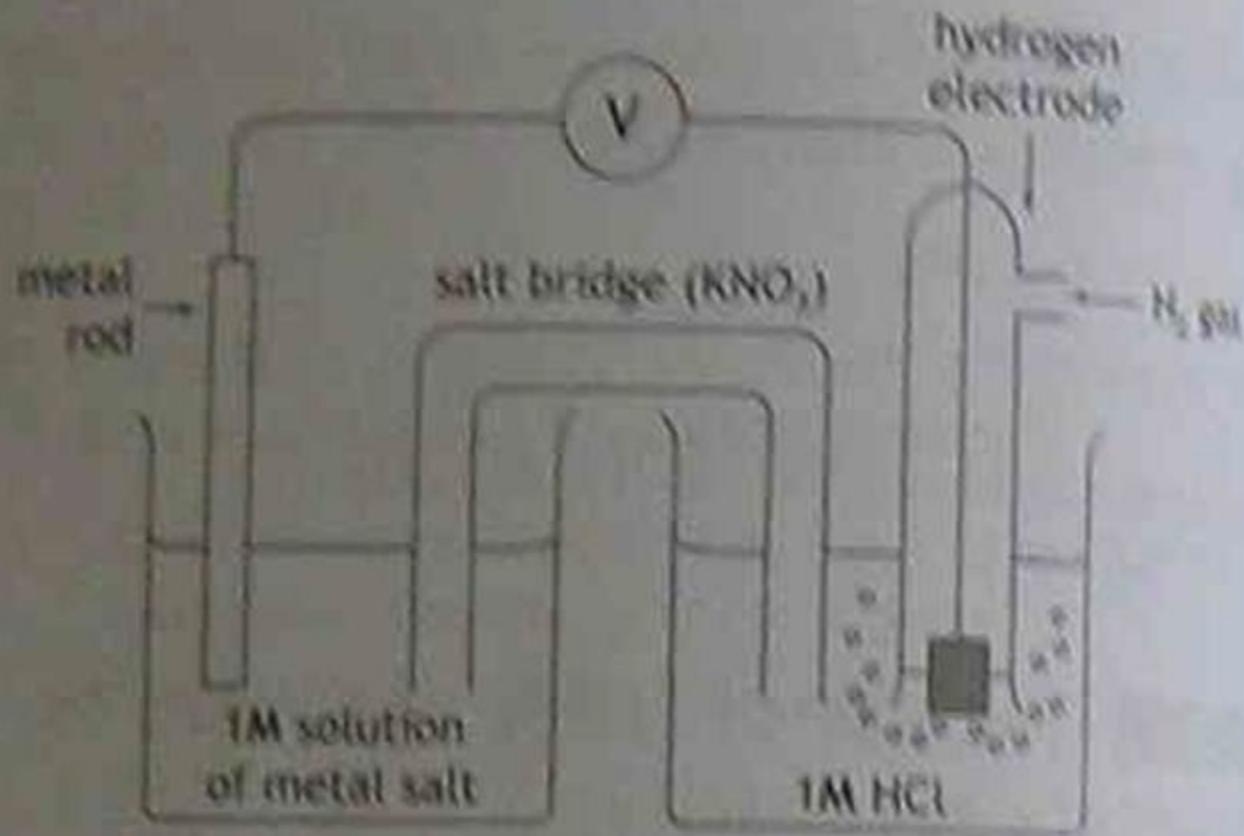
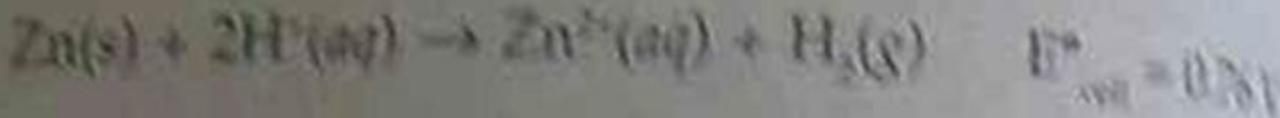


Figure 1.22 A metal electrode coupled with a hydrogen reference electrode

Note 1. The voltage of an electrochemical cell

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

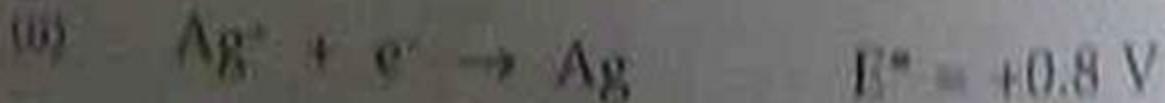
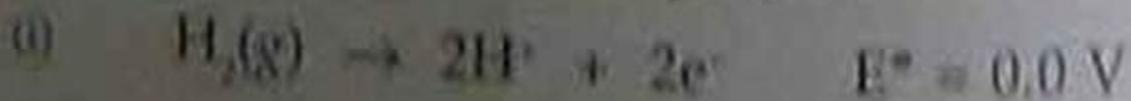
Note 2. If in determining the cell reaction the half-cell equations are balanced, the E° value for each half-cell remains the same.

Case 2

If the metal used in Figure 1.22 is silver, the reduction potential for $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ is $E^\circ = +0.8\text{ V}$

This shows that the tendency for Ag^+ ions to be reduced to Ag in the half-cell is greater than the tendency for H^+ ions to be reduced to H₂ in the reference cell.

We then have two half-equations:



Then $2 \times (\text{ii}) + (\text{i})$ gives cell reaction



$$E_{\text{cell}}^\circ = +0.8\text{ V}$$

1.3

Calculation of a cell voltage

So far we have calculated E°_{cell} using hydrogen as one of the electrodes. In the following example we will use two metal electrodes, zinc and silver.

Example

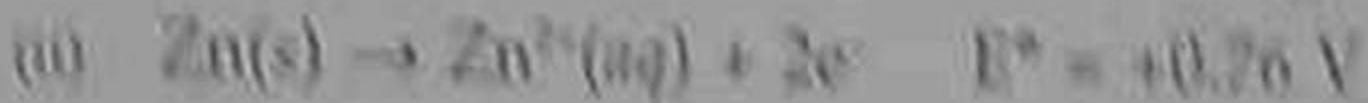
- Draw a diagram for the $\text{Zn}/\text{Zn}^{2+} // \text{Ag}^+/\text{Ag}$ cell.
- Find the overall reaction and the emf for the cell.

Step 1. Inspect the half-cell equations and their E° from Table 1.14.

Step 2. Write the half-equation which has the more positive E° as the reduction reaction.



Step 3. Reverse the direction of the other equation and change the sign of E° so that it becomes the oxidation reaction.



Step 4. The E_{cell}° can now be calculated by adding $E_{\text{oxidation}}^\circ$ and $E_{\text{reduction}}^\circ$.

Step 5. Balance the half-cell equations for electrons.
 $2 \times (\text{i}) + (\text{ii})$ gives

Cell reaction



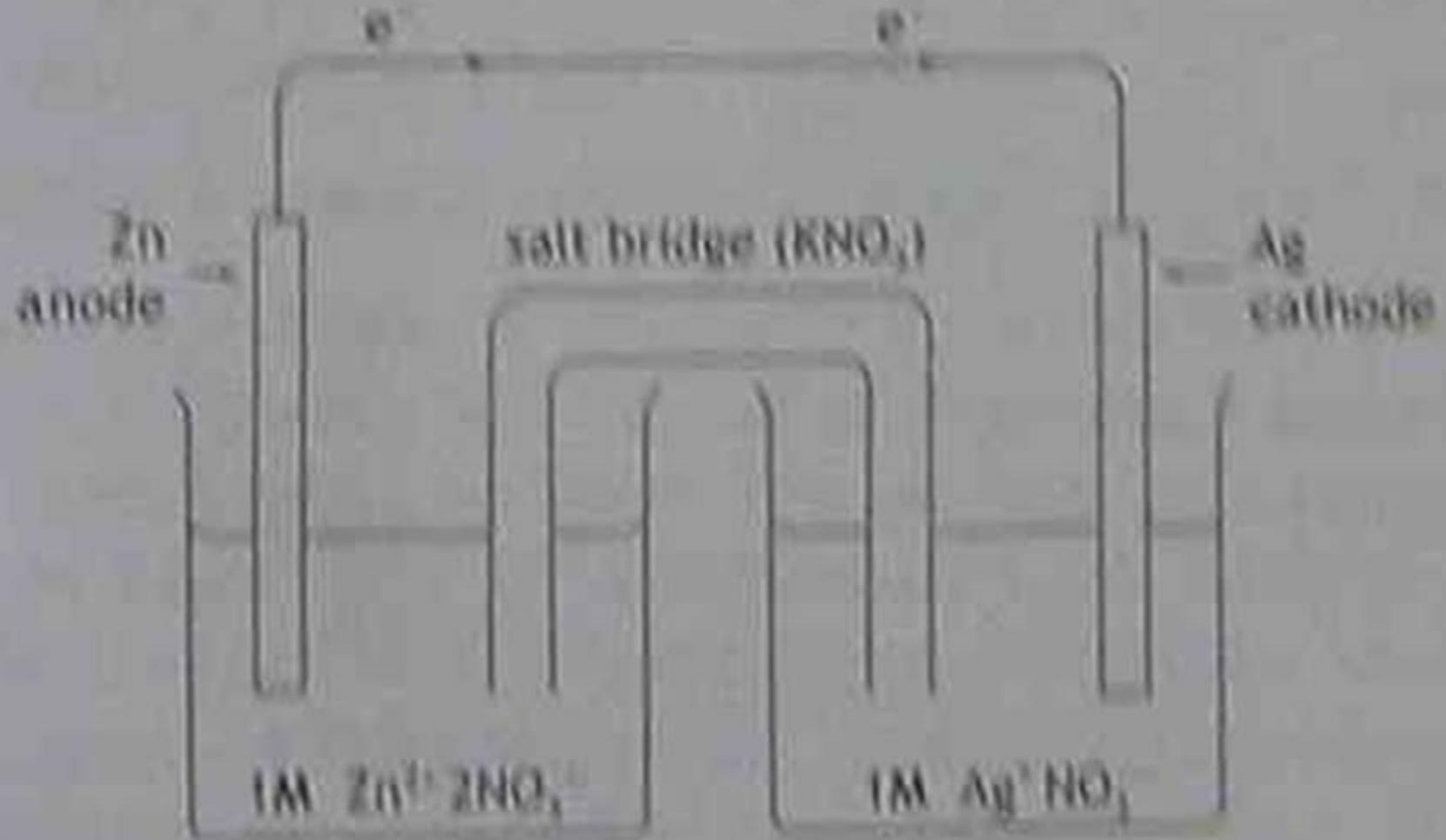


Figure 1.23 $\text{Zn/ZnO}^{2+}\text{//Ag}^{+}/\text{Ag}$ cell

For the cell to operate as a galvanic cell, there must be:

- (a) two half-cell reactions (one oxidising and one reducing);
- (b) an ion path; and
- (c) an electron path.

Note: The emf generated depends on the nature of the half-cell reactions, the concentration of the electrolytes and the temperature.

A comparison of the oxidising strengths of metals using cell voltages

Instead of drawing diagrams to represent cells, it is simpler to represent them in a symbolic way. The Daniell cell, in Figure 1.20, can be represented as $\text{Zn}|\text{Zn}^{2+}/\text{Cu}^{2+}|\text{Cu}$. By convention, the anode is written at the left, with a single line between the two species present (in this case, Zn and Zn^{2+}). The double lines in the middle shows that a salt bridge is present, providing an ion path. The cathode is written at the right and again there is a single line between the species present (in this case Cu^{2+} ions and Cu).

Lab 9

Given the following information:

- (a) $\text{Cu}/\text{Cu}^{2+} // \text{Ag}^+/\text{Ag}$ cell voltage = 0.45 V
- (b) $\text{Zn}/\text{Zn}^{2+} // \text{Cu}^{2+}/\text{Cu}$ cell voltage = 1.11 V
- (c) $\text{Mg}/\text{Mg}^{2+} // \text{Cu}^{2+}/\text{Cu}$ cell voltage = 2.71 V

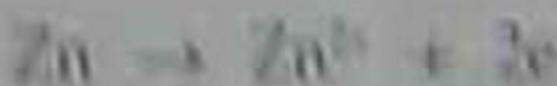
write the four metals, from weak to strong, as reductants. All ions are at the same concentration.

Calculation

For cell (a) at the anode:

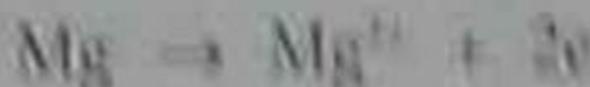


so copper will be a stronger reductant than silver
For cell (b) at the anode



so zinc will be a stronger reductant than copper.

For cell (c) at the anode



so magnesium will also be a stronger reductant than copper.

However the cell voltage of (c) is much higher than that of (b), so magnesium will be a stronger reductant than zinc.

The order from weakest to strongest reductants is
silver, copper, zinc, magnesium.

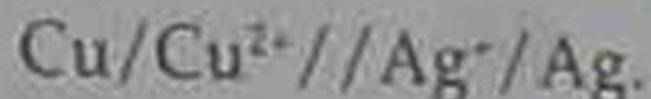
The use of the electrochemical series to predict either the order of reductant strength of metals or the direction of reactions is subject to some restrictions.

1. The order of half-cells alone together in the activity series can be changed with concentration change. The ease with which a metal ion can be reduced depends on concentration.

2. The series only applies to reactions in aqueous solution.
3. The emf of a galvanic cell is temperature-dependent.
4. The emf of a galvanic cell depends in some cases on pH.

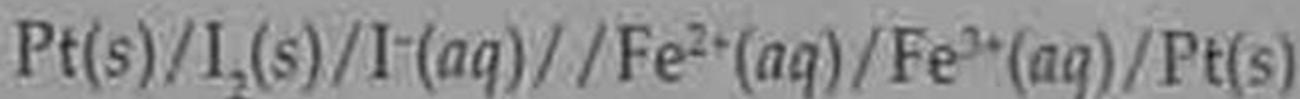
Classification of cells

The types of cells we have discussed so far have had metal/metal ion electrodes, for example,



Another type of electrode involves an inert substance such as platinum or carbon and equimolar amounts of a non-metal and its ion. If the symbol for platinum (Pt) is written on the left of the conducting material the convention is that an oxidising process will occur.

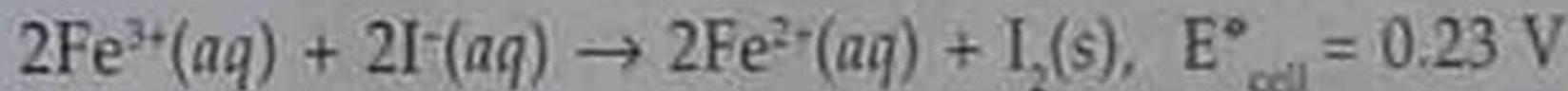
Example



The half-equation with the most positive E° will be the reduction reaction:

- (i) $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}, E^\circ = +0.77 \text{ V}$ (reduction)
- (ii) $2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{s}) + 2\text{e}^-, E^\circ = -0.54 \text{ V}$ (oxidation)

Overall reaction $2 \times (\text{i}) + (\text{ii})$ gives



Another type of electrode involves an inert substance such as platinum or carbon, and ions of different oxidation states. This can be seen in Figure 1.24 where $\text{Fe}^{2+}/\text{Fe}^{3+}$ solutions are used. Hydrogen electrodes are also used. They involve an inert platinum electrode and, for example, hydrogen or chlorine gas at SLC. The gas is bubbled into a 1 M HCl solution.



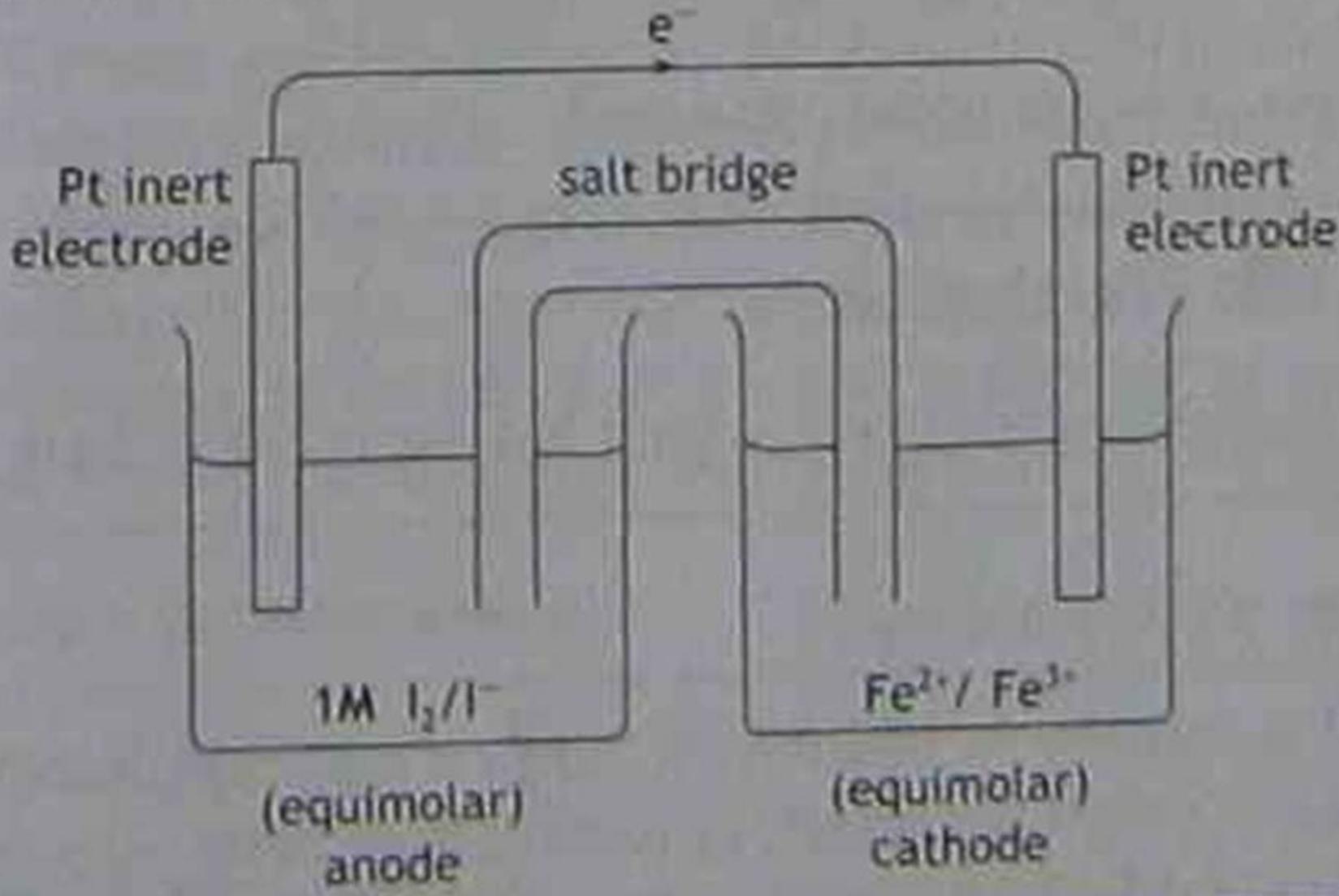


Figure 1.24 Cell with inert electrodes

The hydrogen electrode has already been mentioned as the standard reference electrode. Another reference electrode, used in pH meters, is the calomel electrode.

The pH meter measures the potential difference between a reference half-cell (the calomel electrode) and a half-cell (the glass electrode) whose potential changes as the $[H^+]$ varies.

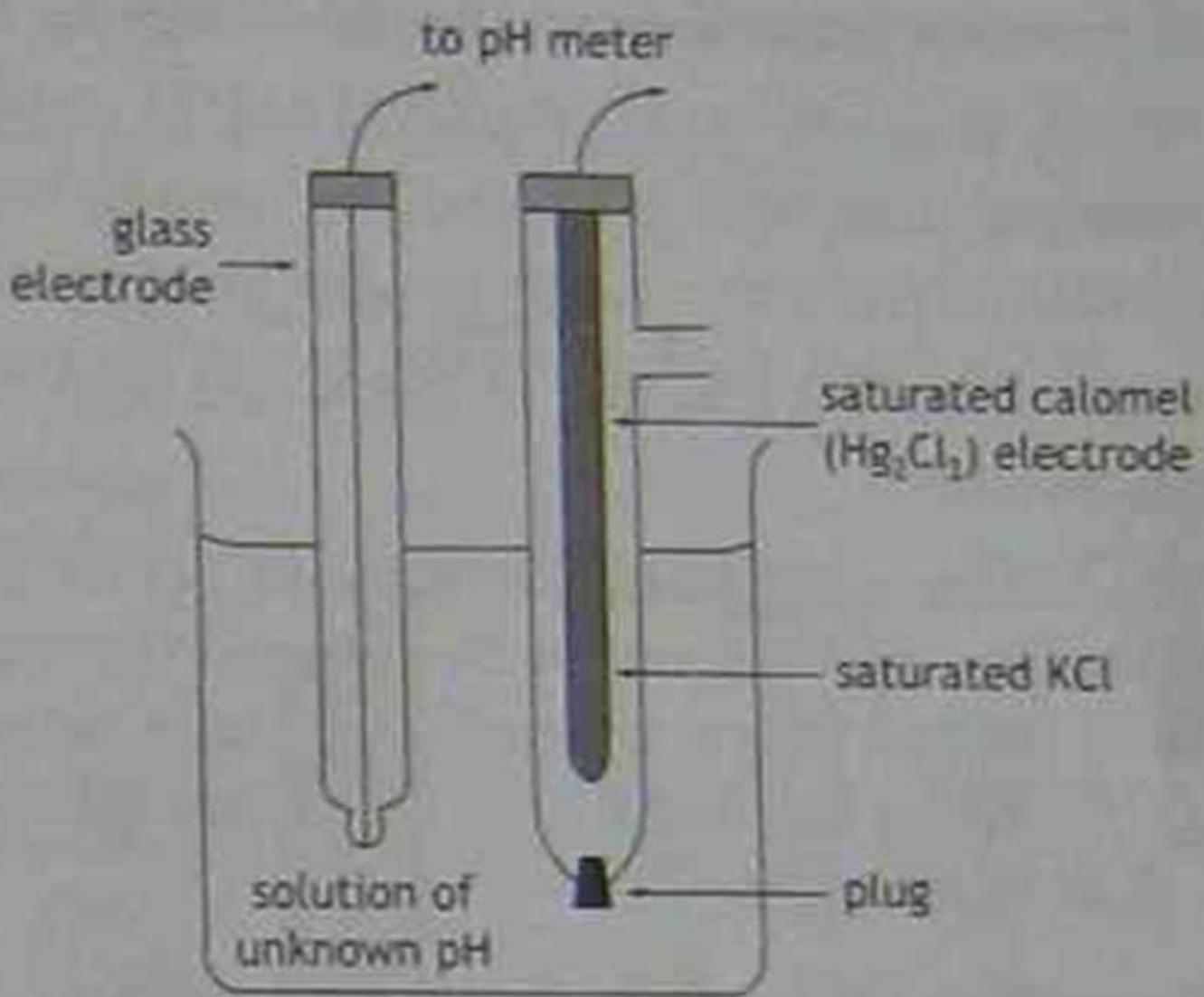


Figure 1.25 Electrodes used in a pH meter

The half-cell reaction for the calomel electrode is



The KCl solution is 1M.

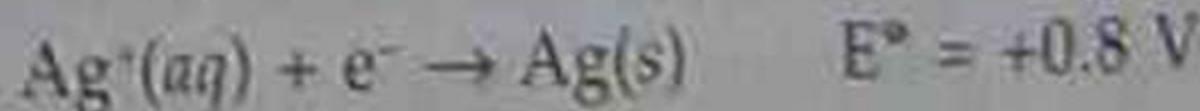
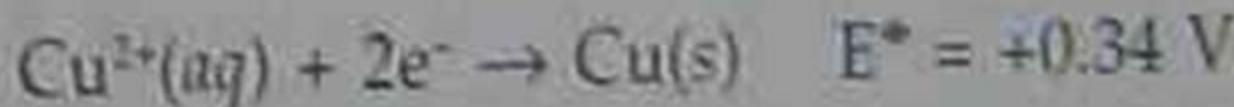
How to predict reactions tendencies

Without actually performing the experiments, students can determine whether a redox reaction can take place by referring to Table 1.14.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

If a piece of copper metal is placed in a solution of silver nitrate, the silver is deposited and the copper metal goes into solution as Cu^{2+} ions.

Half-cell equations:



We already know that the cell with the most positive E° is the reduction reaction, so $\text{Ag}^+ + e^- \rightarrow \text{Ag}$ is the reduction reaction and $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$ is the oxidation reaction.

After balancing the electrons in the half-equations the reaction is



This means that we can predict that when we place a strip of copper metal in a solution of silver nitrate, a reaction will occur. It also allows us to predict that if a strip of silver is placed in copper sulfate solution, no reaction will occur.

This reasoning can be extended to cell reactions:

- A cell reaction can only take place if the cell emf has a positive value. This indicates a spontaneous reaction. If a cell shows a negative value, the reverse reaction will occur. The cell voltage for the cell, $\text{Cu(s)}/\text{Cu}^{2+}(\text{aq})//\text{Ag}^+(\text{aq})/\text{Ag(s)}$, under standard conditions is $0.8 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V}$

$$(\text{i.e. } E^*_{\text{cathode}} - E^*_{\text{anode}} = E^*_{\text{cell}})$$

This cell should function at 298 K and with 1M electrolytes.

- The farther apart the half-equations are on the table, the larger the emf of the cell, and the more likely the reaction is to occur. In practice, where the cell emf is less than 0.2 V, a significant reaction will not take place.

- In practice, electrochemical cells are unlikely to operate under standard conditions. The emf generated depends on the temperature and on the concentration of reactants and products in the cell. In general, if the concentration of reactants increases relative to products, the cell reaction becomes more spontaneous and the emf increases. As the cell operates, the reactants are used up and more by-products form. This will cause the emf to decrease.

- Predictions of cell emf must fit in with Le Chatelier's Principle which states that if an equilibrium system is subjected to change, that system will react in a way to oppose that change. Consider the $\text{Cu}/\text{Cu}^{2+} // \text{Ag}/\text{Ag}$ cell which is not operating under standard conditions. At the anode, as the concentration of the Cu^{2+} ions increases, the tendency of $\text{Cu} \rightarrow \text{Cu}^{2+}$ decreases. At the cathode, if Ag^{+} ions are added,

and the voltage drops.

At the cathode, if the $[Ag^+]$ is increased, Ag will be deposited at a faster rate, so the voltage will increase. By applying Le Chatelier's Principle, it can be seen that forward tendencies are increased by making the $[Cu^{2+}]$ as small as possible at the anode and by making the $[Ag^+]$ as large as possible at the cathode.

- It should be realised that a positive emf does not ensure that a redox reaction will occur to any significant extent.

Some commercial cells

The Leclanché cell

The Daniell cell was very difficult to use because of the electrolytes but, in 1890, Leclanché developed a 'dry cell' which we now use with very little modification in torches, pocket radios, toys and some calculators. It delivers about 1.5 V.

+ve terminal
(carbon rod) – cathode

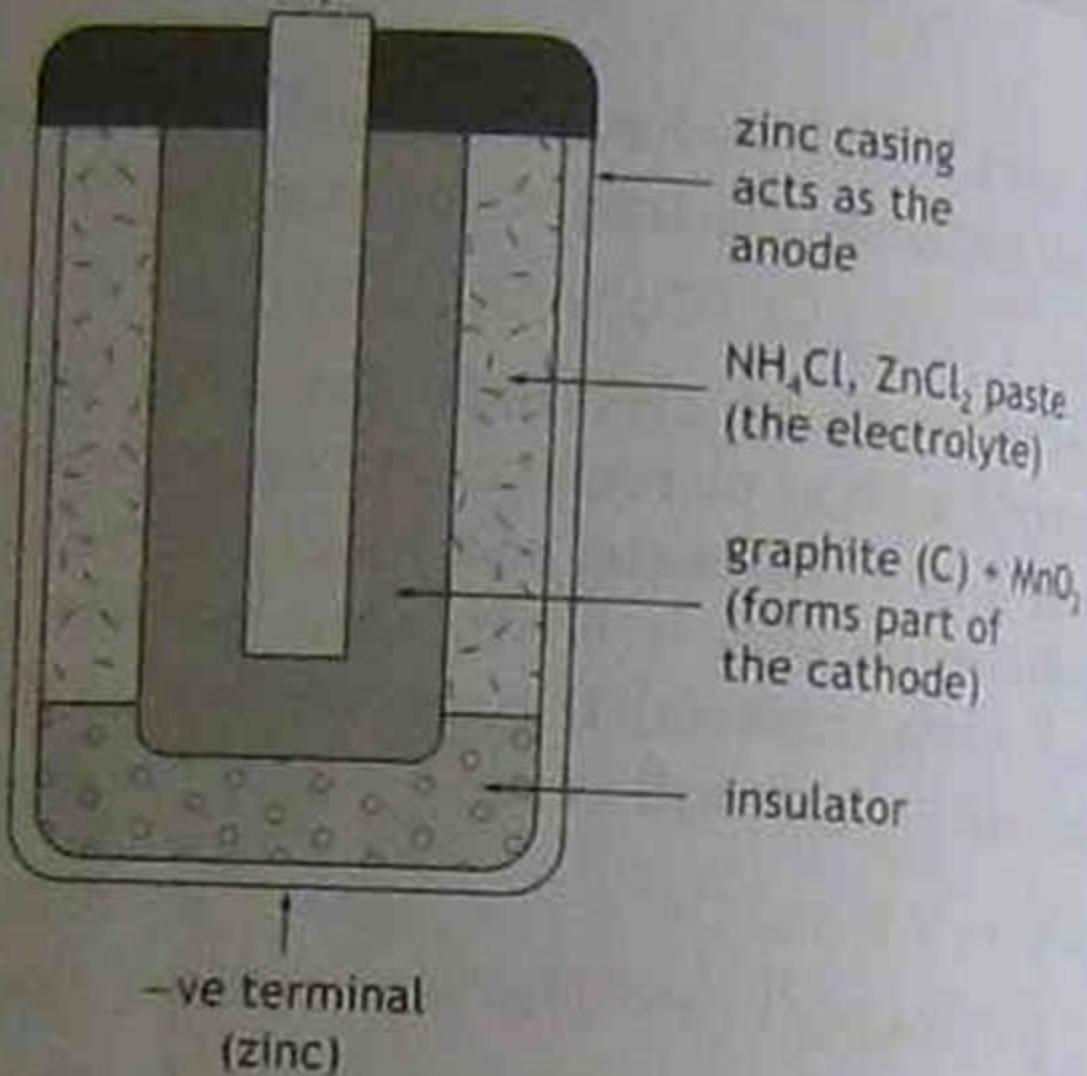
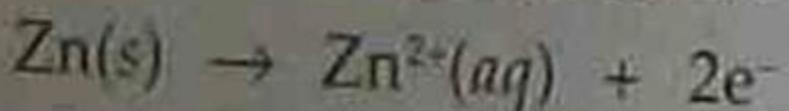


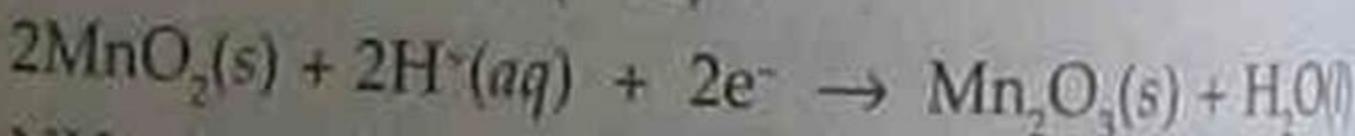
Figure 1.26 Structure of a Leclanché dry cell

Half-cell reactions:

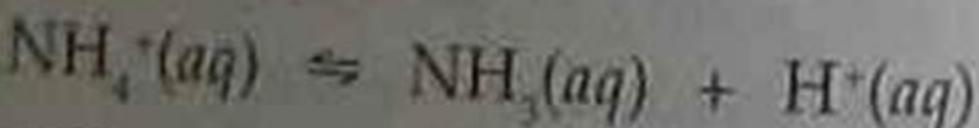
(i) Oxidation reaction at the anode (-ve)



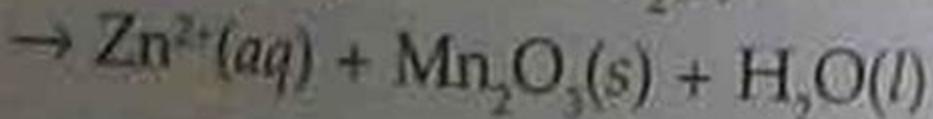
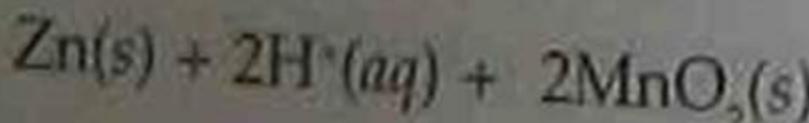
(ii) Cathode reaction (+ve)



NH_4^+ ions provide H^+ ions needed for cathode process.



Overall,



This cell cannot be recharged.

The alkaline battery

This battery is used with 'high drain' appliances such as tape recorders, requiring high total capacity (see Table 1.15) but its size means that it is not

suitable for use in watches and calculators. The electrolyte paste contains potassium hydroxide and is similar in appearance to that in the Leclanché cell.

The alkaline cell can deliver higher currents than the Leclanché cell because the reactions occur more rapidly in the alkaline (KOH) electrolyte paste. It is therefore preferred for use in appliances requiring high currents, such as electronic photographic flash units. It is more expensive than the conventional dry cell but can last up to ten times longer. At present it is the leading type for commercial use. Alkaline batteries are non-hazardous and can be thrown away as waste.

Lithium batteries

(a) Lithium/thionyl chloride cell

The porous carbon cathode is saturated with the electrolyte material [a solution of lithium aluminium chloride (LiAlCl_4) in thionyl chloride (SOCl_2)]. Because lithium reacts strongly with water, only non-aqueous electrolytes can be used for this cell.

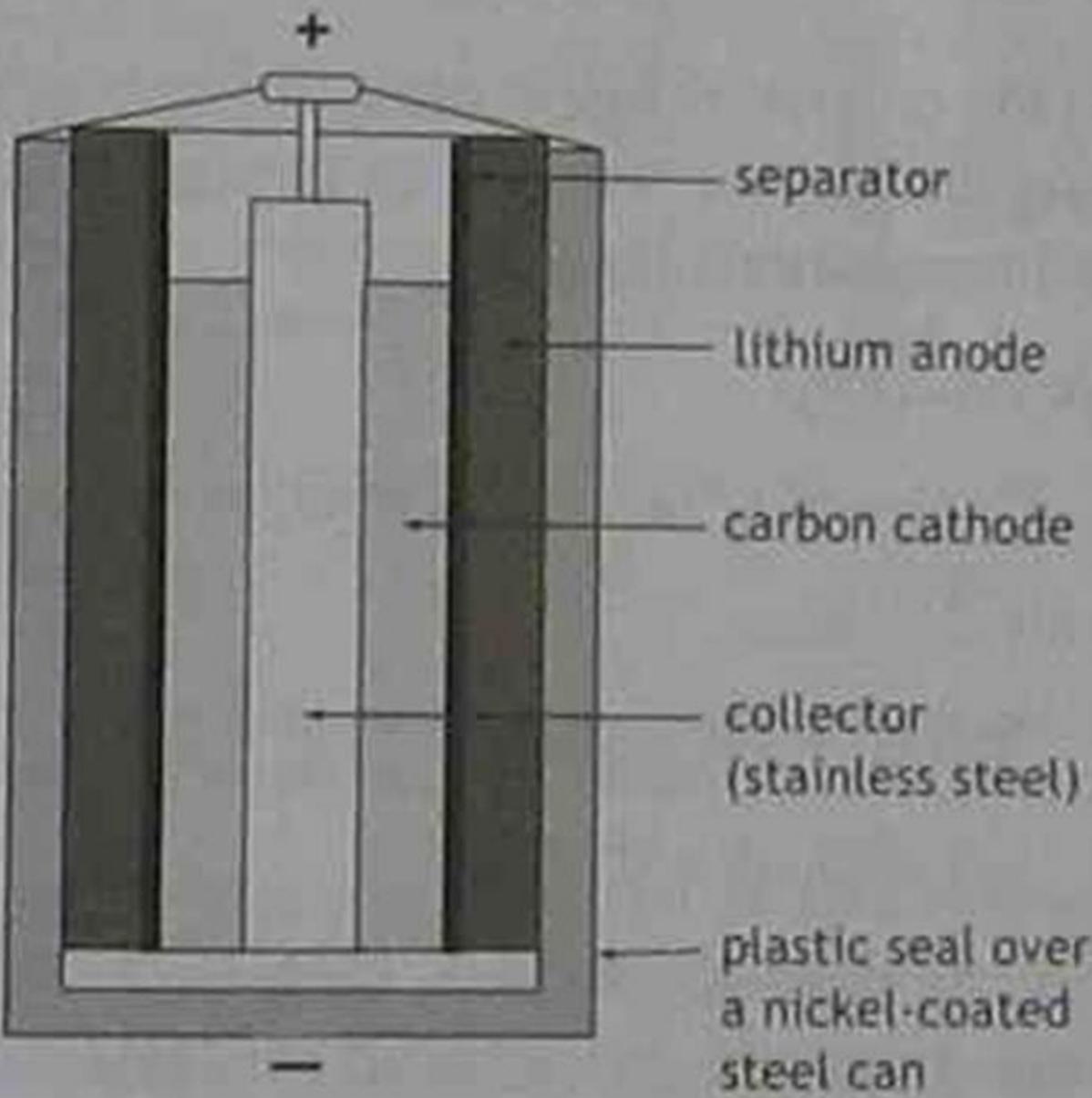


Figure 1.27 Lithium/thionyl chloride cell

demanding environmental conditions, e.g. operating in a temperature range of -55°C to 150°C .

The power source must also provide high voltage per cell, be available in various sizes and shapes, and be able to deliver a good cost/performance ratio. To achieve the safest and most reliable operation of the system, the characteristics of the battery are carefully matched to the conditions of a particular activity.

(b) Lithium 'button' and pacemaker cells

Table 1.16 and Figures 1.28 and 1.29 give details of two typical miniaturised lithium-ion cells in common use as power sources for implanted cardiac pacemakers and small electronic instruments.

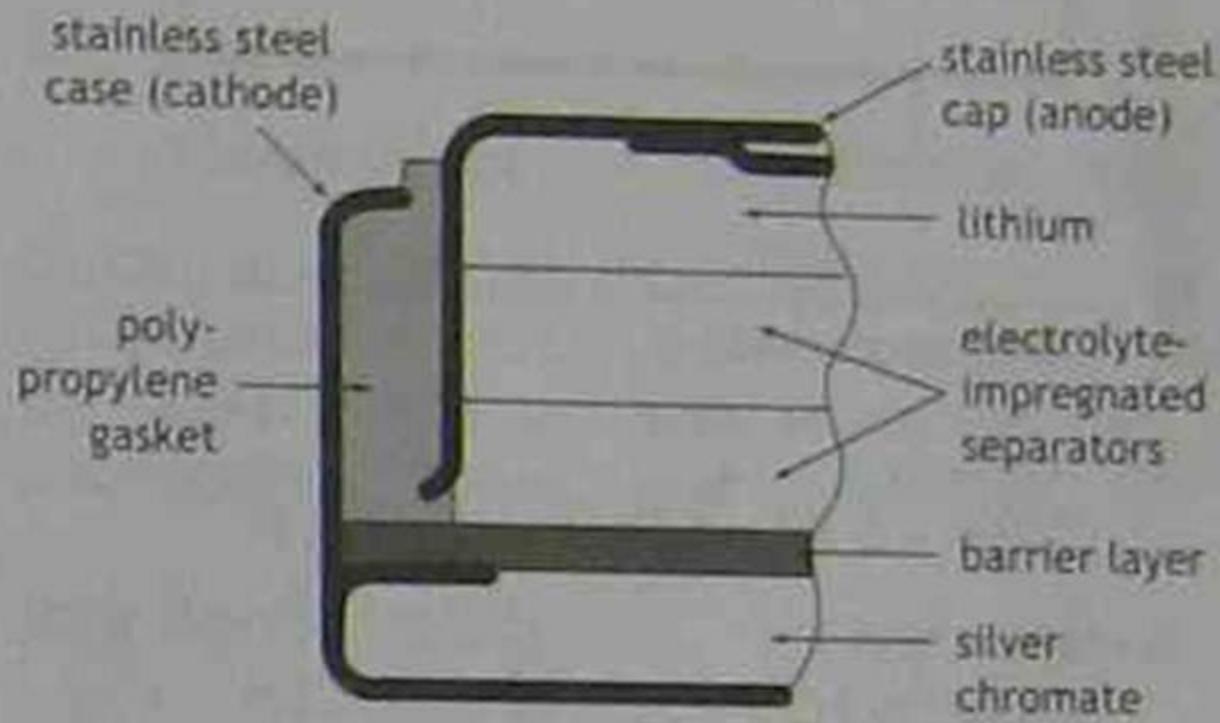


Figure 1.28 Cross-section of a typical lithium-silver chromate button cell

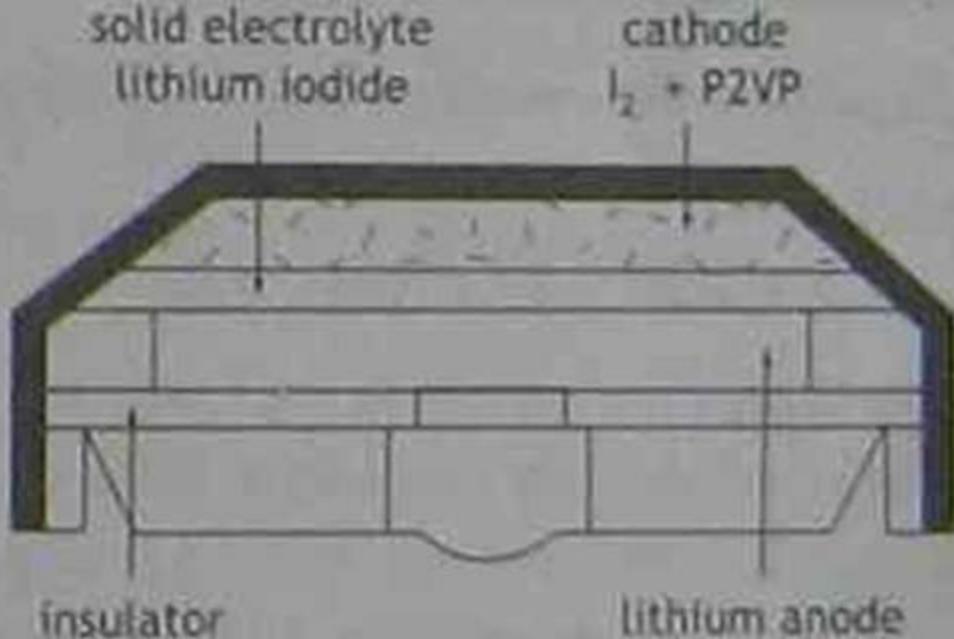


Figure 1.29 Lithium-iodide solid-state cell

Alkaline 'button' cells

(a) Mercury cell (primary)

Many other dry cells are available such as the mercury (II) oxide (button) cell used as a power source for hearing aids, electronic watches, two-way

Table 1.15 The alkaline cell

Name	Anode reaction	Cathode reaction	Uses
Manganese dioxide cell (primary)	$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$	$MnO_2 + 2H_2O + e^- \rightarrow Mn(OH)_3 + OH^-$	shavers, tape recorders

These small cells can provide large amounts of electricity at a constant voltage over a long period of time. Mercury is, however, toxic to the human nervous system. All batteries including button batteries which contain mercuric oxide should be recycled if at all possible. A single cell delivers 1.2 V.

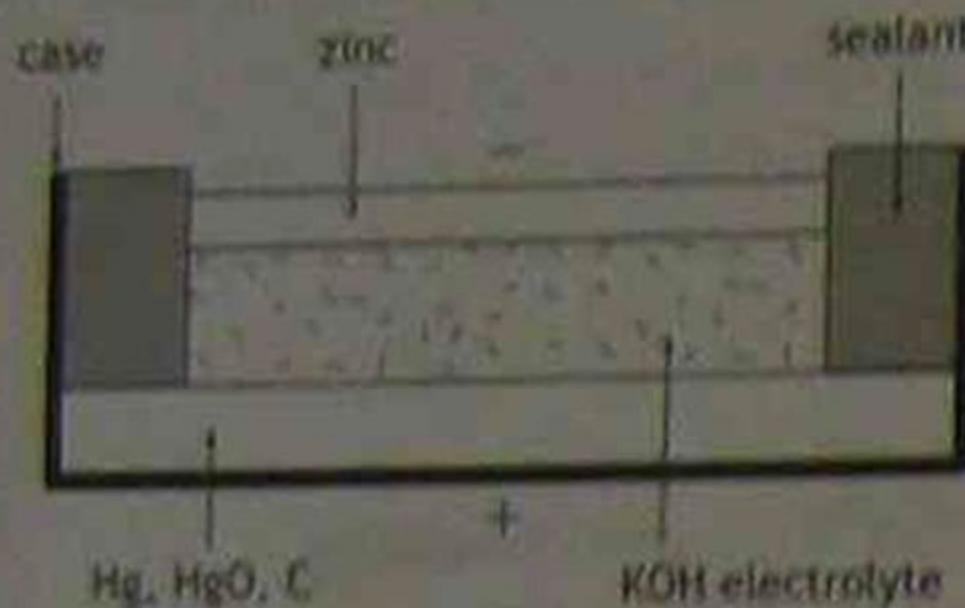
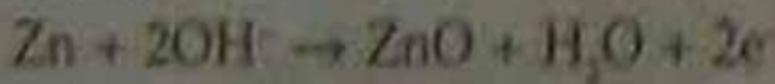
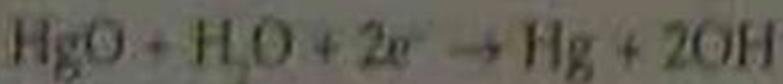


Figure 1-30 A mercury cell

Anode reaction



Cathode reaction



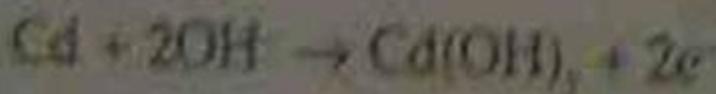
Cell reaction



(b) Silver oxide/cadmium cell (primary)

These cells are used in watches and hearing aids.

Anode reaction



Cathode reaction



Cell reaction



(c) Zinc-air cell

Secondary or rechargeable batteries

The lead-acid accumulator (motor vehicle battery)

This is a storage or secondary battery and can be recharged. It is made up of a series of cells, each of which can deliver about 2 V. A six-volt battery will therefore contain three cells connected in series.

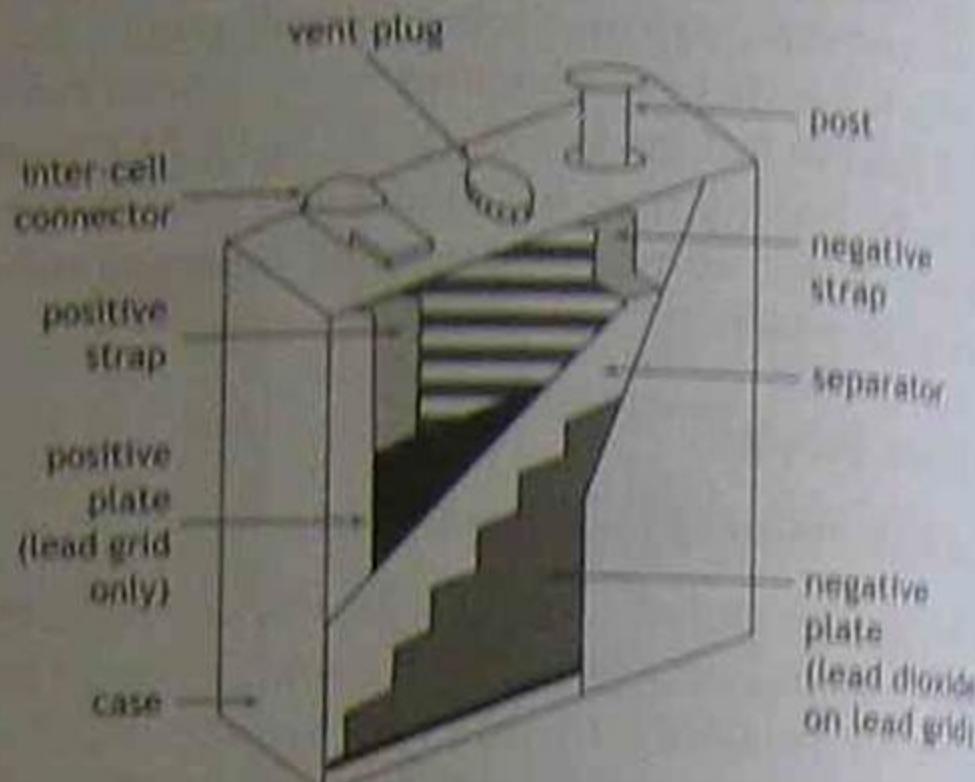


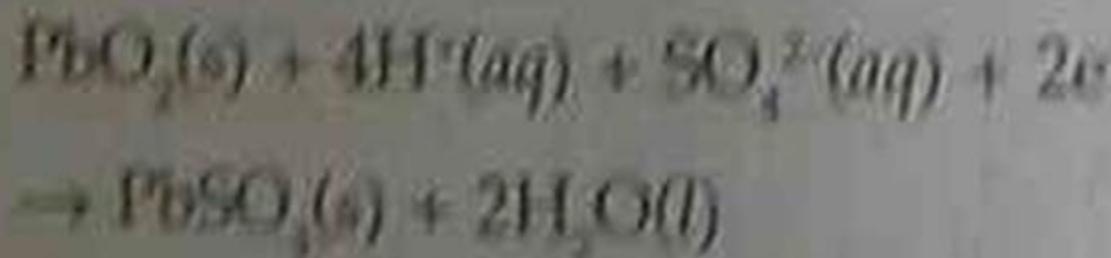
Figure 1.31 The lead-acid accumulator

When the current is being used, for example, when starting the motor vehicle or for headlights, the following reactions take place:

Anode reaction



Cathode reaction



As the cell delivers current, both lead plates then become covered with lead sulfate and the concentration of sulfuric acid falls. When the motor vehicle generator forces current back into the battery, the above reactions are reversed. The cell can be charged and discharged many times.

Disadvantages

- The weight of the battery, especially when being used in golf buggies and carts.
- It requires six hours to recharge.

Topic 5.16: Secondary cells

• It requires six hours to recharge.

Name	Cell reaction	Uses
Lithium-iron disulfide (primary)	$\text{Li}(\text{s}) + \text{FeS}_2(\text{s}) \rightarrow \text{Li}_2\text{S}_2(\text{s}) + \text{Fe}(\text{s})$	caroline pacemaker
Lithium iodine battery	$\text{Li}(\text{s}) + \text{I}_2(\text{l}) \rightarrow \text{LiI}(\text{s})$	caroline pacemaker, electric watches, pocket calculators

- * The electrolyte must be checked regularly using a hydrometer.
- * Irreversible changes in the solids (Pb at the +ve pole; PbO₂ at the -ve pole) can cause permanent damage to the battery.

Disposal

This group includes most motor vehicle and motor cycle batteries. The cases are made of 12% antimonial lead for hardening. They should be recycled.

The Vanadium redox battery

This durable battery was developed for use in electric vehicles. The battery operates on stored charge contained in vanadium chemical solutions.

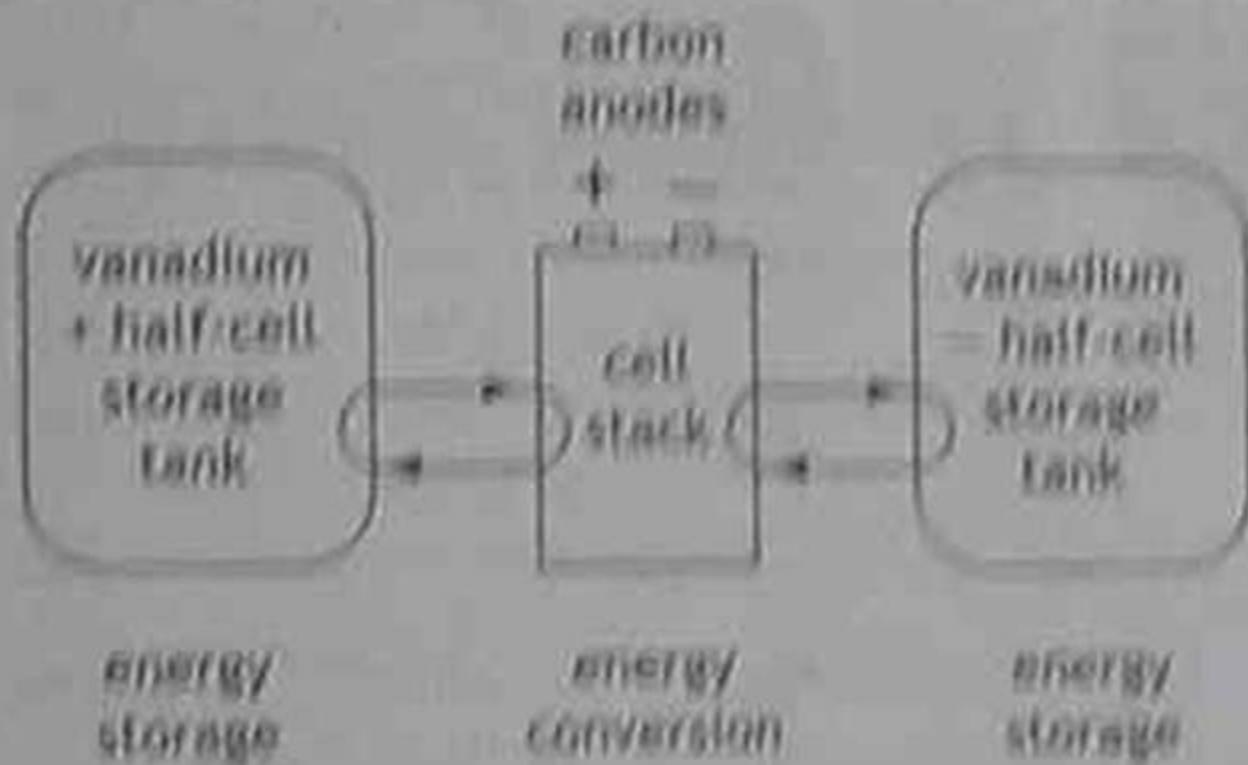


Figure 1.32 The vanadium redox battery

The battery's capacity is stored in two electrolytes which flow into a cell unit. The charged electrolytes are V(+5) and V(+2) salts. During discharge they change to V(+4) and V(+3) salts. The electrolytes are separated in the cell by an ion-selective membrane.

The battery stores charge in the vanadium chemical solutions. The vehicle draws its power from this stored energy. When the solution needs recharging, it is drained from the vehicle's storage tank and placed in recharging tanks. The electric vehicle is then supplied with another fully charged battery solution so that the recharge/refuel process takes less than 10 minutes. The vehicle needs only two sets of solution for continuous use plus a recharging station for the battery solutions.

Nickel-cadmium rechargeable battery

These batteries are widely used in cellular phones, portable hand tools and toys. Nickel-

cadmium (NiCd) batteries contain regulated amounts of cadmium which should be recycled or disposed of as hazardous waste.

The electrodes are made of nickel powder sintered onto a steel plate. Anode plates are impregnated with nickel salts and cathode plates with cadmium salts. The electrolyte is potassium hydroxide. A single cell delivers 1.3 V.

Ni-Cd reactions

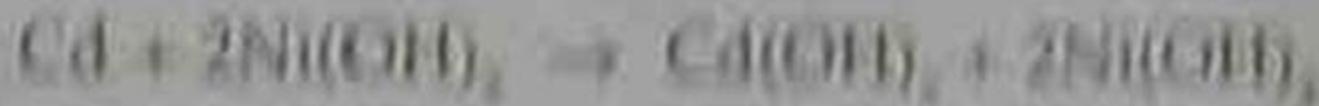
Anode



Cathode



Cell reaction



Larger Ni-Cd batteries are finding increasing use as an alternative to the lead-acid accumulator. The cells are lighter, stronger and more resistant to electrochemical abuse, e.g. short-circuiting.

New developments

Lithium ion batteries

Only lithium ions are involved in charge/discharge reactions.



The unit cells are made in flat shapes that can be connected in series and parallel to reach required voltages. Lithium ion batteries are smaller and lighter than Ni-Cd batteries, can operate at higher temperatures and have an average discharge voltage of 3.7 V.

Table 4.17 Some reported uses of lithium ion batteries

Non-military uses	Military and space uses
Cellular phones	Backpack radio battery
Laptop computers	Missile launch battery
Portable radios	Helmet battery (military)
Flying radios	Satellite batteries
Electric vehicles	

New Dyes for Photovoltaic Applications
C. J. Brabec

The working principle of nanocrystalline-crystalline thin-film solar cell (TCSC) degradation and
failure mechanism.

- Die exhaustion
- Electron injection into porous nano-crystalline titanium oxide (TiO_2)
- Fast reduction of the oxidized dye by a redox couple

This type of cell is based on the principle of the regenerative photovoltaic/chemical process. The active layer is nc-TiO₂. A monomolecular layer of dye on the nc-TiO₂ surface absorbs the incoming light. The device is completed by a counter-electrode which is made up of a platinum catalyst and an organic solvent-based electrolyte containing the redox couple iodide/triiodide.

For low power devices, e.g. calculators and solar-powered watches, an nc-TiO₂ plastic cell is used. For high power outdoor use, a sealing and interconnection technique is used. Introduction of the new nc-DSC cell will depend on low-cost production, efficient marketing and device stability.

Fuel cells

Fuel cells differ from electrochemical cells in several ways.

1. They do not store reactants, products or electrolytes.
2. They obtain electricity direct from the redox reaction.
3. They supply energy at a constant rate as reactants enter and products leave the cell.
4. The electrodes do not undergo permanent change.
5. The reactants are usually gases.
6. Their energy/mass ratio is much higher than for electrochemical cells.

Cathode reaction



2 x (ii) + (iii) gives cell reaction



Latest fuel cells being developed are methanol with a special catalyst on a highly efficient anode from non-conductive silicon.

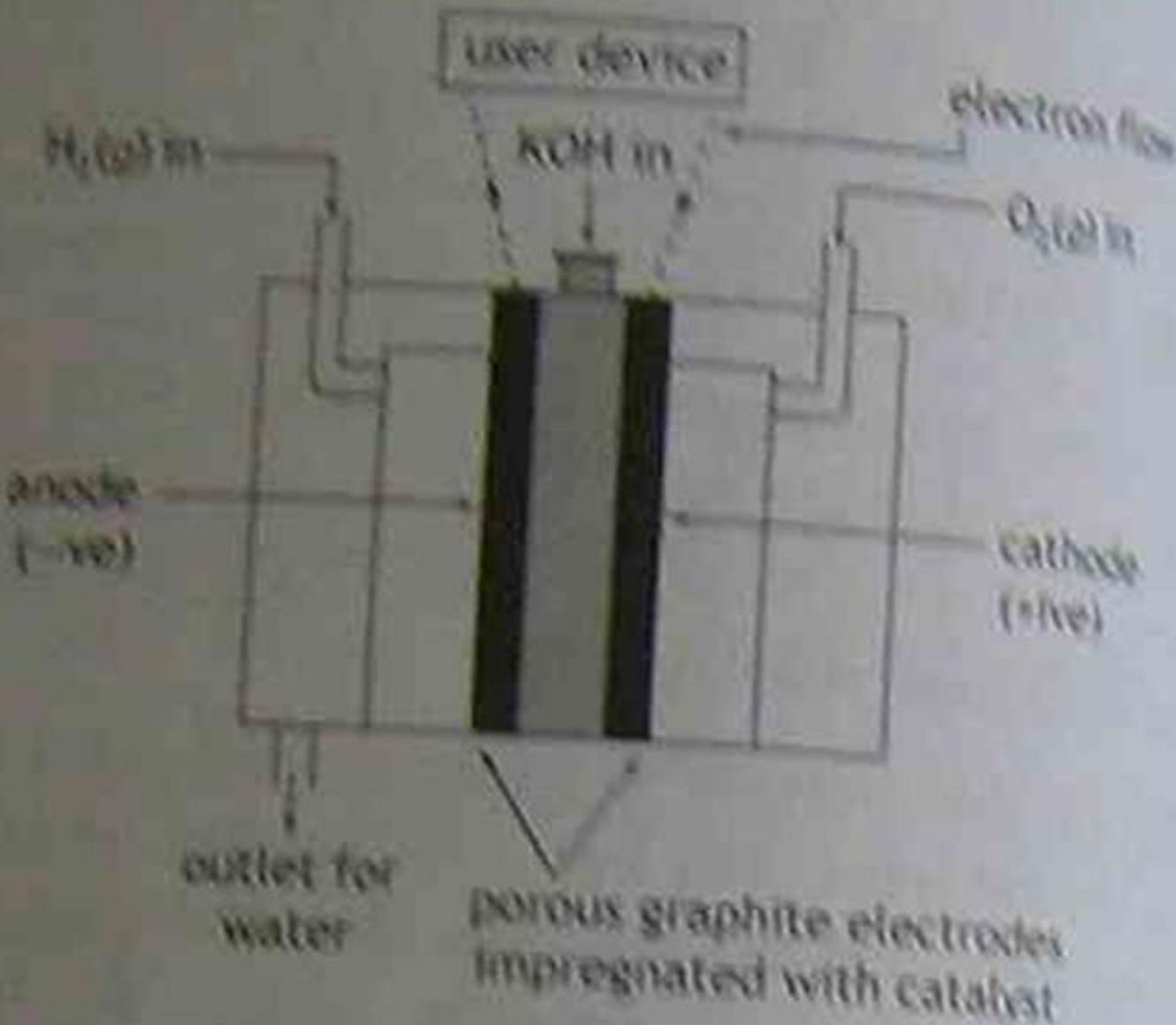


Figure 1.35

A simplified hydrogen-oxygen fuel cell

Nuclear chemistry

The term **nuclear chemistry** is now used to refer to the reactions in the nucleus of an atom in which particles or ionising radiations are emitted, or in which the nucleus is bombarded by particles and radiations and captures them.

1.23

Some nuclear reaction equations

Conditions under which a nucleus is unstable

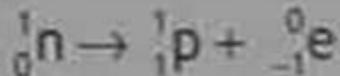


- An unstable nucleus will release particles and/or energy to become more stable. This nucleus is *radioactive* and the stabilising process is called *radioactive decay*.

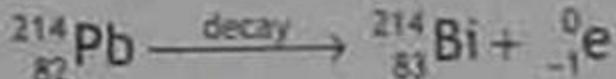
Reasons for instability of the nucleus

- (a) Too many neutrons for the number of protons present

In this case a neutron in the nucleus changes to a proton and an electron.



Example

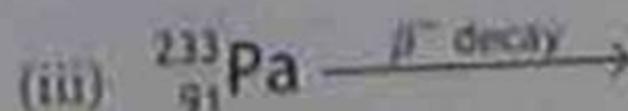
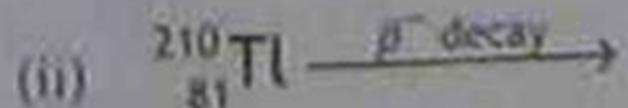
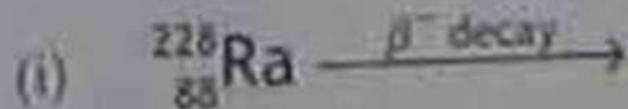


Note:

1. The element has changed from Pb \rightarrow Bi because the atomic number has changed.
2. The symbol β^- can be used in equations instead of ${}^0_{-1} e$.

Exercise 1

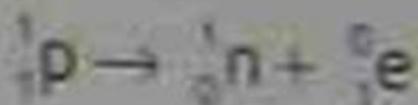
Complete the following nuclear equation:



(b) Too many protons for the number of neutrons

In this case the proton changes into (i) a neutron and
(ii) a positron (a positively charged electron) called

a beta (β^-) particle or e^- (${}_{-1}^0 e$).

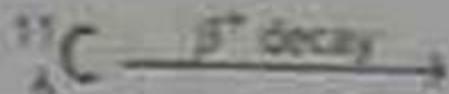


Example



Exercise 2

Complete the following nuclear equation:



- (c) Too many protons and neutrons (the nucleus is too heavy)

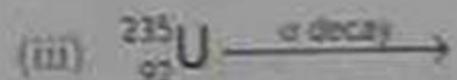
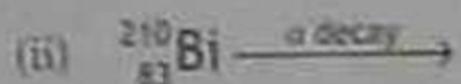
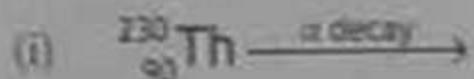
In this case the nucleus loses mass by emitting an alpha (α) particle which consists of two protons and two neutrons. It is positively charged and can also be called a helium nucleus (${}^4_2\text{He}$); this symbol represents the alpha particle in equations.

Example



Exercise 3 _____

Complete the following nuclear equations:



Exercise 4 _____

Starting with $^{238}_{92}\text{U}$ and ending with $^{226}_{88}\text{Ra}$, look up the four missing isotopes and complete the radioactive decay scheme.

Note: Energy in the form of gamma (γ) rays is often released by an atom undergoing radioactive decay. This can be included in a nuclear equation by writing 'energy' or ' γ ' as a reaction product.

Answers to exercises _____

124 Nuclear fuel processing and waste disposal

The nuclear fuel cycle

Most but not all nuclear reactors require uranium 'enriched' in U-235 as their fuel. The enrichment process is one step in a chain of processes from crude uranium ore (see Figure 1.5).

At present there are three types of enrichment in commercial use or under consideration:

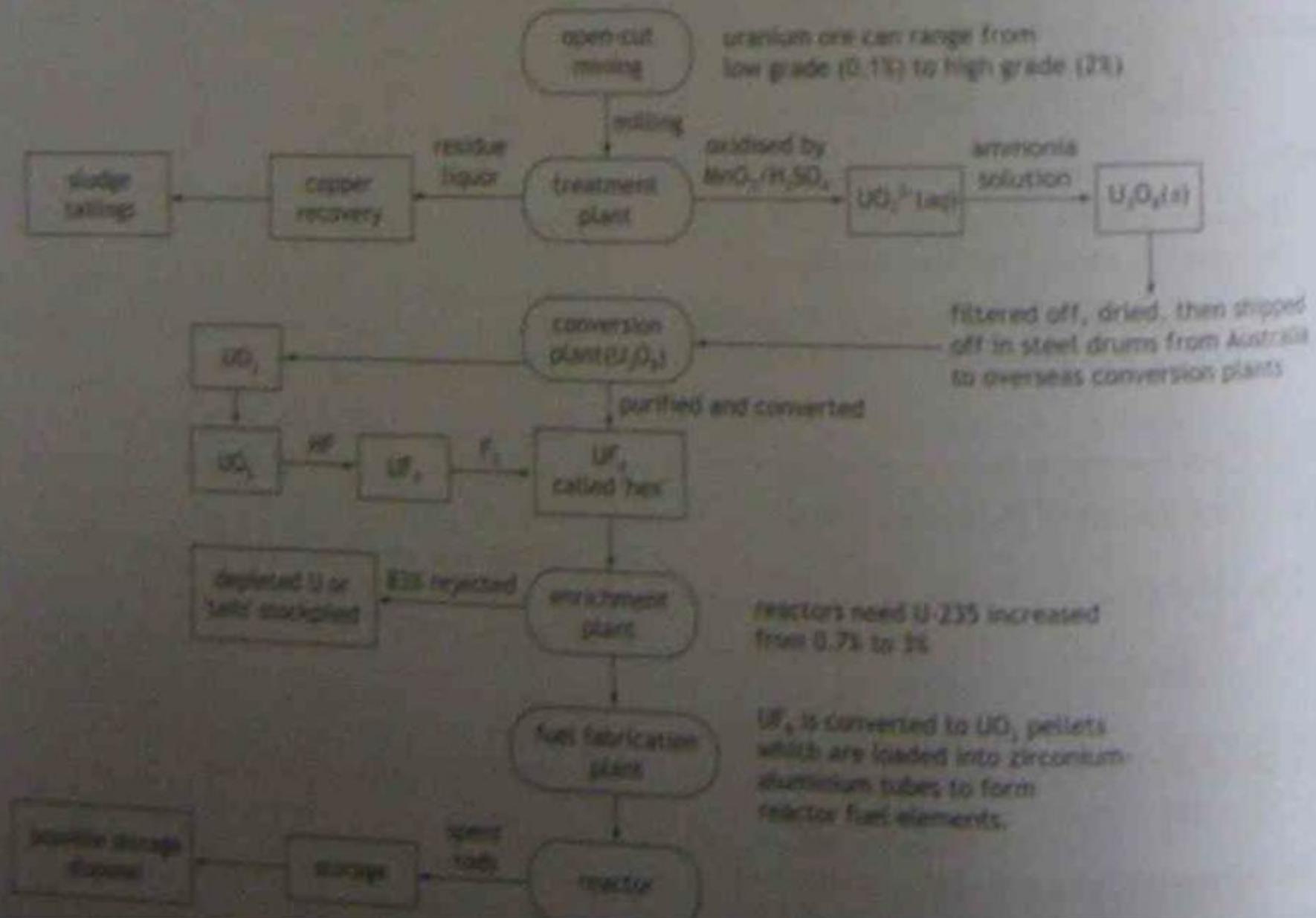
- (a) Gaseous diffusion
- (b) Centrifuge enrichment
- (c) Two types of laser enrichment technologies.

Of these, (a) and (b) are both widely used, but the enrichment is still at the developmental stage. A laser-based selective photo-ionisation process was developed in Australia, but as yet this has not been commercialised.

Uranium found in nature consists largely of two isotopes U-235 (0.7%) and U-238 (approx. 99%). These isotopes differ in their mass with U-235 containing 143 neutrons and U-238 containing 146 neutrons in its nucleus. All enrichment processes are based on this mass difference.

After completion of enrichment to the uranium hexafluoride stage, the UF₆ is turned into 10 pellets which are assembled into fuel rods. Examples of typical reaction products are





Disposal and storage

Stockpiled 'tails'

This material cannot be used in current types of reactors. It can only be utilised in fast breeder reactors and is stored as UF₆ in steel containers. About 0.025% U-235 remains in it. Fast breeder reactor programs have ceased for the time being.

Storage and possible waste disposal

Several methods have been used for the disposal of dry radioactive wastes produced after the evaporation of liquid.

- (a) Deep burial of drums of wastes in mines where hopefully no earthquake activity will occur. These sites should also be free from ground water and be remote from population centres.
- (b) Drums of wastes have been dumped by Belgium, the Netherlands, Switzerland and the UK in deep parts of the oceans where any escaping material would be diluted by seawater.

- (c) The use of solids to contain the high level radioactive wastes. Such a solid must be chemically stable, resistant to pressure, irradiation damage, structural change and especially to high temperatures and have a low susceptibility to leaching. It must be able to incorporate a wide range of waste elements. The solid must contain the waste for almost a million years to allow radioactivity to reduce to former levels.

Nuclear reactors

The fission process

Most atoms are stable, but U-235 is an unstable atom and is therefore radioactive. If a U-235 atom is bombarded with a neutron it will split in two and a few neutrons will fly off. If the free neutrons can be controlled so that they hit successive atoms, the process becomes a chain reaction. When the U-235 atom is split, the free neutrons travel at very high speeds and must be quickly slowed down by passing them through 'heavy water' (water made from deuterium and oxygen).

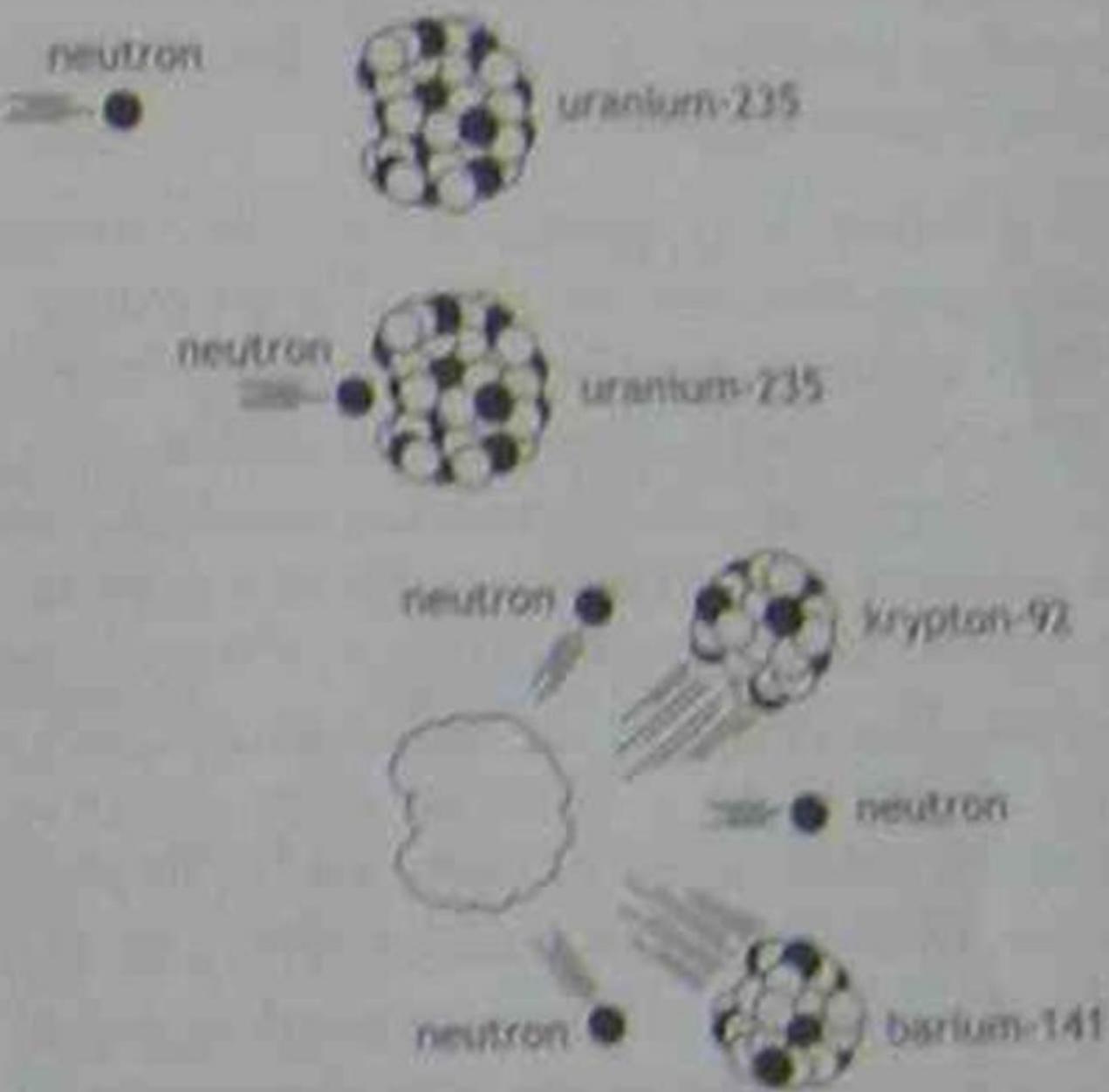


Figure 1.35: Schematic diagram of the fission of the U-235 nucleus

Uses of nuclear reactors

Nuclear reactors are used for a number of commercial purposes. These include:

- (a) the production of thermal heat to drive electric power turbines;
- (b) the production of specific radioisotopes for use mainly in industry and diagnostic or therapeutic nuclear medicine; and
- (c) the provision of a range of scientific research facilities (e.g. for X-ray diffraction studies).

Some nuclear reactors are dedicated to the production of weapons grade plutonium, but this is expected to reduce as more nations sign on to the Nuclear Non-proliferation Treaty.

1.26

Isotopes, radiation and radioactivity

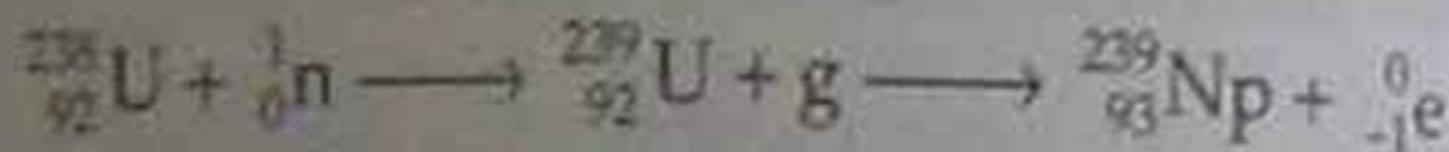
Transuranic elements

The initial attempts to convert the largest naturally occurring element, uranium (U-238), into heavier elements by neutron bombardment resulted in nuclear fission. The nucleus was split in two. This event ultimately led to the Manhattan Project. The first atomic bomb was exploded in 1945.

The first transuranic element (element 93) was found in 1940 at Berkeley in California; it was named neptunium (Np). In 1941 element 94 was formed by bombarding uranium with hydrogen nuclei using a cyclotron (a type of particle accelerator). This element was named plutonium (Pu). The formation of larger nuclei from smaller ones is called nuclear fission. Research teams headed by Glenn Seaborg led the world in making transuranic elements for the next decade. In 1944, elements 95 (americium) and 96 (curium) were

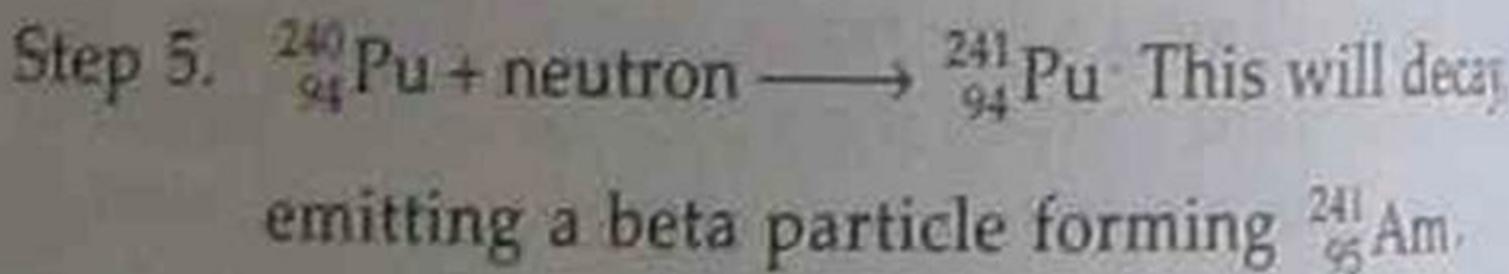
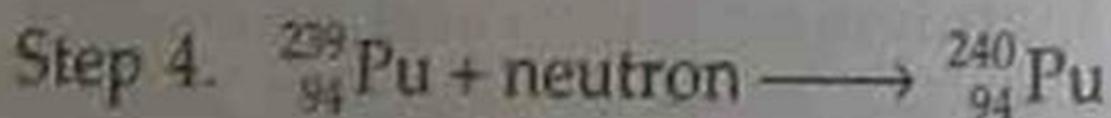
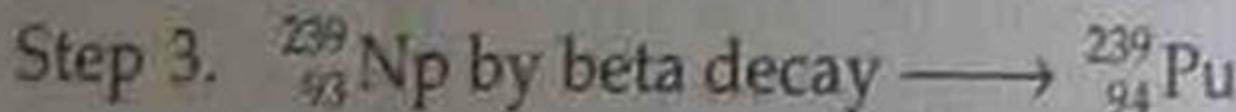
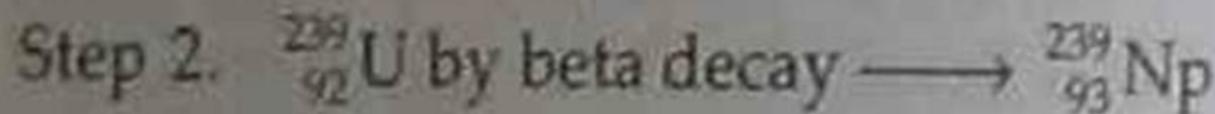
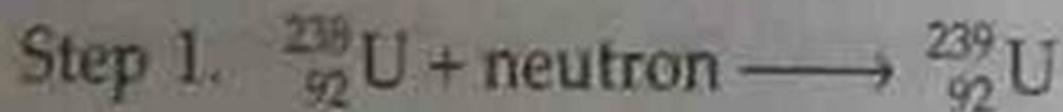
produced by bombarding plutonium. Element 98 (californium) was followed by discoveries of elements 99–103. Element 104 is californium (Cf), element 105 is unnilquadium (Unq) and element 106 is unnilpentium (Unp). Elements up to 109 have been reported, but they are so short-lived that they are not considered to be important. Nuclear reactors were used to produce the following elements:

Equations:



Plutonium-241. This element is formed from uranium-238 in nuclear reactors by bombardment with neutrons followed by beta-decay in several steps.

Detailed steps:



Note: $^{241}_{94}\text{Pu}$ has a half-life of 14 years. $^{241}_{95}\text{Am}$ has a
half-life of 432 years and is used in smoke detectors.

Isotopes

The nucleus of an atom consists of two subatomic particles, the proton and the neutron. These particles are called nucleons. Atoms of the same element have the same number of protons (atomic number). Atoms of a given element can have different mass numbers ($p + n$) and are called isotopes.

 Isotopes are atoms with the same atomic number but a different mass number. They therefore contain a different number of neutrons.

Many naturally-occurring elements have two or more isotopes, e.g. three neon isotopes contain 10, 11 or 12 neutrons. The symbol $^{21}_{10}\text{Ne}$ shows the particular isotope of neon which contains 11 neutrons.

mass no.
atomic no. X

is the **comprehensive symbol** for element X.

Different isotopes of the same element are chemically similar because the chemical properties of atoms are determined by the electrons and not the nuclei. There are 82 stable elements with a total of 275 isotopes.

Natural radioactivity

Natural sources of atmospheric radioactivity include:

- cosmic rays from the sun;
- radioactive substances found in rocks and minerals.

Becquerel in 1896 found that uranium ore gives off invisible rays which can penetrate the light-proof covering of a photographic plate and affect the film. Substances which give off these invisible rays are called radioactive. Radioactivity is the spontaneous breakdown of an unstable atomic nucleus, releasing rays and often particles. Polonium, radon, radium, actinium and protactinium have natural radioactive nuclides. Members of the actinide series after uranium include artificially produced radioactive nuclides.

Table 1.18 Nuclear radiation products

Radiation	Type	Penetration
α particle	He nucleus (${}^4_2\text{He}$)	least (about 5 cm of air)
β particle	high speed electron (${}^{-1}_1\text{e}$)	greater (about 5 m of air)
γ radiation	short-wave electromagnetic radiation	greatest (at least 2 cm of Pb)

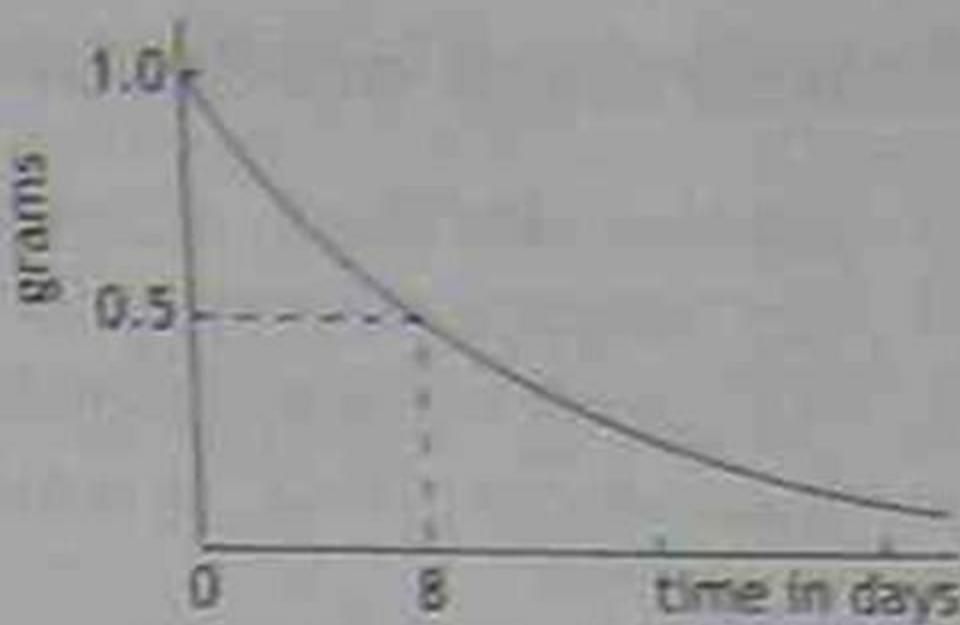


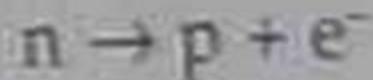
Figure 1.36 Decay curve for iodine-131

Table 1.19 Examples of radioisotopes

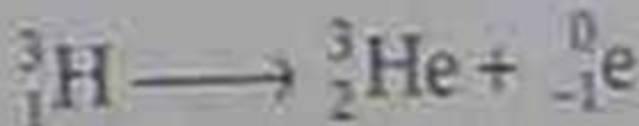
Name	Symbol	Half-life	Mode of decay
Uranium-238	$^{238}_{92}\text{U}$	4.5×10^9 years	α
Plutonium-239	$^{239}_{94}\text{Pu}$	24 000 years	α
Carbon-14	$^{14}_6\text{C}$	5740 years	β
Strontium-90	$^{90}_{38}\text{Sr}$	28 years	β
Cobalt-60	$^{60}_{27}\text{Co}$	5.27 years	β
Iodine-131	$^{131}_{53}\text{I}$	8 days	β
Bismuth-210	$^{210}_{83}\text{Bi}$	5 days	β

Gamma radiation is also emitted in most cases. Two conditions for radioactive isotopes to form:

- (a) Too high a ratio of neutrons to protons. A neutron changes to a proton and an electron (β particle) is emitted.

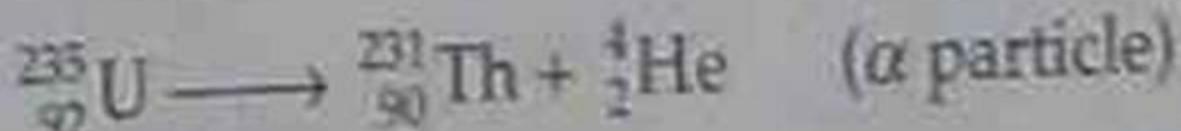


Example — 3_1H is tritium, a radioactive isotope of hydrogen.



- (b) The nucleus is too large (where mass number is >209). An α particle will be emitted.

Example

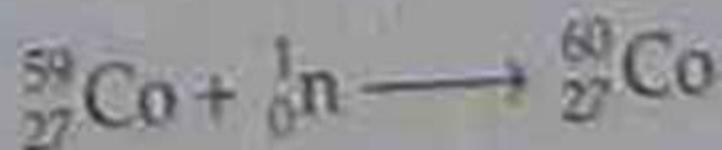


In writing nuclear equations, the atomic numbers and mass numbers must balance.

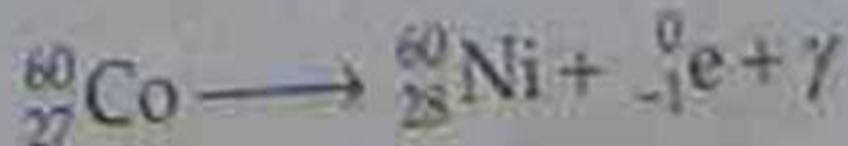
and mass...

Many radioisotopes are made by neutron irradiation of stable isotopes in a nuclear reactor.

Example



Cobalt-60 decays to produce β and γ radiation.



Radiisotope production

The most common method of radiisotope production is by neutron activation in a nuclear reactor. This involves the capture of a neutron by the nucleus of an atom resulting in an excess of neutrons (neutron-rich).

This may be manufactured in a cyclotron (an accelerator) in which protons are introduced to the nucleus, resulting in a deficiency of neutrons (proton-rich). The cyclotrons use high voltages and electric fields to accelerate hydrogen atoms through a vacuum chamber. When they collide with the target substance they produce radioactivity. It can be more difficult to make a radioisotope in a cyclotron than in a reactor. The Australian government has recently agreed to a new nuclear research and radioisotope production reactor to be installed and operated by ANSTO at the Lucas Heights Science and Technology Centre.

The least frequently used medical radionuclide, technetium-99m, evolves by radioactive decay from a precursor radionuclide, molybdenum-99 (half-life 66 hours) produced in the reactor. Because of its longer half-life, appropriately large activities of the "Mo/Tc" generator can then be transported to nuclear medicine departments around the country for immediate diagnostic use.

Radioisotopes in medicine

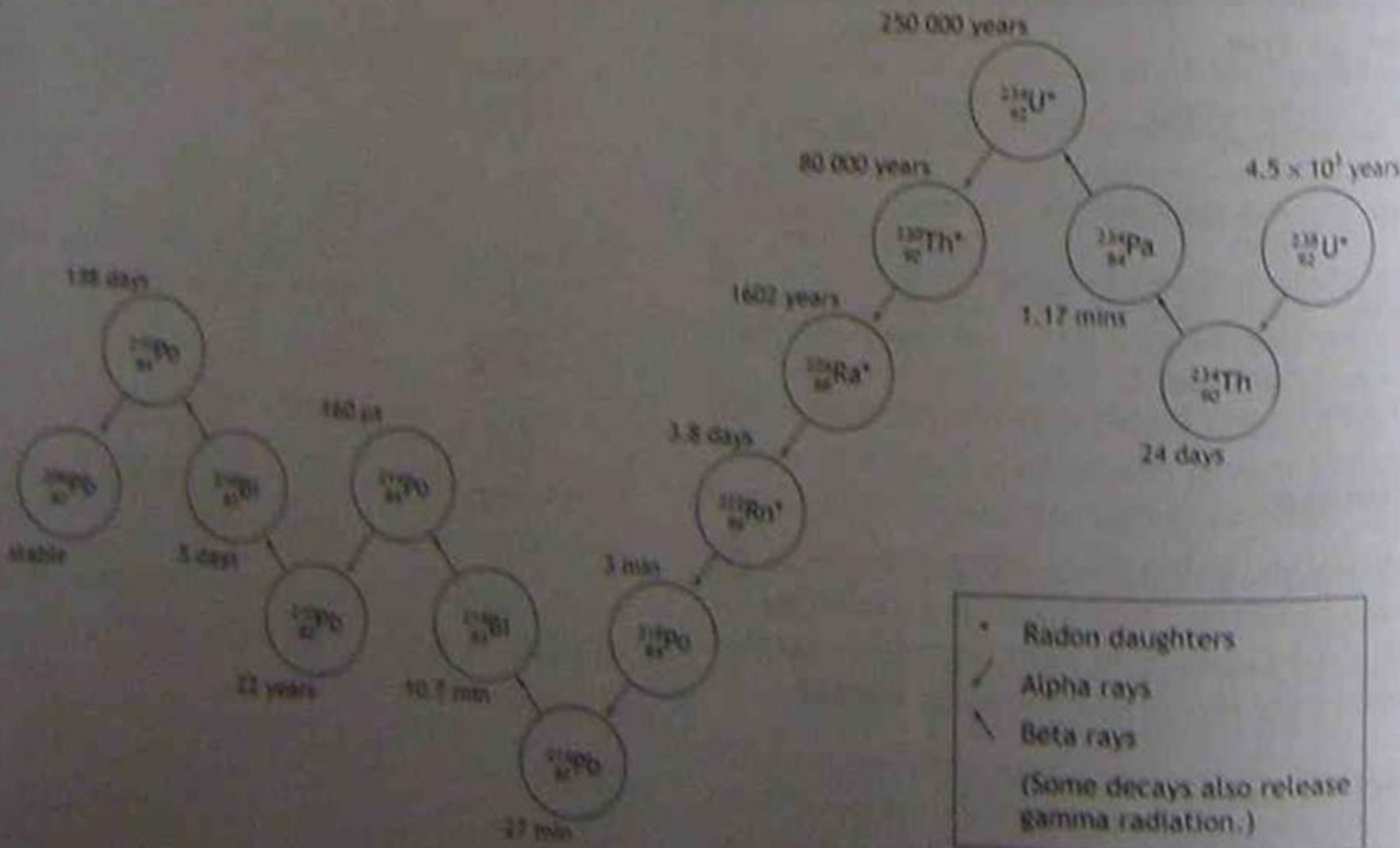
There are three main uses of radioisotopes in medicine:

(a) Diagnostic

In nuclear medicine radioisotopes, combined with suitable chemical 'carriers', are used to target and provide essential diagnostic information on the functioning of specific organs.

(b) Therapeutic

Radiotherapy using radiation from a radioactive source is used to treat cancer by weakening or destroying diseased cells. This is possible since rapidly dividing cells are very sensitive to radiation damage. Some cancerous growths can be controlled by radiation from a cobalt-60 source. Internal radiotherapy can also be carried out using a small



(c) Biomedicine

Because they are easily detected in low concentrations, radioisotopes can be used to label molecules of biological samples on which pathologists can carry out *radioimmuno assays*.

Diagnostic radiopharmaceuticals

These are used to examine, for example, the functioning of organs such as the liver, heart or kidneys. The amount of radiopharmaceutical given to the patient is the minimum needed to obtain the information before it undergoes radioactive decay. The selected radiopharmaceutical must emit gamma rays of sufficient energy to escape from the body and have a half-life short enough for it to decay away soon after imaging is completed. Iodine-131 based radiopharmaceuticals are used for therapy in cases of thyroid cancer. Another, based on phosphorus-32, can be used to control the number of red blood cells.

The radioisotope most widely used in nuclear medicine is technetium-99*m*, 'milked' from the artificially produced $^{99}\text{Mo}/5$ generator, which comprises a lead pot enclosing a glass tube containing the radioisotope supplied by Australian Radioisotopes (ARI) from its laboratories at the Lucas Heights Science and Technology Centre. The molybdenum-99 progressively decays to technetium-99*m*. When it is received at the point of use, the technetium is washed out of its container with saline solution. After about two weeks, the generator is returned to ARI for recharging.

As a producer of radioisotopes the cyclotron complements the neutron-rich reactor products but does not replace them. In other words, reactor-produced radioisotopes have different uses to the equally important 'proton-rich' cyclotron radioisotopes.

Selection of radiolsotopes in nuclear medicine

In nuclear medicine, a radioisotope is administered to a patient either to aid the diagnosis of disease or for the treatment of disease.

Table 1.20 Selection of the isotope depends on its use

For diagnosis	For treatment
A short half-life (hours) depending on the length of the investigation.	A half-life which will not cause extended hospital stay due to excessive radiation.
Must not emit alpha or beta particle radiation since these particles would be trapped in the patient's tissues and not be detected externally.	Must emit alpha and beta radiation to penetrate the lesion being treated.
Must emit gamma radiation of an energy which will allow its position in the body to be reliably assessed.	Must emit gamma radiation to assess that the appropriate target region of the body has been reached.

The characteristics of technetium-99m

Technetium-99m has the following almost ideal characteristics for a nuclear medicine scan:

- It has a half-life of six hours which enables metabolic processes to be examined yet minimises the radiation dose to the patient.
- It decays by an 'isomeric' process which emits gamma rays and low energy electrons. Since there is no high energy beta emission, the radiation dose to the patient is low.

- The low energy gamma rays easily pass out of the body, so they can be detected by the gamma camera.
- The chemistry of technetium is versatile and can be incorporated into a range of biomolecules (carriers) which concentrate in specific organs.

1.29

Radioisotopes in industry

Modern industry uses radioisotopes in a variety of ways to improve productivity and/or gain specific information.

Industrial gamma radiography

Gamma rays are produced by a small pellet of radioactive material, e.g. cobalt-60 or iridium-192, in a sealed titanium capsule. The capsule is placed on one side of the object being radiographed and photographic film is placed on the other. Like X-rays, gamma rays show flaws in metal castings or welded joints. Because of ease to transport and since no power is needed, gamma radiography is especially useful in remote areas, e.g. to check welds in natural gas or oil pipelines.

Gauging

The radiation that comes from a radioactive source has its intensity reduced by matter placed between source and detector. Detectors can be used to measure this reduction without contact with the material being gauged. This method can be used to measure the thickness of plastic film, the detector signal strength being used to control the plastic film thickness.

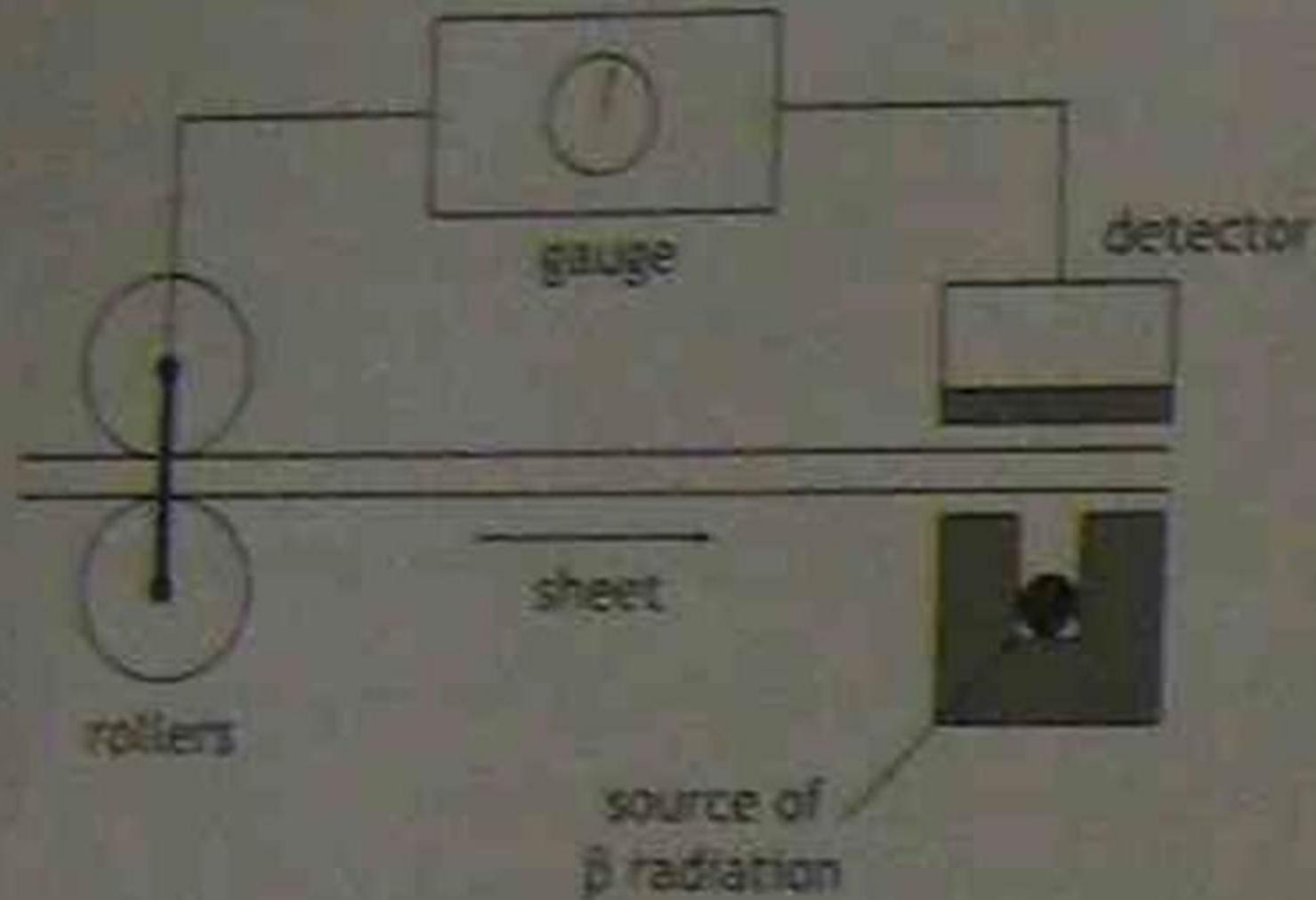


Figure 1.38 Thickness control gauge

Gamma sterilisation

This technique is used for sterilising medical products, e.g. disposable syringes, gloves, sutures and instruments, many of which would be damaged by heat sterilisation. Cobalt-60, an energetic gamma emitter, is widely used. It is produced in nuclear reactors and has a half-life of 5.27 years.

Raw wool for export can also be treated by this method to kill parasites. Food preservation also benefits from gamma irradiation treatment. More than 50 foods have received extended shelf lives and the risk of food-borne diseases has been reduced.

Environmental studies

Radioisotopes provide an ultrasensitive analysis technique for studying the age, movement and depletion of water resources.

All water originally contained minute amounts of radioisotopes of hydrogen and carbon. Surface water may seep underground into porous rocks and sand. The Great Artesian Basin is the largest underground water resource in Australia. After water goes underground the radioisotopes are no longer replenished from cosmic rays so they decay. The radioisotope of hydrogen (tritium) has a half-life of 12 years, while carbon-14 has a half-life of 5740 years.

CARBON-14 has a half-life of 5740 years.

Table 1.21 Examples of other reactor radioisotopes

Radiation	Element	Half-life	Use
α	chromium-51	27.7 days	to label red blood cells
$\beta^- \alpha$	iodine-131	8 days	widely used in functional imaging and therapeutic applications for the thyroid gland
$\beta^- \alpha$	potassium-42	22 hours	determination of exchanged potassium in blood flow
$\beta^- \alpha$	sodium-24	15 hours	studies of body electrolytes
γ	ytterbium-169	3 days	brain scan

Table 1.22 Examples of other cyclotron radioisotopes

Radiation	Element	Half-life	Use
γ	gallium-67	3.3 days	tumour-seeking agent
γ	krypton-81m	13 seconds	lung ventilation studies
Positron emitters	carbon-11 nitrogen-13 oxygen-13	ultra short-lived	used in positron emission tomography (PET) for studying brain physiology and pathology for epilepsy and dementia

Table 1.23 Naturally occurring radioisotopes for studying water resources

Isotope	Use
Chlorine-36	to measure sources of chlorine and the age of water (up to 2 million years)
Carbon-14	to measure the age of water (up to 50 000 years)
Tritium	to measure the age of groundwater (up to 30 years)

By measuring the minute amounts of these radioisotopes taken from various bores, the 'age' of each sample can be determined and used to determine the rate and direction of flow. For example, water found at the south-western extremity of the Great Artesian Basin entered the Basin in Central Queensland about half a million years ago and has been travelling in a south-westerly direction ever since at a rate of a few metres per year.

Information about the age of water in underground bores can be used to indicate if groundwater is being used faster than the rate of replenishment.

Tracing/mixing uses

Since very small quantities of radioactive material can be easily detected, if it is added to sewage from ocean outfalls, the radioactivity can be traced to study sewage dispersion. The half-life of the tracer isotope chosen should be just long enough to obtain the required information so that no long-term residual radiation remains. Flow rates of large rivers can also be measured in this way.

The tandem accelerator

ANSTO's tandem particle accelerator at the Lucas Heights Science and Technology Centre produces an ion beam which is accelerated by an electrostatic field. Electrons are stripped by a carbon foil stripper from the outer orbits of the ions so that they become positively charged. On leaving the accelerator, they finally enter the target room where they can be measured directly to determine the amount of rare isotope in the original samples.

Archeometry

Archeometry is the term used to describe a range of scientific techniques, including radioisotopic dating and other nuclear techniques, to resolve problems posed by archaeologists.

Radiocarbon dating

This is a method for determining the age of objects up to 50 000 years old that contain matter which was once living. Natural carbon consists mainly of the stable isotope carbon-12, some carbon-13 and a small proportion of carbon-14. Carbon-14 has a half-life of 5740 years and is produced by the action of cosmic rays on atmospheric nitrogen. All living organisms absorb carbon from atmospheric carbon dioxide until their death. The once constant carbon-14:carbon-12 ratio then decreases as carbon-14 decays.

To determine the ^{14}C in this ratio, measurements with a tandem accelerator enable a fast analysis of submilligram carbon specimens, e.g. for dating Aboriginal artefacts and middens.

Smoke detectors

Americium-241 is a reactor radioisotope that evolves as a decay product of plutonium-241. It has a half life of 432 years and emits alpha particles during radioactive decay to become neptunium-237; it also emits low energy gamma rays.

The alpha particles are absorbed in the detector and gamma radiation is lower than normal background radiation. The alpha particles ionise oxygen and nitrogen particles in the air in the detector's ionising chamber. When smoke enters the detector, the alpha radiation is absorbed by smoke particles so the rate of ionisation of the air falls and an alarm is triggered.

Safety requirements for smoke detectors in Australia

Domestic smoke detectors must be labelled with the following information:

- The words 'Warning - radioactive material'
- Trefoil symbol



(this is the usual symbol)

- Identity and amount of radioactive material in the source (each detector uses less than 37 kBq of americium-241 which is a minute amount)
- The words 'return to supplier or Department of Health for disposal'.

Detection of radioactivity

Radiation effects

Becquerel discovered radioactivity because of the effects of radiation on photographic plates. The radiation affects photographic film like ordinary light — the greater the extent of exposure to radiation, the darker the area of the developed negative. Radiographers and other radiation workers wear film badges which are later developed to record the extent of their exposure to radiation over a given period.

The Geiger counter

This instrument is used to detect and measure radioactivity in a particular area. Its operation is based on the ionisation of matter by radiation. The ions and electrons produced permit conduction of an electrical current. (See Figure 1.39)

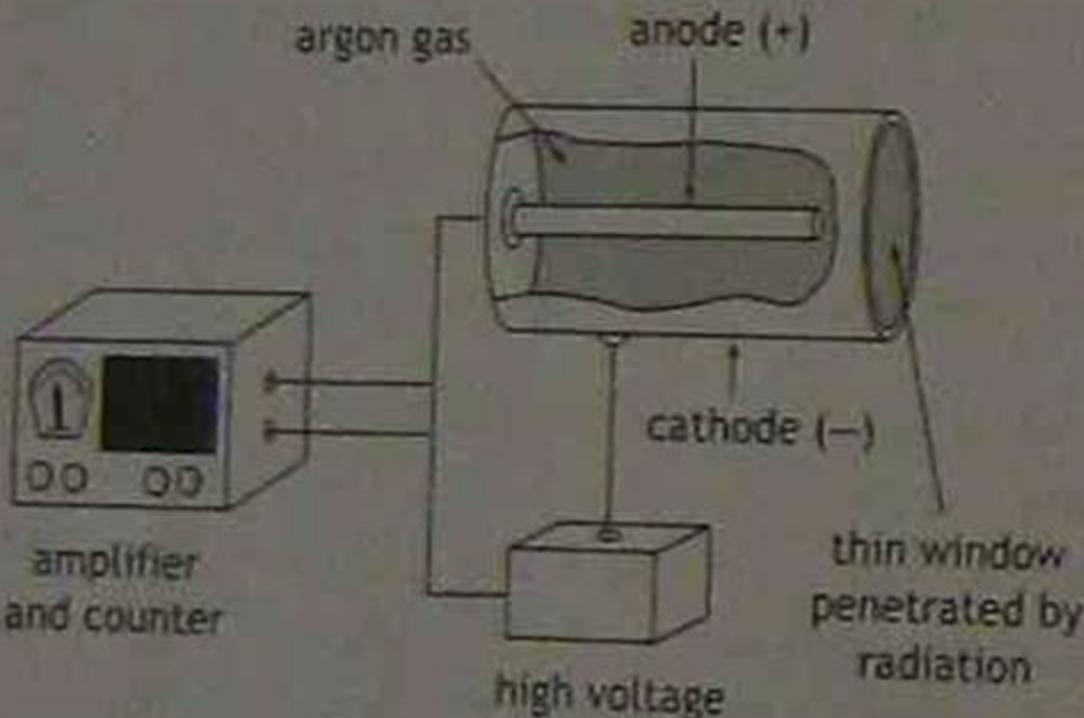


Figure 1.39 A simple diagram of a Geiger counter

Note: School sources are used as a practical means of training students in the basic concepts of radiation.

- **Cobalt-60:** a gamma-emitting radioisotope. Gamma radiation is long range and has high penetration. Dense substances, e.g. lead, are used as a shield.
- **Strontium-90:** a beta-emitting radioisotope. Beta radiation is shorter in range and less penetrating

than γ radiation. It can be stopped by a thin sheet of aluminium.

- **Americium-241:** an alpha-emitting isotope. Alpha radiation can be stopped by a thin sheet of paper and the radiation cannot penetrate the skin.

The scintillation counter

Certain substances that are electronically excited by radiation, fluoresce (give off light) as electrons return to their lower energy state. A scintillation counter measures the fluorescence and hence the radiation causing it.

The gamma camera

Nuclear medicine techniques use radioactive tracers which emit gamma rays from within the body. These are detected by a gamma camera which can view organs from many angles. The camera builds up an image based on the points from which radiation is emitted. This image is then enhanced on a computer and viewed by a physician on a monitor to indicate indications of abnormalities.

A distinct advantage of nuclear imaging over X-ray methods is that both bone and soft tissue can be successfully imaged.

Positron Emission Tomography (PET)

This technique can be expensive because it employs ultra short-lived positron-emitting radioisotopes e.g. oxygen-15, nitrogen-13 and carbon-11, produced at a nearby cyclotron. In a PET study, the patient is surrounded by a ring of stationary radiation detectors.

Single photon emission computer technology

This latest development in nuclear medicine is referred to as SPECT. To produce 3-D images, classical gamma cameras are rotated around the patient. The advantages are a reduced overall cost and convenience since longer-lived radioisotopes,

e.g. technetium- 99m with a half life of six hours, can be used so that an on-site cyclotron is not needed.

Units of measurement of radioactivity

In material, the becquerel (Bq) is the unit of radioactivity present with reference to the number of nuclear disintegrations per second (1 Bq = 1 disintegration/s). Older units include the curie which was the activity of 1 g of radium-226 and is equivalent to 3.7×10^{10} Bq.

In humans, the amount of ionising radiation absorbed in tissue is expressed in grays (Gy), where $1 \text{ Gy} = 1 \text{ J kg}^{-1}$. Since neutrons and alpha particles cause more damage per gray than gamma or beta radiation, another unit, the sievert (Sv) is used when setting radiological protection standards. One gray of beta or gamma radiation has one sievert of biological effect, one gray of alpha particles has a 20 Sv effect, and one gray of neutrons is equivalent to around 10 Sv. A typical background radiation for Australians is 2 mSv/year. In underground uranium mines, such as Olympic Dam in South Australia, the individual workers' doses are by law kept below 10 mSv/year.

Classification and properties of acidic oxides

Group IV

GROUP IV	Carbon dioxide (CO_2)	Silicon dioxide (SiO_2)
Structure	covalent molecular	covalent network
Physical properties	gas at room temperature	solid at room temperature
Effect on living things	essential as a source of carbon for photosynthesis	
Effect on atmosphere	the rate of emission of CO_2 and other greenhouse gases is increasing; in the case of CO_2 this is mainly due to fossil-fuel burning and deforestation	
Chemical properties	soluble in water forming an acidic solution containing H_2CO_3 ($K_s = 4.3 \times 10^{-7}$), this accounts for the acidity of carbonated water; reacts with hydroxide ions to form carbonates and hydrogen carbonates in solution	almost insoluble (K_s = about 10^{-10}) forms a wide range of silicates with the hydroxide ion

Group V

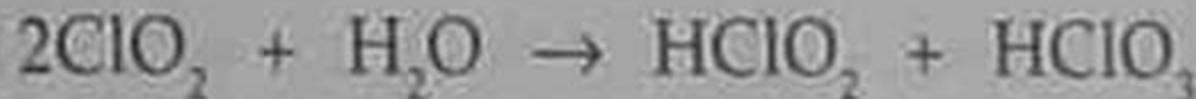
GROUP V	Acidic oxides of nitrogen nitrogen dioxide (NO_2), dinitrogen trioxide (N_2O_3), dinitrogen pentoxide (N_2O_5)	Acidic oxides of phosphorus phosphorus (III) oxide (P_2O_3), phosphorus (IV) oxide (P_4O_{10})
Structure	covalent molecular	covalent molecular
Effect on atmosphere	NO_2 is a serious atmospheric pollutant in photochemical smog formation in cities	
Chemical properties	both the stated oxides of nitrogen are water soluble N_2O_3 is the anhydride of nitrous acid HNO_2 (weak acid) N_2O_5 is the anhydride of nitric acid HNO_3 (strong acid)	both oxides of phosphorus are water soluble; P_2O_3 is the anhydride of orthophosphorous acid H_3PO_2 ; P_4O_{10} is the anhydride of orthophosphoric acid H_3PO_4
Acid properties of the oxides	N_2O_5 is strongly acidic; N_2O_3 is weakly acidic	P_2O_3 is weakly acidic (weaker than N_2O_5) P_4O_{10} is strongly acidic
Note: The acidic nature of the oxides of Group V decreases down the group.		

Group VI

GROUP VI	Sulfur dioxide (SO_2)	Sulfur trioxide (SO_3)
Structure	covalent molecular	covalent molecular
Physical properties	SO_2 is a gas at room temperature	SO_3 is a solid at room temperature (melting point 62°C)
Effect on atmosphere	Increases in the amount of sulfur dioxide in the atmosphere have led to 'acid rain', particularly in cities in the Northern Hemisphere	
Chemical properties	SO_2 has a low solubility in water and forms sulfurous acid H_2SO_3 ; it reacts with hydroxide ions to form sulfites and hydrogen sulfites in solution	SO_3 dissolves in water to form H_2SO_4 , which is a strong acid; it reacts with hydroxide ions to form sulfates and hydrogen sulfates in solution

Group VII

- With the exception of F_2O , all the oxides are acidic.
- The oxides of chlorine are strong oxidants.
- ClO_2 is used for bleaching in the paper industry and as a germicide. It is also used as an improving agent for flour.



- Another oxide of chlorine, Cl_2O_7 , dissolves in water to form a powerful oxidising acid called perchloric acid (HClO_4).
- The rest of the oxides of Group VII are not important.

2.3

Periodic trends of some oxides

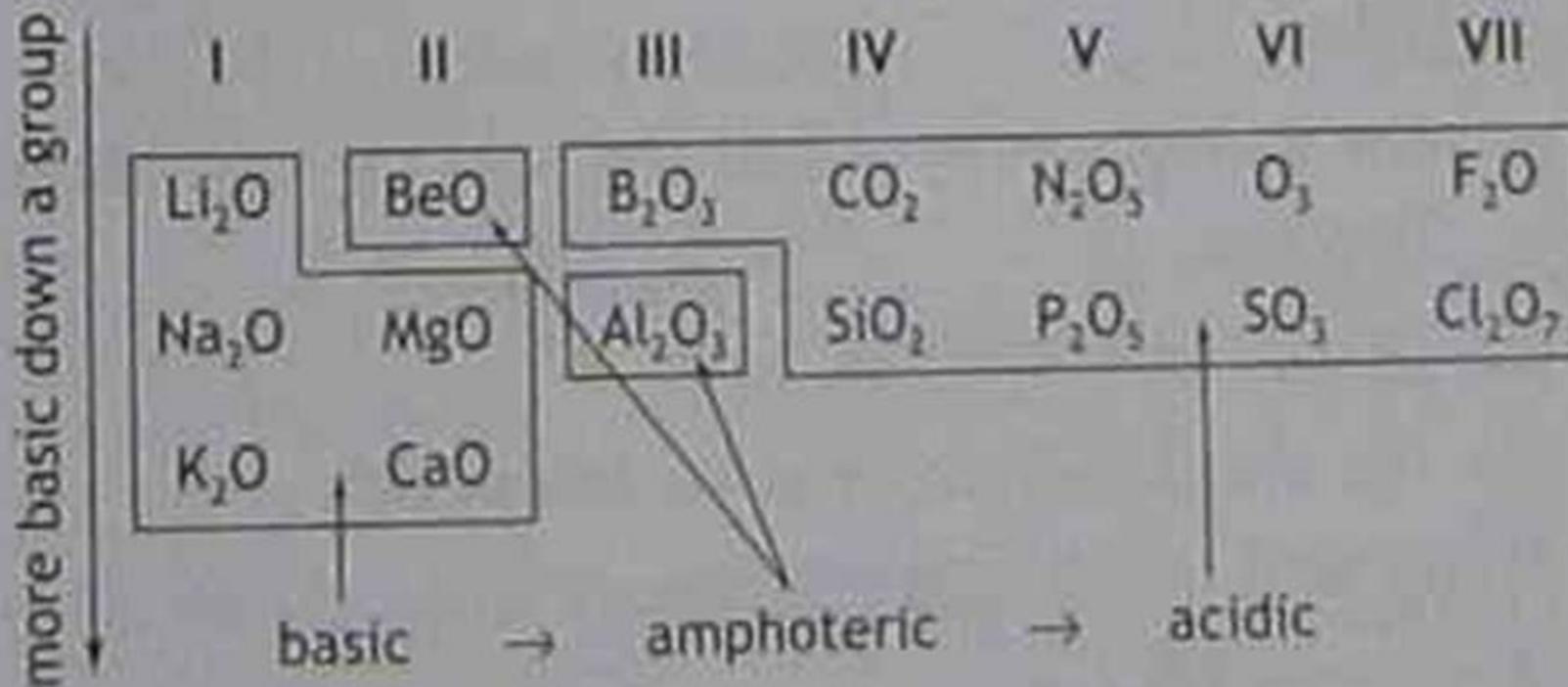


Figure 2.1 Periodic trends of some oxides

Other oxides formed

Peroxides: H_2O_2 , Li_2O_2 , Na_2O_2 , K_2O_2

Neutral oxides: CO , N_2O , NO

- Most oxides of metals are bases and, if soluble in water, e.g. Group I oxides and CaO and BaO , they form alkaline solutions. Some insoluble oxides are MgO , CuO , Fe_2O_3 and Ag_2O .

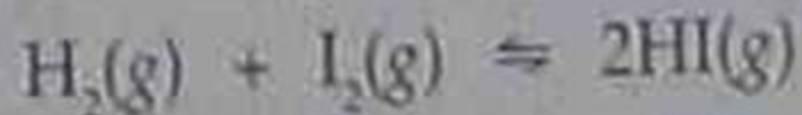
2.4

Disturbing an equilibrium

- If any chemical system at equilibrium is upset, it will re-establish itself.
- Le Châtelier's Principle states that if any chemical system is subjected to a change in concentration or temperature, the system will react in the direction to minimise the effect of the change.

Concentration changes

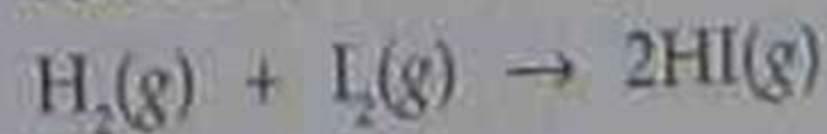
[R] and [P] are moles per litre of reactants and products. Increase [R] — equilibrium shifts to decrease [R] by consuming some of the added R, for example



Increase [H₂] — equilibrium shifts to right.

Temperature changes

Increase temperature — equilibrium shifts to minimise the effect of the change for the forward reaction, for example

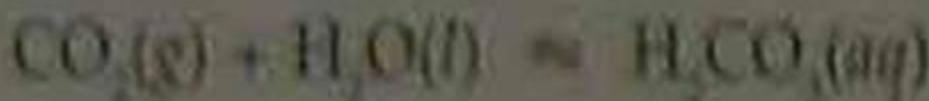


$$\Delta H = 47.7 \text{ kJ}$$

Equilibrium process of CO₂ dissolving in water

- The solubility of carbon dioxide (g) in water decreases as the temperature of the water increases.
- The solubility of carbon dioxide in water increases with pressure. Any increase in pressure of the gas means that there is an increase in its concentration. This can be readily observed by decarbonating a fizzy soft drink.

↓ increased temperature



Usually when a gas dissolves in a liquid, heat is evolved, so the above reaction is exothermic. As the solution is heated, the equilibrium will move to the left to oppose the change. $\text{CO}_2(g)$ will evolve according to Le Chatelier's Principle.

When the pressure (concentration) is increased, at constant temperature, the equilibrium will move to the right to reduce the concentration of CO_2 , according to Le Chatelier's Principle.

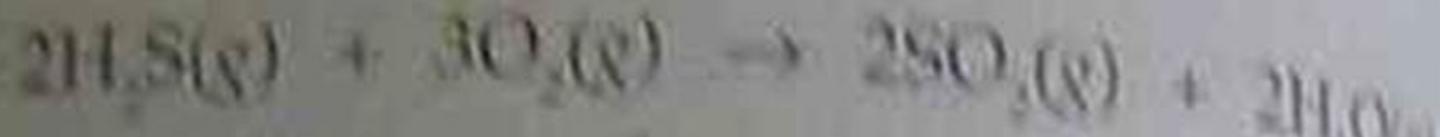
Atmospheric gaseous pollution

When present in sufficiently high concentrations, pollutants have a detrimental effect on the environment and the community. When introduced into the atmosphere they are called air pollutants. Many common pollutants such as sulfur dioxide (SO_2), nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are poisonous gases. Many air pollutants are released into the atmosphere in large quantities by natural processes.

Natural pollution due to sulfur dioxide

- About half of the sulfur dioxide in the atmosphere is due to the oxidation of hydrogen sulfide produced during the decay of organic matter.

Equation:



- Volcanic eruptions release sulfur dioxide as dust and other gases into the atmosphere.

Artificially produced sulfur dioxide emissions

- Humans can generate both local and global effects on atmospheric pollution. About 40% of sulfur compounds are discharged into the atmosphere around large cities where populations are concentrated.
- About 80% of the SO₂ generated by artificial emissions is a result of the combustion of fossil fuels (coal and oil). The presence of sulfur in fossil fuels is a result of the protein material in the original living matter where, after fossilisation, the free element and compounds of sulfur remained.

- Australian fuels have a relatively lower sulfur content when compared with fuels from other regions. Fossil-fuelled power plants are the major culprits for the release of SO_2 pollution.
- Smelters release sulfur dioxide in the process of roasting sulfide ores such as those of copper, lead and zinc. This can produce high local SO_2 levels.
Equation:
$$2\text{ZnS}(s) + 3\text{O}_2(g) \rightarrow 2\text{ZnO}(s) + 2\text{SO}_2(g)$$

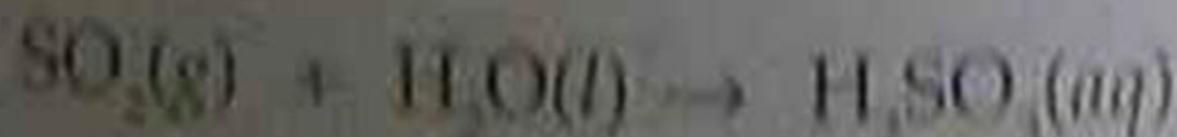
- Other industries which contribute to SO₂ pollution include
 - (a) the manufacture of sulfuric acid by the contact process,
 - (b) petroleum refining, and
 - (c) the manufacture of coke from coal.

Note: Motor vehicles contribute only about 1% of SO₂ emission.

Effects of SO_2 as a pollutant

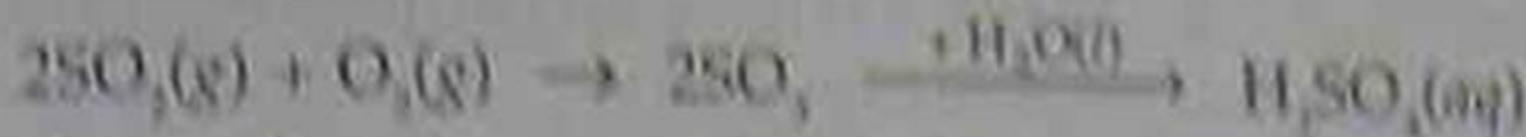
- The main effect on humans is irritation of the respiratory system.

Equation:



- Plants are very sensitive to SO_2 . Low concentrations retard the production of chlorophyll while high concentrations result in the formation of sulfuric acid and plant death.

Equation



- Sulfur dioxide can form a 'reducing' smog.

Control of SO_2 pollution

- Use low sulfur content fuels.
- Remove sulfur from oils in refineries.
- Remove SO_2 from flue gases of power and other industrial plants.

A manganese compound which can absorb SO_2 and convert it to H_2SO_4 is currently being assessed.

Measurement of pollution

The Environmental Protection Authority (EPA) bases its scale, the Air Pollution Index (API), on the amount of pollutants in the air divided by a weighting factor, e.g. SO₂ is a far worse pollutant than NO. The units for pollutant concentration are in parts per hundred million (pphm). The API is not used throughout the world.

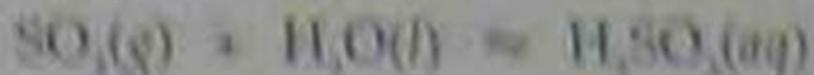
Acid rain

Because of modern industrial pollution in the atmosphere, there has been an increase in acidity due mostly to the formation of sulfuric and nitric acids. Toxic gases such as sulfur dioxide and oxides of nitrogen are released from motor vehicles and industrial smokestacks.

- Sulfur dioxide can be removed from the air by rain in which it forms a weakly acidic acid solution of

sulfurous acid.

Equation:

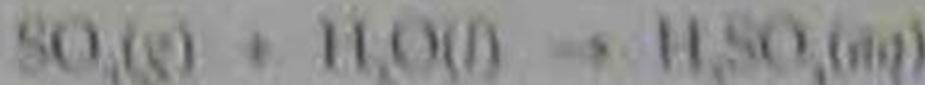


sulfur dioxide

sulfurous acid

- Sulfur dioxide can be gradually oxidised to sulfur trioxide which is quickly converted in moist air to sulfuric acid.

Equation:

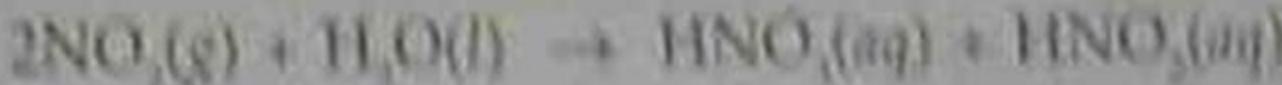


sulfur trioxide

sulfuric acid

- Acid rain may also contain nitrous acid and nitric acid formed from oxides of nitrogen.

Equation:



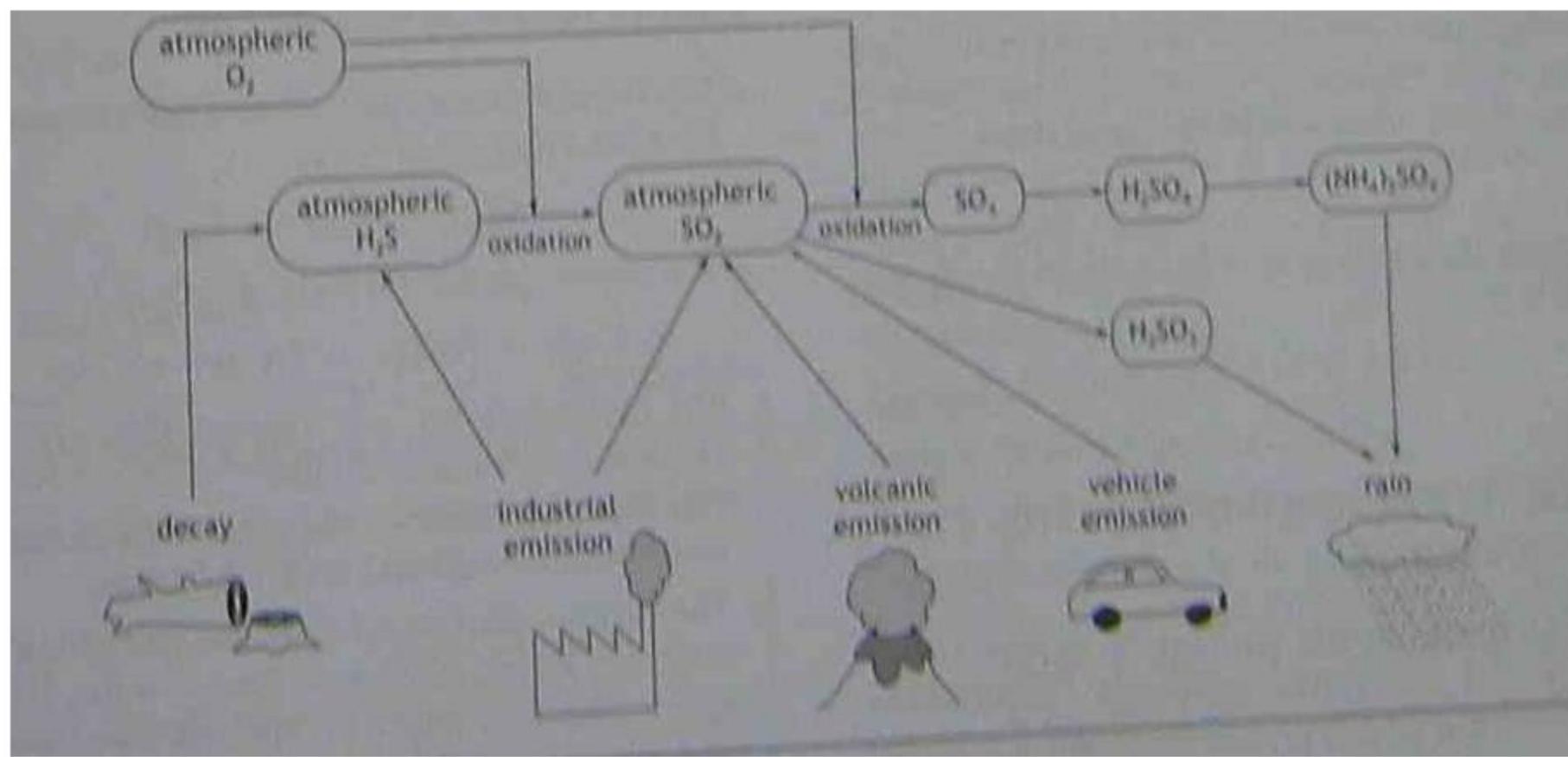
Note: The pH of unpolluted rain water is about 5.2 but in a Los Angeles fog, the pH has been known to drop to 2.2.

Effects of acid rain

Acid rain refers to a form of environmental pollution which results in damage to buildings and marble statues in cities. The calcium carbonate present is 'dissolved' by the acid rain, soluble calcium hydrogen carbonate being formed.



Even more devastating are the effects of acid rain on forests and the extermination of aquatic life forms from lakes and rivers. Acid rain has a pH below 5.6, while rain from an unpolluted atmosphere has an acidity close to 6.0 due to the reaction of water



By upsetting the vital process of photosynthesis acid rain has resulted in more than 75% of the pine trees in the Black Forest being severely damaged. Acid rain in extreme conditions can also leach aluminium from the soil into ground water and into lakes and rivers. Not only do small concentrations of aluminium poison fish but they also threaten the aquatic life at the bottom of the food chain. Eggs and larvae are particularly vulnerable. The leachant can also poison plant and tree roots.

Sources which release oxides of nitrogen

Natural sources

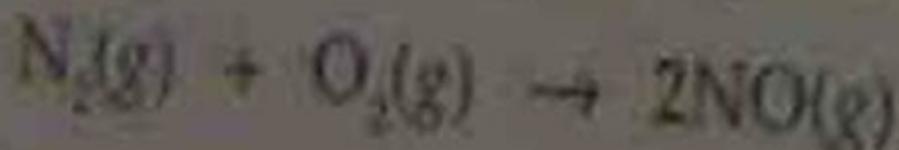
The activities of modern human society now discharge into the atmosphere three oxides of nitrogen: dinitrogen monoxide (N_2O), nitrogen monoxide (NO) and nitrogen dioxide (NO_2). The last two are often analysed together as NO_x .

Oxides of nitrogen (NO_x) form naturally when lightning passes through the atmosphere, and are emitted by volcanoes and by some biological processes.

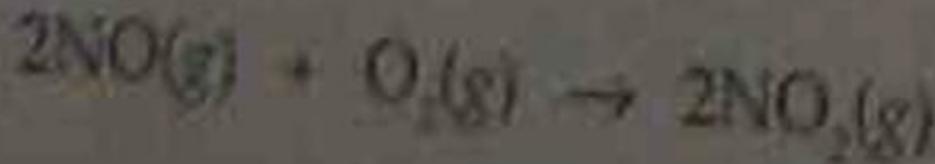
Some chemical reactions which release oxides of nitrogen

These include the burning of fossil fuel and vegetation. Gas-fired power stations and nitric acid manufacture also lead to oxides of nitrogen entering the atmosphere.

Nitrogen monoxide (NO) is formed in internal combustion engines by the direct combination of nitrogen with oxygen at high temperatures:



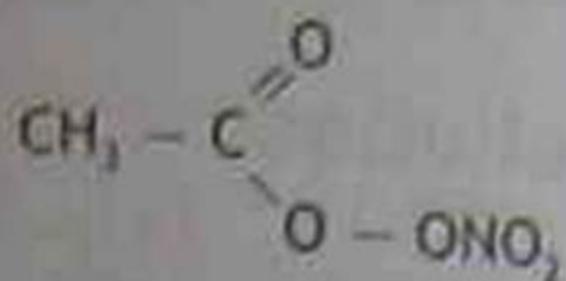
Nitrogen monoxide is readily oxidised to nitrogen dioxide (NO_2).



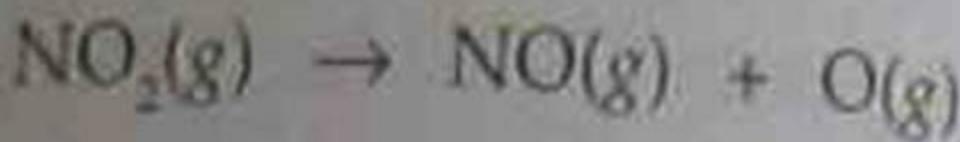
23 The production of photochemical smog

Photochemical smog oxidises in nature and is formed from the primary pollutants, hydrocarbons and oxides of nitrogen discharged by motor

vehicles. These react with oxygen in the presence of sunlight to form various harmful secondary pollutants including ozone, aldehydes and peroxyacetyl nitrate (PAN).



In the presence of u.v. light from the sun, nitrogen dioxide decomposes.



Smog formation needs the following conditions

- Plenty of sunshine.
- Temperature inversion. Pollutants accumulate in the lower inversion layer.
- The presence of tetraethyl lead (C_2H_5)₄Pb. This is used as 'anti-knock' in leaded petrol and deactivated catalytic exhaust devices.

Sydney's climate is conducive to smog formation.

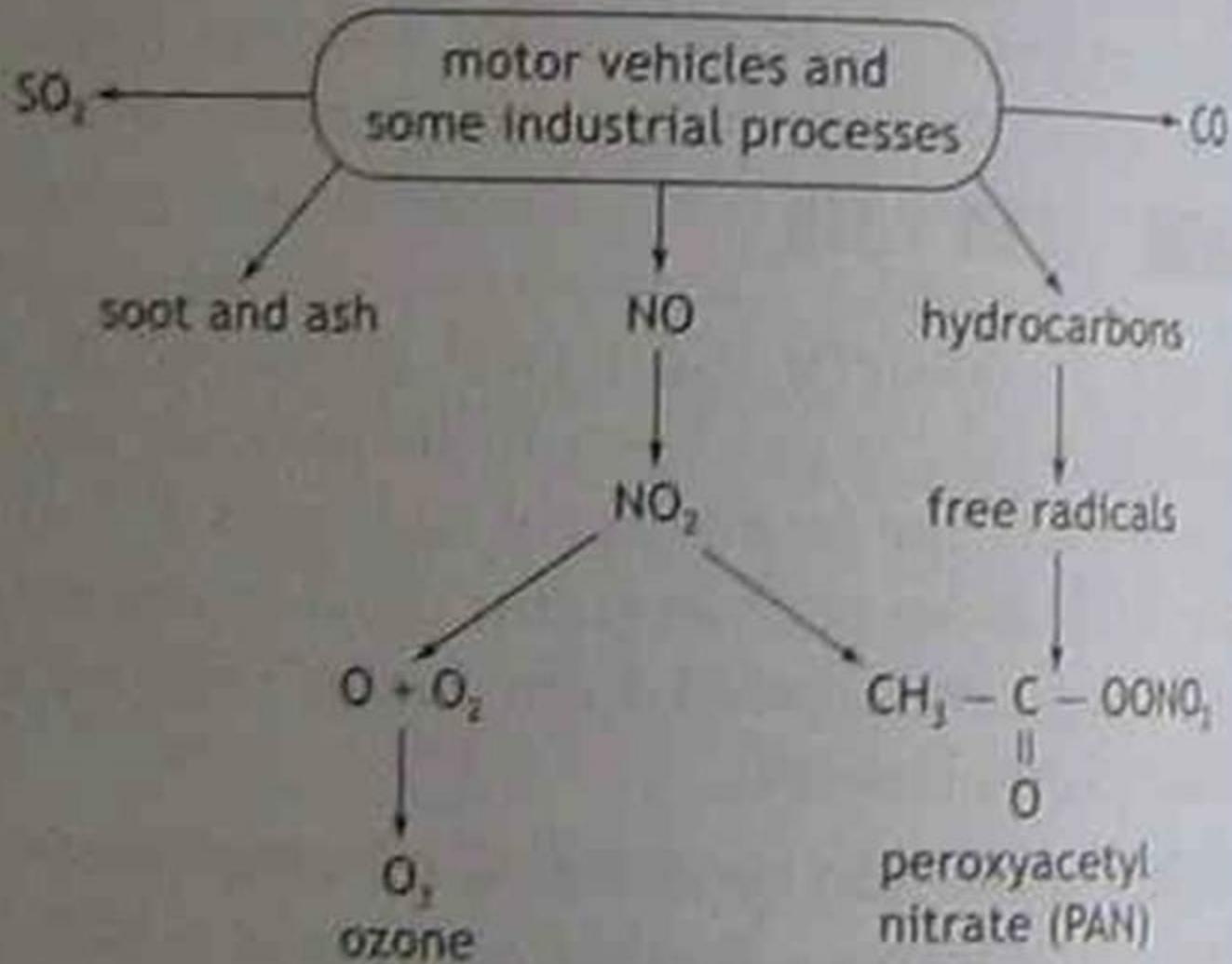
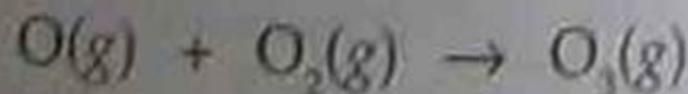


Figure 2.3 Formation of photochemical smog

- * The oxygen atoms react with oxygen to produce harmful ozone.



- * The normal photolytic cycle of NO_2 is



but hydrocarbons can disrupt this cycle by causing competing reactions.

- * The ozone accumulates and other irritants such as aldehydes, ketones and PAN are formed.

- * The accumulation of pollutants below an inversion layer, i.e. when a layer of warm air lies above a layer of cooler air, aids the development of a photochemical smog.

2.9 Calculations involving mole/volume problems

All thermochemical data should be stated at standard state pressure of 100 kPa (1 bar) and a temperature of 25°C. (Refer to G. Aylward and T. Findlay, *SI Chemical Data*, 5th edition, John Wiley & Sons, 2002.)



The key relationship is that one mole of any gas occupies 24.82 L at 25°C and 100 kPa. One mole of a compound contains its molecular mass.

Step 1. Write a balanced equation.

Step 2. Work out the first part of the problem as a mass/mass type.

Step 3. Use the above relationship of the mole to convert mass of gas to volume of gas.

Example 1

Problem

A student carried out an experiment to decarbonate a bottle of soft drink. The volume of gas released was to be found from the loss in mass which occurred when all the gas was released at 25°C and 100 kPa.

Results

Original mass of stoppered bottle
of carbonated drink = 531.25 g

Final mass of stopper, open bottle
and carbonated drink = 529.80 g

Difference in mass due to loss of
 CO_2 (molar mass = 44) = 1.45 g

Calculation

$$\begin{aligned}\text{Volume of } \text{CO}_2 &= n\text{CO}_2 \times 24\ 820 \text{ mL} \\ &= 0.0330 \times 24\ 820 \text{ mL} \\ &= 819 \text{ mL}\end{aligned}$$

The Mole Method

- 
- Step 1.** Write a balanced equation.
 - Step 2.** Find the moles of known substance (the one for which information is given).
 - Step 3.** Determine the mole ratio.

$$\text{mole ratio} = \frac{\text{moles of unknown}}{\text{moles of known}}$$

Step 4. Find the moles of unknown by multiplying the moles of known (Step 2) by the mole ratio (Step 3).

Step 5. Answer the question by converting moles of known into the units asked for.

In performing the calculations in Steps 2 and 5, there is a choice of equations:

$$n = \frac{N}{N_A}, \quad n = \frac{m}{M}$$

$$n = \frac{V}{MV} \text{ (gases only)}, \quad n = CV \text{ (solutions)}$$

Example 2

Problem

What volume of hydrogen gas is produced when 6.5 g of magnesium metal is dissolved in excess hydrochloric acid under standard conditions (25°C and 100 kPa).

Step 1. Write equation



Step 2. Moles of known substance $n = \frac{m}{M}$

(molar mass for Mg = 24.3),

$$n = \frac{6.5}{24.3} = 0.267 \text{ mol.}$$

Step 3. From equation, number of moles of
 $\text{H}_2 = 0.267 \text{ mol.}$

Step 4. Volume of H_2 at 25°C and 100kPa
= $V = n \times MV$
= 0.267×24.82
= 6.63 L

In many problems where the quantities of two substances are given, the limiting reagent is often unknown. To solve such problems, the limiting reagent must first be identified and then used as the known substance in the '5 step mole method'.

Note: It is important to understand that the limiting reagent depends on the mole ratio, not just on which one has less mass.

Method

- Step 1.** Write a balanced equation.
- Step 2.** Find the moles of both known quantities.
- Step 3.** Find (a) the mole ratio of the quantities from Step 2; and (b) the mole ratio from the balanced equation. By comparing the actual mole ratio with the one from the equation, the limiting reagent can be identified.

Step 4. Use the limiting reagent as your known to find the moles of unknown substance (as in previous questions).

Step 5. Answer the question as before.

Example 3

Problem

What volume of carbon dioxide is produced at 25°C and 100 kPa when 20 g of calcium carbonate is heated (atomic mass: Ca = 40, C = 12, O = 16)?



$$\frac{\text{mass CaCO}_3}{\text{formula mass CaCO}_3} = \frac{\text{vol. CO}_2}{\text{molar volume}}$$

$$\frac{20}{100} = \frac{\text{vol. CO}_2}{24.82}$$

$$\text{Step 3. Volume CO}_2 = \frac{20}{100} \times 24.82 \text{ L} = 4.96 \text{ L}$$

Example 4

Problem

0.22 g of a gas is found to occupy 0.124 L at 25°C and 100 kPa. Find the molar mass of the gas.

Step 1. Formulate a ratio.

0.22 grams occupies 0.112 litres at 25°C and
100 kPa

M grams occupies 22.4 litres at 25°C and

$$100 \text{ kPa}, \frac{M}{0.22} = \frac{24.82}{0.124}$$

Step 2. Solve for M.

$$M = 44$$

Molar mass of the gas is 44.

Limiting reagent

Limiting reagent problems

In a chemical equation, the numbers in front of any chemical formula can only tell us what happens when the reactants are mixed in the correct molar ratio so that they will both be completely used up in the reaction. Usually more of one of the reactants than is needed is present. This is called the excess reagent. The other reagent which is completely used up is called the limiting reagent. The limiting reagent depends on the mole ratio, not on the masses of the reactants present. For example, if we place a large piece of zinc in a small amount of hydrochloric acid so that after the reaction some zinc is left, then the zinc will be in excess and the limiting reagent will be the hydrochloric acid.

When quantities of both reactants are given, the limiting reagent must first be identified. It is then used as the known solution in solving the problem.

(a) Mass/mass limiting reagent problems

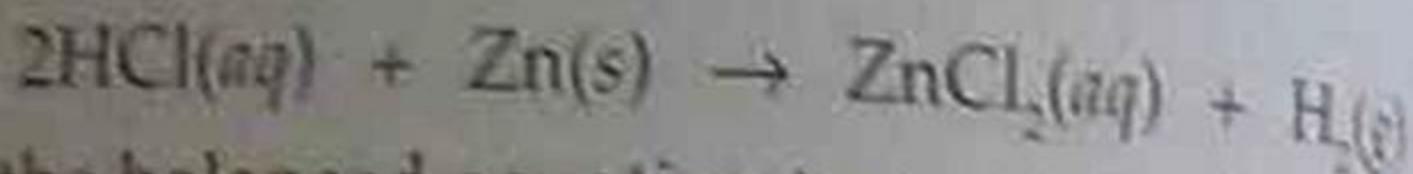
- Write a balanced equation.
- Find out which reagent is in excess.
- Use the limiting reagent to calculate the mass of the product.

Example 1

Problem

A solution containing 100 g of hydrochloric acid added to 100 g of zinc. Find the mass of zinc chloride formed.

Equation:



From the balanced equation two moles of HCl react with one mole of Zn, so $\frac{100}{36.5}$ moles of HCl is added

to $\frac{100}{65.4}$ moles of Zn.

2.74 moles of HCl are added to 1.529 moles of Zn. From equation, for all the Zn to react, $1.529 \times 2 = 3.058$ moles of HCl is needed, i.e. 3.058 moles of HCl. Since only 2.7 moles of HCl is present, then zinc is in excess and 1.37 mole ZnCl₂ is formed.

$$\text{Grams of ZnCl}_2 = 1.37 \times 136.4 \text{ g}$$

Therefore, 186.9 grams of ZnCl₂ are formed.

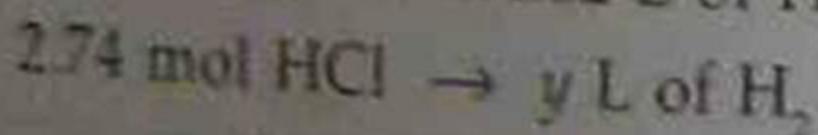
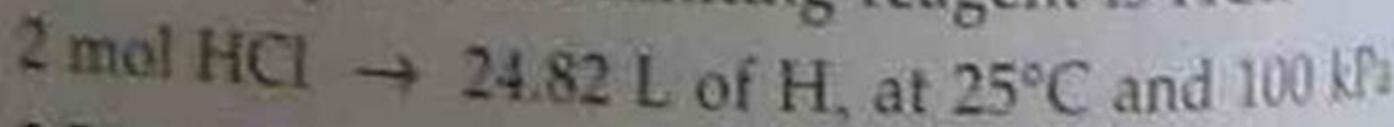
- (b) Mass/volume problems with a limiting reagent

Example 2

Problem

A solution containing 100 g of hydrochloric acid is added to 100 g of zinc. find the volume of hydrogen gas evolved under standard conditions of 25°C and 100 kPa.

From Example 1, the limiting reagent is HCl.



$$\frac{y}{24.82} = \frac{2.74}{2}$$

$$y = \frac{2.74 \times 24.82}{2} = 34.0 \text{ L}$$

34.0 litres of H₂ are produced at 25°C and 100 kPa

Natural acids

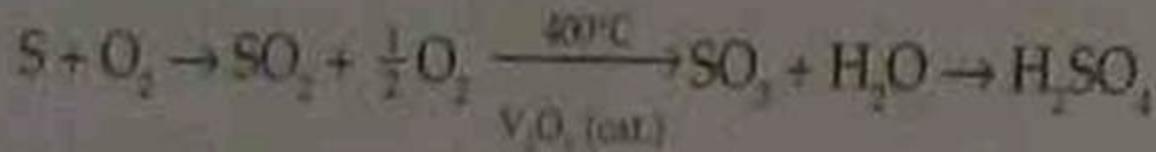
These include the following:

- (a) Acetic acid (ethanoic acid). Vinegar of 0.5 – 1.0 M solution of acetic acid.
- (b) Citric acid found in lemons and other citrus fruit. It is used by soft drink manufacturers to give an acid taste.
- (c) Ascorbic acid (Vitamin C) found in fruit and vegetables.
- (d) Tartaric acid found in grapes.
- (e) Dilute hydrochloric acid (0.1 M) found in gastric juices.

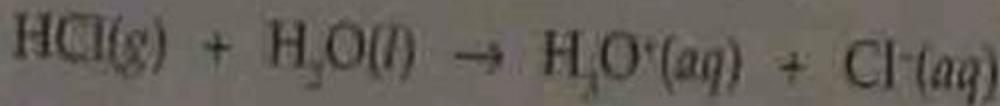
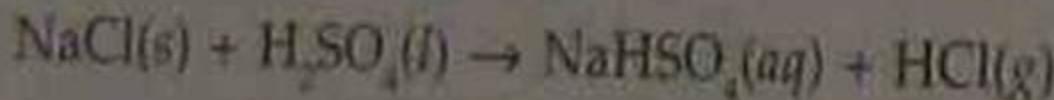
Manufactured acids

These include the following:

- (a) Sulfuric acid, which is the most widely used industrial acid. It is usually manufactured by the contact process.



- (b) Hydrochloric acid, made by

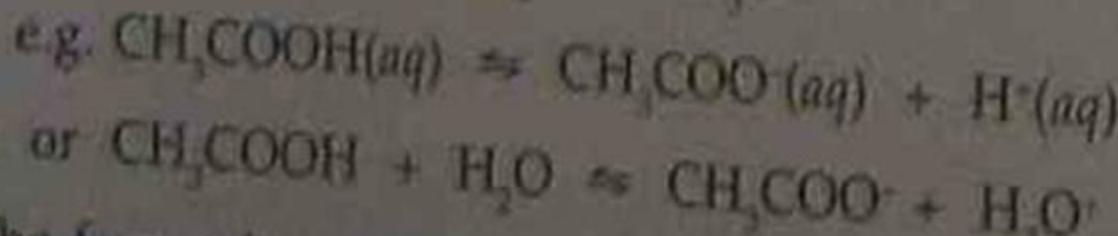
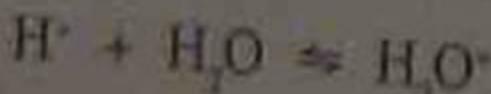


Note: Hydrochloric acid occurs naturally in the stomach and is also manufactured. It is used widely by builders for brick cleaning.

2.11

Acids as proton donors

Acids in aqueous solutions are called *proton (H⁺) donors*.



The forward reaction shows acetic (ethanoic) acid acting as an acid by releasing hydrogen ions.

For water

$[\text{H}^+] [\text{OH}^-] = K[\text{H}_2\text{O}] = K_w$. K_w is called the ionic product of water, and equals 1×10^{-14} at 25°C.

Pure water is a neutral solution.

$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$ at 25°C.

Acidic solutions, e.g. CH_3COOH , HCl , produce H^+ ions in aqueous solutions so $[\text{H}^+] > [\text{OH}^-]$.
The pH scale = $-\log_{10} [\text{H}^+]$.
For pure water $\text{pH} = 7$ at 25°C .
As the $[\text{H}^+]$ increases the pH will decrease.

Concentration of acids

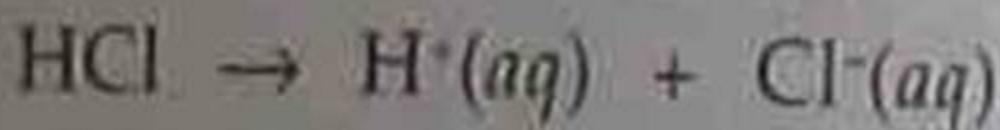
Concentration of acids

In a concentrated acid there is a large amount of acid/unit volume, e.g. 10 M HCl is a concentrated acid, 0.1 M HCl is a dilute acid.

Strength of acids

This is *not* the same as concentration. The strengths vary between strong and weak according to the extent that the acids ionise in solution and are indicated by dissociation constants. A strong acid dissociates completely into hydrogen ions and anions in aqueous solutions.

Example 1



$$\text{The equilibrium constant } K = \frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]}$$

If the [HCl] is almost zero, then K is too large to measure.

A *weak acid* does not dissociate completely in aqueous solution. The weaker the acid, the smaller is the dissociation constant.

Note: If we compare the pH of a 0.1 M solution of HCl and a 0.1 M solution of CH_3COOH ($K_a = 1.8 \times 10^{-5}$) we find that the pH of 0.1 M HCl = 1, but the pH of 0.1 M CH_3COOH = 2.87. Equal concentrations of acids do *not* have equal pH values.

Relative strengths of acids

Relative strengths of weak acids (extension work)

Table 2.1 Some weak acids in water at 25°C

Acid	Formula	K_a
Ascorbic (vitamin C)	$C_6H_7O_6$	$K_{a_1} = 8.0 \times 10^{-5}$ $K_{a_2} = 1.62 \times 10^{-11}$

O=C1C(O)=C(O)C(H)=C(O)C1O

continued next page

Acid	Formula	K_s
Acetic (ethanoic)	CH_3COOH	1.8×10^{-5}
	$ \begin{array}{c} \text{H} & & \text{O} \\ & & = \\ \text{H} - \text{C} - & \text{C} & \text{OH} \\ & & \\ \text{H} & & \end{array} $	
Citric (hydrate $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$)	$ \begin{array}{c} \text{C}_6\text{H}_8\text{O}_7 \\ \\ \text{COOH} \\ \\ \text{CH}_3 \\ \\ \text{HO} - \text{C} - \text{COOH} \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array} $	$K_{s1} = 7.1 \times 10^{-4}$ $K_{s2} = 1.68 \times 10^{-5}$ $K_{s3} = 8.4 \times 10^{-6}$

Note 1: Polyprotic acids, e.g. citric acid, have more than one ionisable proton. These acids have more than one dissociation constant, K_{a_1} , K_{a_2} , K_{a_3} .

Note 2: In multiprotic acids the value of K_{a_1} is always the highest since it is more difficult to remove a hydrogen ion from a negatively charged substance than from a neutral molecule.

2.12

Changes in conductivity of weak acids with dilution

The conductivity of a strong acid, e.g. HCl, increases approximately in proportion to concentration. The conductivity of a weak acid, e.g. acetic acid, does not vary linearly with the acid concentration. This happens because the percentage of acid ionised varies with the acid concentration (see Section 2.13).

Example

$$\text{Percentage ionised} = \frac{\text{concentration ionised}}{\text{original concentration}} \times \frac{100}{1}$$

Dilution

By applying Le Chatelier's Principle to the case of equilibrium in solution, the effect of diluting the solution in water is similar to changing the volume of gaseous equilibria. Dilution causes the reaction to shift in the direction that produces the larger number of particles. For example, the dilution of a 1 M solution of acetic acid by a factor of 10 (to a 0.1 M solution) results in an increase in the percentage of molecules ionised by about a factor of 3.

2.13

Ionisation constants for weak acids (extension work)

- Strong acids (HCl , HNO_3 , H_2SO_4) are completely dissociated ($K_a = \infty$) in aqueous solution.
- Weak acids have a small K_a and are partially dissociated in aqueous solution, e.g. CH_3COOH . At 25°C , $K_a = 1.8 \times 10^{-5}$. The higher the K_a , the stronger is the acid.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$



- Relationship to pH

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{acid strength} \longrightarrow K_a = \frac{[\text{H}^+] [\text{A}^-]}{[\text{HA}]}$$

↑
[H⁺] [A⁻]
[HA] ← undissociated acid
concentration

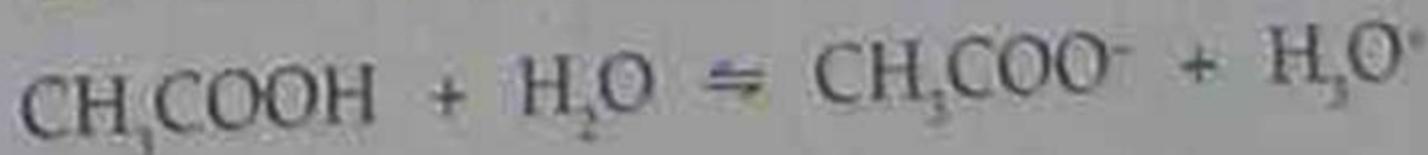
Any one unknown can be calculated from this relationship.

Table 2.2 Ionisation constants for some common weak acids at 25°C

Acid	Formula	K_i at 25°C
*Sulfurous acid	H_2SO_3	1.5×10^{-2}
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-3}
*Phosphoric acid	H_3PO_4	7.5×10^{-3}
Hydrofluoric acid	HF	7.0×10^{-4}
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	6.5×10^{-5}
Acetic acid	CH_3COOH	1.8×10^{-5}
*Carbonic acid	H_2CO_3	4.2×10^{-7}
Hypochlorous acid	HClO	3.5×10^{-8}
Hydrocyanic acid	HCN	4.0×10^{-11}

Example 1

Consider the weak acid, ethanoic acid (acetic acid)



Because water is the solvent,

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
$$= 1.8 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

Note: The stronger the acid, the weaker is its conjugate base.

Example 2

Given the molarity of a 0.001 M solution of acetic acid and that its K_a is 1.0×10^{-5} at the temperature of reaction, find

- (a) the hydrogen ion concentration, and
- (b) the pH of the solution.

Step 1. Write the expression for K_a .

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1 \times 10^{-5}$$

Step 2. Find the relationship between the $[H^+]$ and its conjugate base. Let x be the degree of dissociation.

For each mole of hydrogen ions there is one mole of acetate ions, so

$$[H^+] = [CH_3COO^-]$$

x

x

Step 3. Rewrite the K_a expression

$$K_a = 1 \times 10^{-5} = \frac{[\text{H}^+]^2}{0.001}$$

(Assume that undissociated acid = molarity.
In fact it is molarity - x .)

Step 4. Calculate $[\text{H}^+]$ and hence pH.

$$[\text{H}^+]^2 = 10^{-5}$$

- (a) $[\text{H}^+] = 10^{-2.5}$
(b) $\text{pH} = 2.5$

Example 3

A student carried out an experiment to find K_a for ethanoic acid (acetic acid) given an exactly 0.1 M solution of CH_3COOH and Universal Indicator paper (or a pH meter). The 0.1 M solution was tested with the UI paper and the pH recorded. Using volumetric flasks, the 0.1 M solution was diluted to produce a 0.01 M and a 0.001 M solution of CH_3COOH .

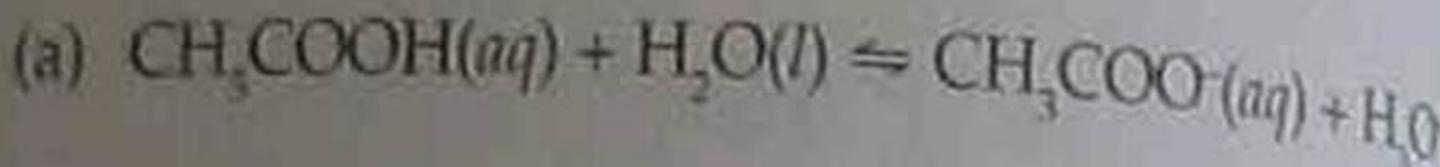
The results were as follows:

Acid concentration	pH
1. 0.1	
2. 0.01	3.0
3. 0.001	3.5
	4.0

- (a) Write an equation to show the ionisation of ethanoic acid in water.

- (b) Write an expression for the equilibrium constant K_a for the reaction.
- (c) Use the student's experimental results to evaluate K_a .
- (d) Would you expect the pH of the 0.1 M solution to increase or decrease if a few millilitres of 1 M $\text{CH}_3\text{COONH}_4$ were added? Explain.

Answers:



(b) $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$

(c) $K_{a_1} = \frac{[10^{-3}]^2}{10^{-1}} = 1 \times 10^{-5}; K_{a_2} = \frac{[10^{-35}]^2}{10^{-2}} = 1 \times 10^{-5};$

$$K_{a_3} = \frac{[10^{-4}]^2}{10^{-3}} = 1 \times 10^{-5}$$

$$K_a = 1 \times 10^{-5}$$

(d) The addition of $\text{CH}_3\text{COONH}_4$ increased the $[\text{CH}_3\text{COO}^-]$ so, according to Le Chatelier Principle, the equilibrium would shift to form more CH_3COOH . This causes the $[\text{H}^+]$ to decrease so that the pH will increase.

pH and pK_w

- Water is a weak electrolyte that ionises slightly to form H^- and OH^- ions.
- K_w is the ionic product of water at 25°C .
$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

- $pK_w = pH + pOH$.
pH is calculated from $pH = -\log_{10} [H^+]$. In a neutral solution $[H^+] = [OH^-]$ or $pH = pOH = 7$. If $pH > 7$ solution is basic, $pH = 7$ neutral, $pH < 7$ acidic
- Strong acids and bases are completely ionised in solution.
- Weak acids such as organic acids are partly ionised in solution.

2.14

The pH scale

As we become more environmentally aware, the acid/base properties of water are seen to be extremely important. The pollution of our beaches, river systems and wetlands has aroused considerable concern.

Not only the suitability of an aquatic environment for support of plant and animal life, but also the rate of corrosion of man-made metallic structures, are very much dependent on the acidity or basicity of the water. The degree of this depends then on the $[H^+]$ and $[OH^-]$ in the water and this is commonly expressed in terms of pH and pOH.

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

$$pOH = -\log_{10}[OH^-]$$

In a *neutral* solution,

$[H^+] = [OH^-] = 1 \times 10^{-7}$, so $pH = pOH = 7$.

Since $[H^+] [OH^-] = 1 \times 10^{-14}$, taking negative logs,
 $pH + pOH = 14$.



pH is < 7 in acidic solutions
and > 7 in basic solutions

Remember that pH is a measure of the $[H^+]$ at equilibrium for substances that do not ionise completely.

The pH scale operates for the convenience of the chemist. If we consider the range to be at one end equal to 1 M HCl and the other end to be equal to 1 M NaOH, we can see that strong acids can have a pH of < 0 and strong alkalis can have a pH of > 14.

Table 2.3 pH and pOH for some solutions

Solution	pH	pOH
1 M HCl	0	14
0.1 M HCl	1	13
Gastric juice	2	12
Coca cola	3	11
Wine	4	10
Coffee	5	9
Tap water	6	8
Pure water	7	7
Blood	7.4	6.6
Sea water	8.5	5.5
Detergents	10–11	4–5
0.1 M NaOH	13	1
1 M NaOH	14	0

Indicators and their pH range

Indicators can be used to determine the acidic or basic nature of a substance over a range that can be

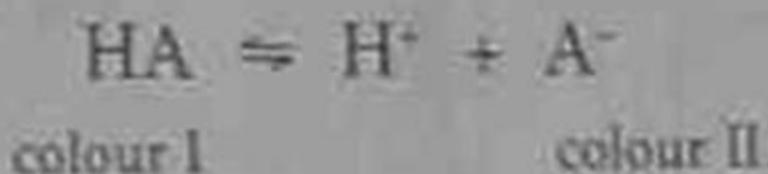
determined by an indicator colour. Chemists have introduced a scale which can be used to measure how acid or alkaline a solution is. It is called the pH scale and ranges from 1 M HCl having a pH = 0 to 1 M NaOH having a pH = 14, so that it operates for the convenience of the chemist. pH = 7 is neutral whereas values below that level are acidic and above are alkaline. Universal Indicator, which is a mixed selection of indicators changing over different pH ranges, can be used in liquid or paper form. A colour chart matching colour to pH present is provided.



Indicators are dyes that change colour if their pH is changed

Practical work should include indicators commonly used in titrations, such as methyl orange, bromothymol blue and phenolphthalein. Universal Indicator is a range of indicator blends. A natural universal indicator can be made by boiling a small amount of chopped red cabbage and straining off the red liquid.

The remarkable properties of this indicator called cyanidin is the variety of colours it produces over a pH range of 1-12. The usual acid-base indicators are weak acids HA whose conjugate bases A⁻ undergo structural changes that result in colour changes.



Cyanidin belongs to a group of substances called bioflavonoids which are widely distributed in plants.

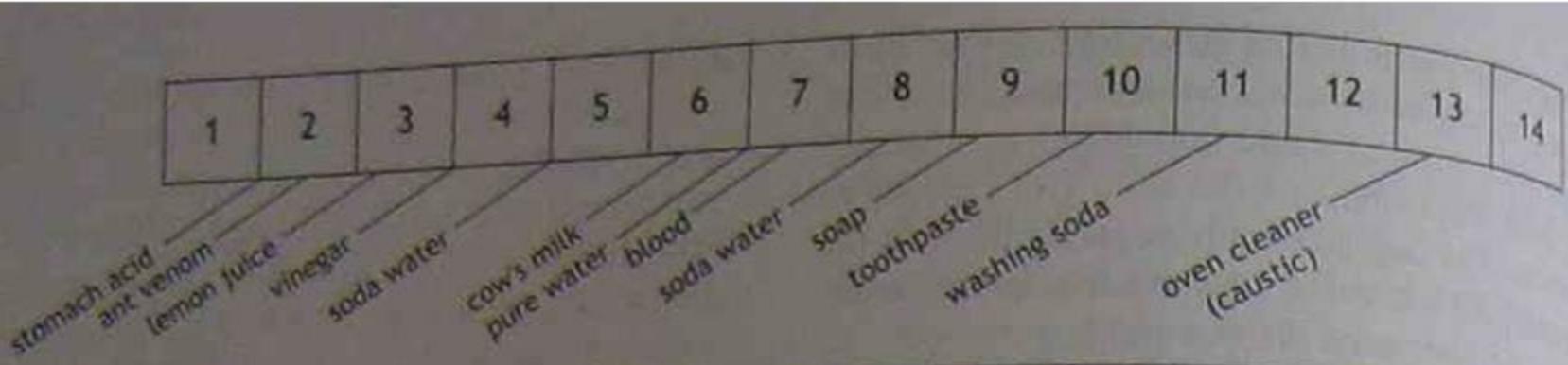


Figure 2.4 pH values of some common substances

Table 2.4 Indicators

Indicator	Colour on acid side	Colour on basic side	pH range of colour change
Methyl orange	red	yellow	3.2 – 4.4
Methyl red	red	yellow	4.8 – 6.0
Bromothymol blue	yellow	blue	6.0 – 7.6
Phenolphthalein	colourless	pink	8.2 – 10
Litmus	red	blue	unsuitable for titration

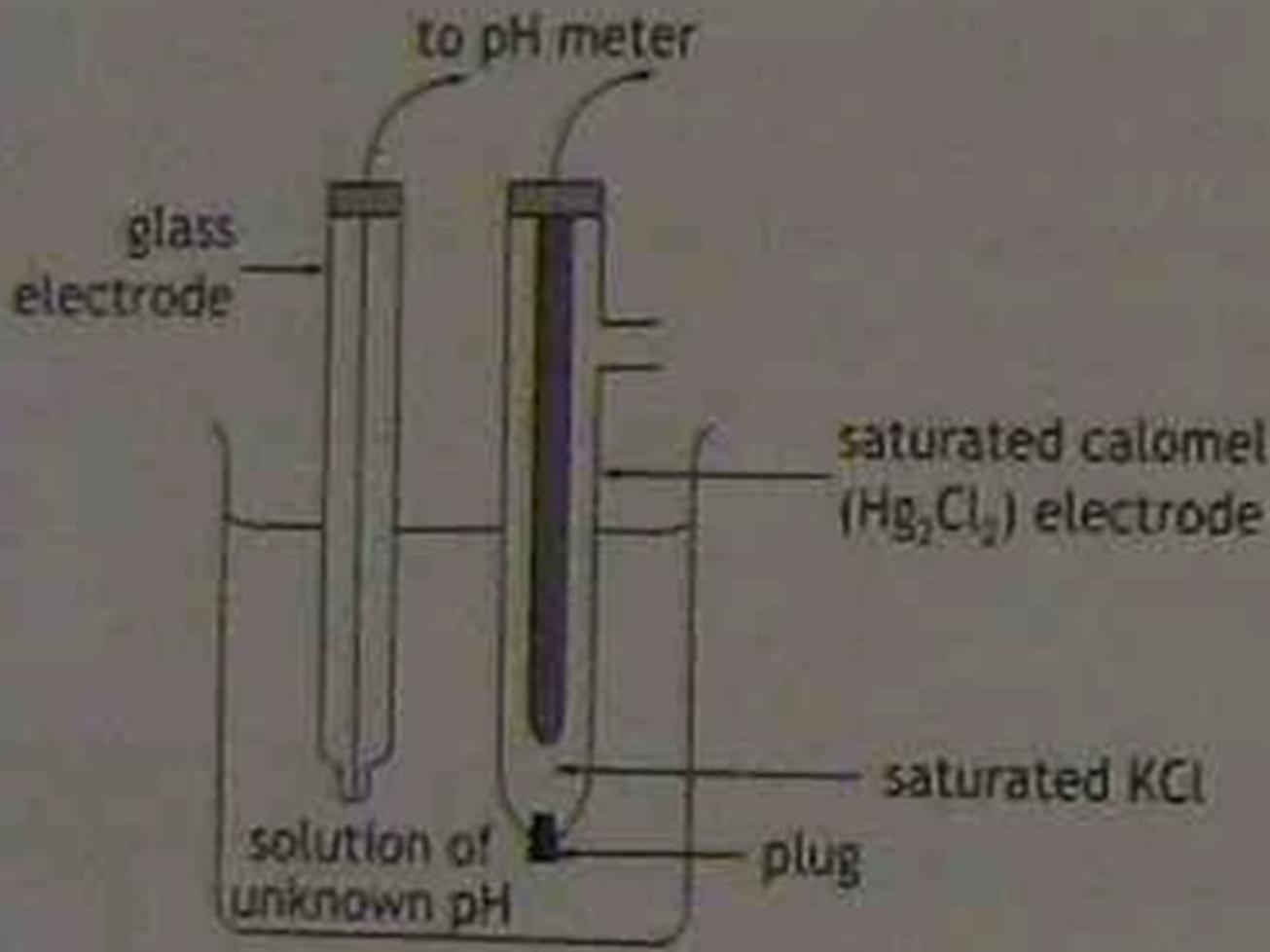


Figure 2.5 Electrodes used in a pH meter. (Enclosed probe types of electrodes are also used, e.g. for determining pH of soils.)

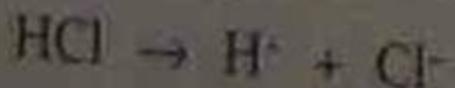
2.16

Calculations involving pH

Strong acids and bases are said to be completely ionised in water, so it is relatively easy to calculate their pH and pOH from known molarities.

Example 1

Find the pH of a 0.001 M solution of HCl at SLC.



so for each mole of HCl, one mole of H^+ ions will be produced.

$$[\text{H}^+] = 0.001 \text{ M} = 10^{-3} \text{ M}$$

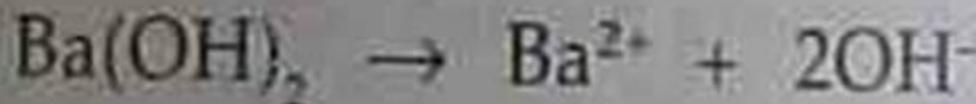
From the definition of pH, negative logs are taken so that $\text{pH} = 3$.

$$\text{Hence } \text{pOH} = 14 - 3 = 11.$$

Example 2

Find the pH of a 0.005 M solution of barium hydroxide.

Note: In finding the pH of alkalis, the pOH is first found using the $[\text{OH}^-]$, then $14 - \text{pOH} = \text{pH}$.



so for each mole of Ba(OH)_2 , two moles of OH^- ions will be produced.

$$[\text{OH}^-] = 2 \times 0.005 = 0.01 \text{ M} = 1 \times 10^{-2} \text{ M}$$

$$\text{pOH} = 2, \text{pH} = 12$$

Example 3

- (a) For 20 mL of a 0.1 M solution of HCl find:
- the pH, and
 - the number of moles of hydrogen ions present.
- (b) If 5 mL of 0.1 M NaOH is then added to the HCl, find
- the number of moles of H⁺ ions left,
 - the concentration of the H⁺ ion, and hence
 - the new pH.

Answers:

- (a) (i) [H⁺] = 10⁻¹, so pH = 1.0
(ii) No. of moles of H⁺

$$= 10^{-1} \times \frac{20}{1000} = 2 \times 10^{-3} \text{ mol}$$

(b) No. of moles of OH^- ions added

$$= 0.1 \times \frac{5}{1000} = 0.5 \times 10^{-3}$$

(i) No. of moles of H^+ left

$$\begin{aligned} &= 2 \times 10^{-3} - 0.5 \times 10^{-3} \\ &= 1.5 \times 10^{-3} \text{ mol} \end{aligned}$$

(ii) Conc. = No. of moles $\times \frac{1000}{V}$

(the new volume $V = 20 + 5 \text{ mL}$)

$$= 1.5 \times 10^{-3} \times \frac{1000}{25} = 0.06 \text{ M}$$

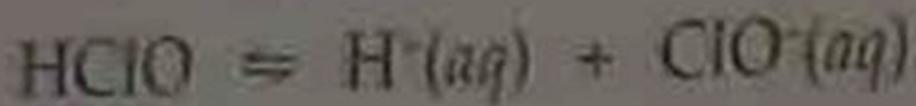
or concentration = $\frac{\text{No. of moles}}{\text{volume of soln. in L}}$

$$= \frac{1.5 \times 10^{-3}}{2.5 \times 10^{-2}} = 0.06 \text{ M}$$

(iii) Hence pH = 1.22

Swimming pools

'Chlorination' in swimming pools depends on keeping the pH of the water close to 7.2. Hypochlorite ions are added as calcium and sodium salts and form an equilibrium with hypochlorous acid.



pH > 7.4 (alkaline)

green algal scum

pH < 7.0 (acidic)

eye problems

Food preservation

A low pH (less than 4) will prevent the development of some dangerous pathogens in food. In pickled onions, for example, vinegar (pH 2.8) is used. Benzoic acid also preserves food by inhibiting the growth of bacteria, and is used particularly in soft drinks where the pH is less than 4.5. Sulfur dioxide is the most effective inhibitor of the deterioration of dried fruits and fruit juices.

Control of pH in soils

In high rainfall areas around the Australian coastal strip, the pH of soils is about 5.5–6.5. Further inland, where the rainfall is less, soils have a higher pH at about 7.5–8. An interesting activity would be to check soils from your area for pH.

Plants grow in a narrow pH range and different species prefer a different pH value for the soil. Azaleas, for example, will only grow in an 'acid' soil. To increase the pH of soil, powdered limestone (CaCO_3) is often used, making it more 'basic'. To decrease the pH of the soil, ammonium sulfate is often used.

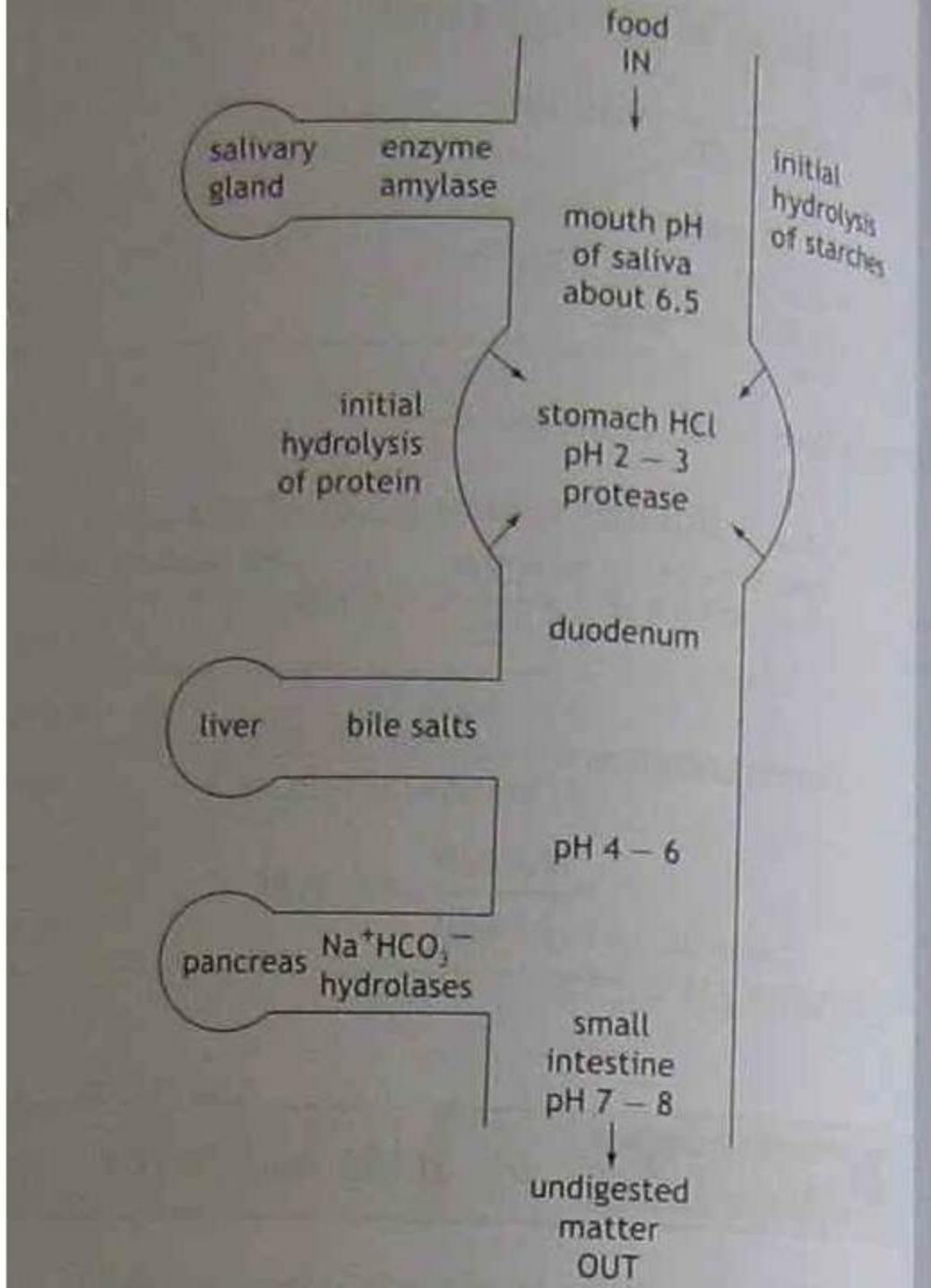
Variation of pH in the human digestive system

Catalytic enzymes function in a narrow pH range.

Because of the low pH of gastric juices in the stomach, antacids are used to reduce the acidity. Some brands use a mixture of calcium carbonate and magnesium carbonate. Others use a mixture of magnesium hydroxide and aluminium hydroxide. (See Figure 2.6.)

Cosmetic applications of pH

During recent years, the topic of pH has been introduced into hair shampoo advertisements.



Claims that pH control not only improves the cleansing of hair but also makes it shinier, bouncier and stronger are found in these advertisements. Most shampoos have a pH range of 4–7.5 for humans. Conditioners lie in the range of 2.6–4.8, being acidic. Perhaps your class would like to test a variety of shampoos and conditioners using pH paper.

The cleansing power of a shampoo refers to its ability to remove grease, dirt and foreign material from the hair and scalp. A good shampoo should not remove all oils since this could cause scalp diseases.

Human skin has a natural acid layer on its surface with a pH range of 3–5. This is why conditioners are used after shampoos to restore the pH balance.

Shampoos can have the pH adjusted for special reasons. For example, for small children the pH is kept near 7 so that it will not cause eye irritation. Dog shampoos are much more alkaline with a pH as high as 8.7.

Many other substances such as antiperspirants and deodorants, mouthwashes, toothpastes and soaps all have a controlled pH.

- An acid is a substance which dissolves in water to produce hydrogen ions as the only positive ion in solution.
- A water soluble base is a substance which produces hydroxide ions as its only negative ion in solution.

Example

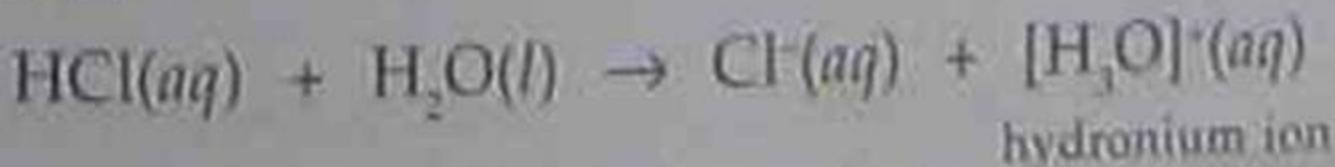
Acids	Ions produced
HCl CH ₃ COOH	H ⁺ ; Cl ⁻ H ⁺ ; CH ₃ COO ⁻
Alkalies	Ions produced
NaOH KOH	Na ⁺ ; OH ⁻ K ⁺ ; OH ⁻

This theory only applies to aqueous solutions.

- An acid is a substance which when in solution donates a proton (H^+ ion).
- A base is a substance which when in solution accepts a proton.

Since an acid is a proton donor, it must contain hydrogen atoms. Acidic solutions are formed when an acid transfers a proton to a water molecule.

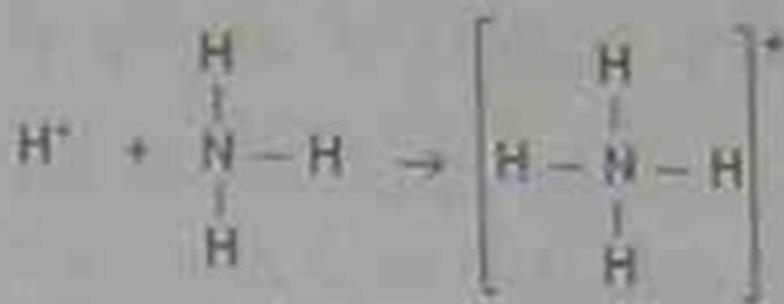
Example



Since the proton is transferred from an acid to a base, acids and bases must exist in pairs which are called conjugate pairs. An acid-base reaction is therefore the transfer of a proton from an acid to a base.

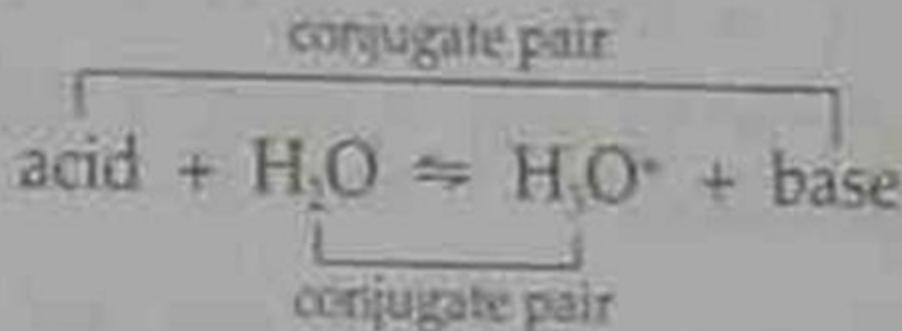
Lewis proposed a definition of a base that emphasises the shared electron pair: an acid is an electron-pair acceptor and a base is an electron pair donor.

Example

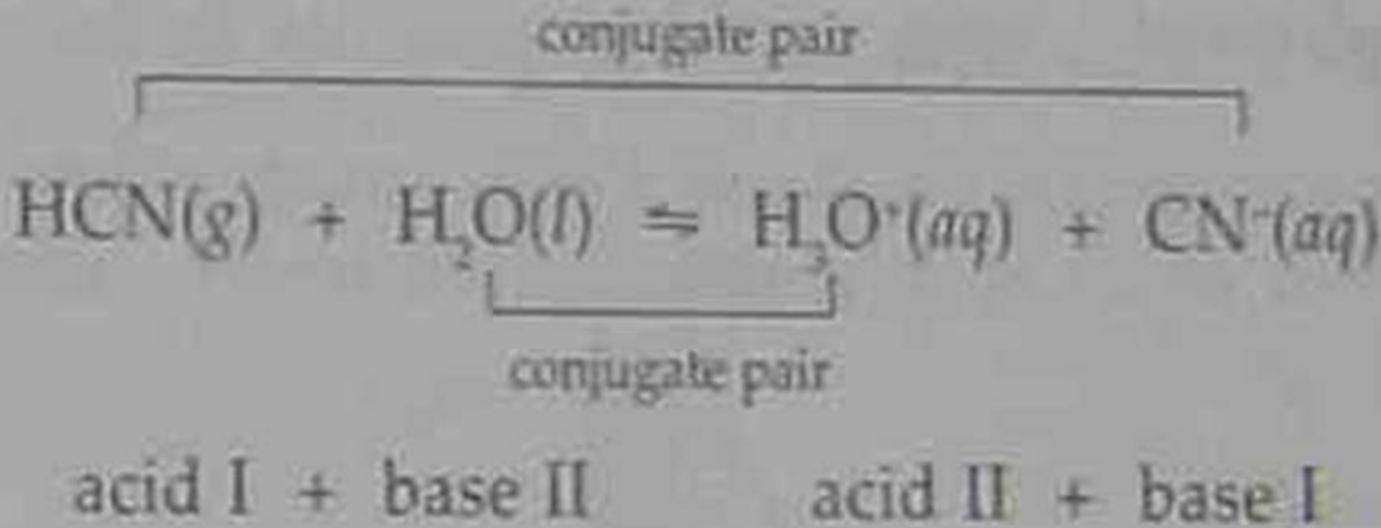


A Brønsted-Lowry base (a proton acceptor) is also a Lewis base (an electron-pair donor).

Acid - base pairs



Example



In the reaction, HCN loses a proton to form its conjugate base CN⁻ while H₂O gains a proton to form its conjugate acid H₃O⁺ for the forward reaction.

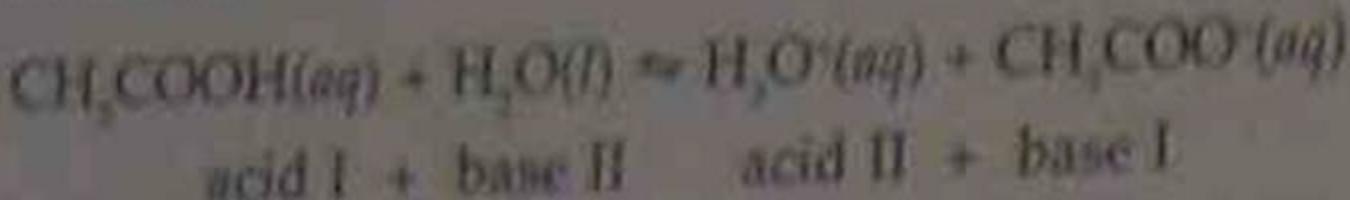
Strength of acids and bases

The strength of an acid is measured by the concentration of H⁺ ions or more precisely [H₃O]⁺ ions in solution. Since many acid-base reactions are examples of equilibrium reactions in aqueous solutions, the concentration of H⁺ ions produced is determined by the value of the equilibrium constant for that reaction.

Table 2.5 Conjugate pairs

Strength	Acid	Base
Strong (fully ionised in water)	H_2SO_4 HCl	HSO_4^- Cl^-
Weak (partly ionised in water)	CH_3COOH H_2CO_3 HSO_3^- NH_3	CH_3COO^- HCO_3^- SO_3^{2-} NH_4^+
Very weak	H_2O	OH^-

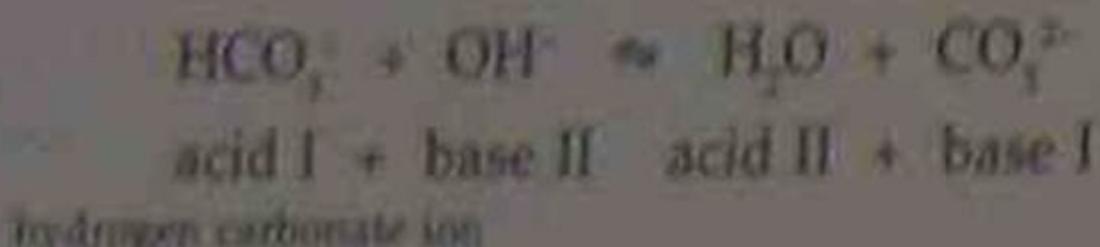
HCl is a strong acid. Its conjugate base is the Cl⁻ ion which is so weak that it is neutral when dissolved in water.



This reaction will go from left to right if acid I is stronger than acid II. If acid II is stronger than acid I then the reverse is the case.

In the Brønsted-Lowry Theory, acids can be ions as well as molecules.

Example

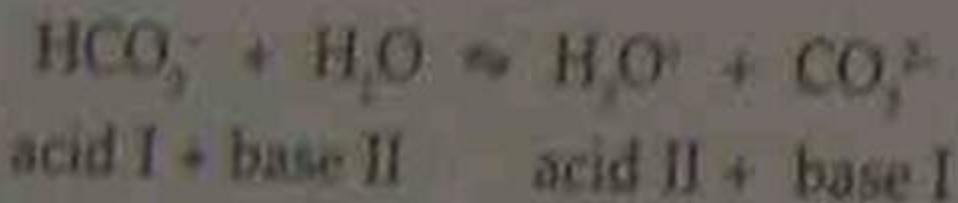


Amphiprotic ions and molecules

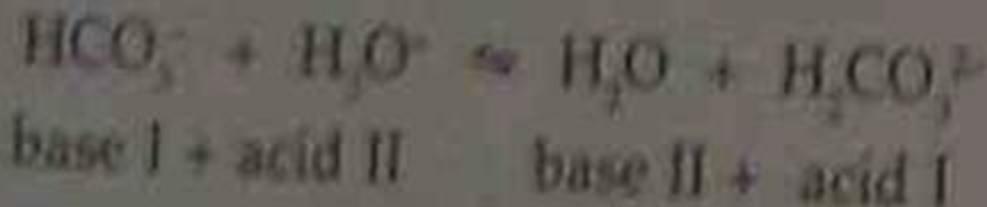
Amphiprotic ions

An amphiprotic ion is one which can act either as a base or as an acid, depending on which reaction takes place.

Example 1



Example 2

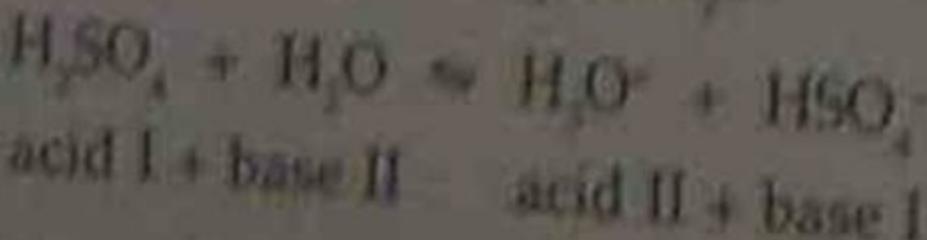


Since the HCO_3^- ion is both the conjugate acid of the base CO_3^{2-} and the conjugate base of the acid H_2CO_3 , it is said to be **amphiprotic**.

Amphiprotic molecule

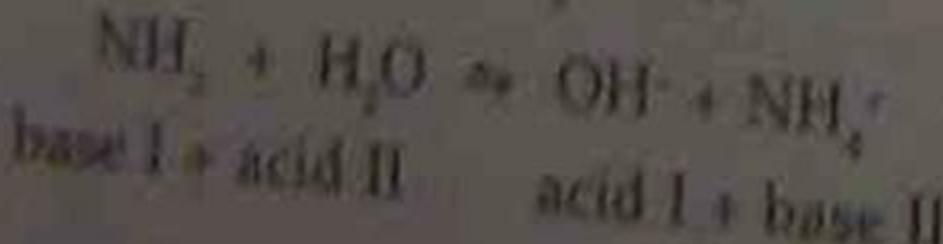
Water as a base:

conjugate acid/base pair: $\text{H}_2\text{O}^+/\text{H}_2\text{O}$



Water as an acid:

conjugate acid/base pair: $\text{H}_2\text{O}/\text{OH}^-$



2.20

The pH of various salts

Only a few common salts are neutral and Brønsted-Lowry Theory can be used to explain the different pH values.

Note: To predict the pH for salts of weak acids and weak bases, the K_a and K_b must be known.

Salts formed from a strong base/weak acid

Example

Sodium acetate

The anion CH_3COO^- is a conjugate base so, in water:

$$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$$

The free OH^- ions increase the pH to > 7 , so aqueous solutions of sodium acetate are alkaline.

Salts formed from a strong acid/weak base

Example

Ammonium chloride

The cation is the conjugate acid of a weak base, NH₃, so in water



Since H⁺ ions have been produced, the pH will be < 7, so solutions of ammonium chloride are acidic.

Salts formed from a strong acid/strong base

Example

Sodium chloride

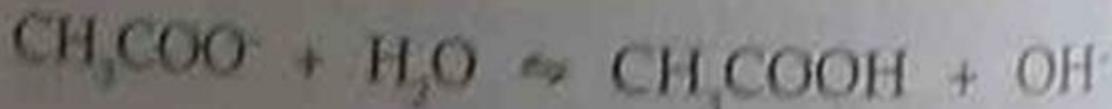
No hydrolysis occurs, so pH = 7.

Salts formed from a weak acid/weak base

Example

Ammonium acetate

Both anion and cation will react with water



Since both anions and cations OH⁻ and H⁺ are present, and in this case K_a = K_b, then the salt will have a pH = 7.

2.21

Volumetric analysis and titration

Volumetric analysis involves determining the volume of a solution of accurately known

concentration (the standard solution) which is to react quantitatively with the solution being determined.

To be useful in volumetric analysis, a reaction should fulfil the following conditions:

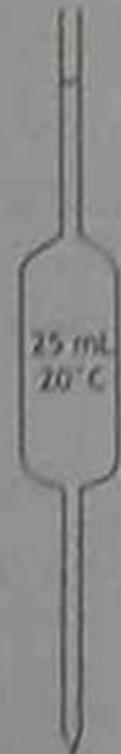
1. The reaction should be rapid.
2. The reaction should be in keeping with a chemical equation.
3. There must be a marked change at the equivalence point.
4. An indicator, or some other method, must be able to detect the change.

The procedure for carrying out a volumetric analysis is called titration.

Titration

In a titration, one reactant is placed in a conical flask and the other solution is delivered in a measured amount from a burette.

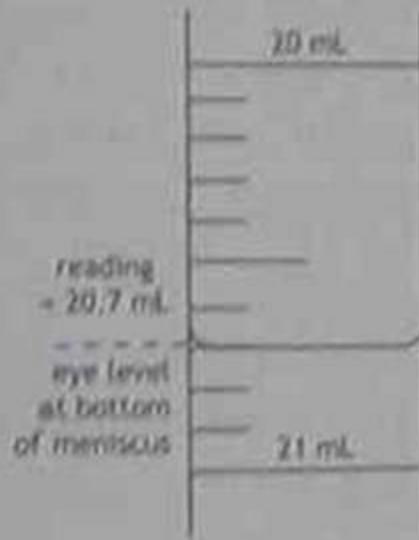
In determining the end point in titrations, an appropriate indicator must be used.



(a) pipette



(b) burette



Note: with practice, the scale should be read to ± 0.05 mL.



(c) volumetric flask



(d) conical flask

Figure 2.7 Equipment used in titration. The volumetric and conical flasks are receiving vessels and are rinsed with distilled water.

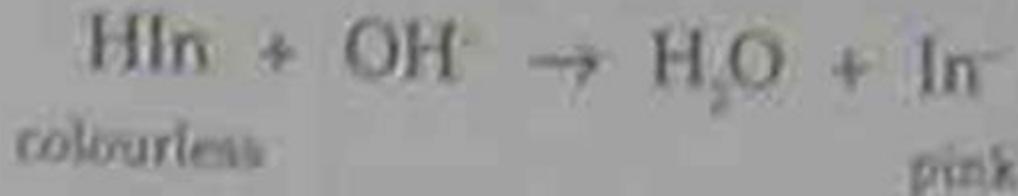
Example 1

Bromothymol blue changes colour around a pH of 7 and can be used in strong acid/strong base titrations.



Example 2

Phenolphthalein changes colour around a pH of 9 and can be used in weak acid/strong base titrations.



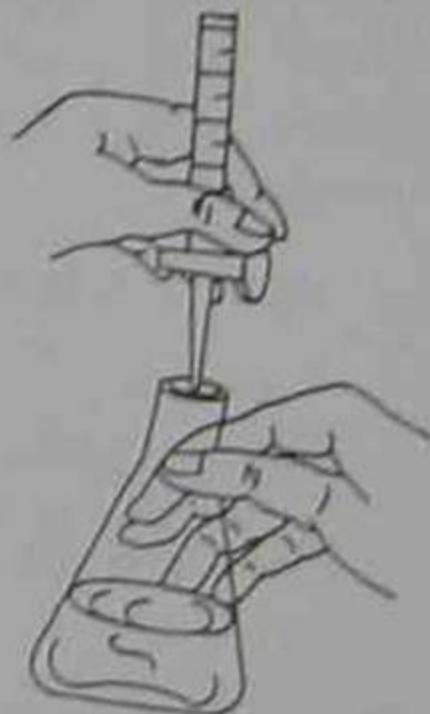
Example 3

Example 3

Methyl orange changes colour around a pH of 4 and can be used in strong acid/weak base titrations.

Colour change: red → yellow

Because of the importance of practical work in volumetric analysis, the following 'worked' experiment has been included.



2.22

Standardisation of solutions of acids and bases

Standardising solutions

This is carried out by using a primary standard which is a solid.

A primary standard has certain requirements.

- (a) It should be easy to purify, dry and store in powdered state.

- (b) It should be unaffected by moisture in the air when it is being weighted.
- (c) It should have a reasonably high molar mass so that weighing errors can be minimised.
- (d) It should be readily soluble in water or a required solvent.

To standardise sodium hydroxide which cannot be used as a primary standard (since it absorbs moisture and carbon dioxide from the air), two methods are frequently used:

- (a) Anhydrous Na_2CO_3 is used as the primary standard to determine the exact molarity of a HCl solution. The standardised HCl is then used in a titration with an NaOH solution.
- (b) A solid organic acid, usually oxalic acid or benzoic acid, is used as the primary standard. This method is detailed in the following experiment.

Table 2.6 Choice of indicators

Titration	Indicator used	Salt formed
Weak base/strong acid Na ₂ CO ₃ /HCl	methyl orange pH 3.1 – 4.4	In this case NaCl + H ₂ CO ₃ , H ₂ O + CO ₂ , acidic
Strong base/strong acid NaOH/HCl	bromothymol blue pH 6.0 – 7.6	NaCl, neutral salt, no hydrolysis, pH = 7
Weak acid/strong base CH ₃ COOH/NaOH	phenolphthalein pH 8.3 – 10.0	CH ₃ COONa, basic salt, hydrolysis, CH ₃ COO ⁻ + H ₂ O → OH ⁻ + CH ₃ COOH, pH > 7
Weak base/strong acid NH ₃ /HCl	methyl red pH 4.4 – 6.2 or methyl orange	NH ₄ Cl, acidic salt, pH < 7, NH ₃ ⁺ + H ₂ O → NH ₄ ⁺ + H ₃ O ⁺
Weak base/weak acid	bromothymol blue	pH = 7

Typical problems in volumetric analysis

In volumetric analysis, one mole of solid is its molar mass in grams. A one molar solution is the molar mass of the solid in grams dissolved in a litre of solution. (Expressed as 1 M or 1 mol L⁻¹.)

Various substances are used as primary standards.

- Anhydrous sodium carbonate is often used to standardise strong acids such as HCl and H₂SO₄, using methyl orange as indicator. (Methyl orange is not affected by any H₂CO₃ formed.)
- Oxalic acid (COOH)₂.2H₂O is used to standardise strong alkalis, for example NaOH, KOH.

Other organic acids or acid salts used are benzoic acid C_6H_5COOH (solution in alcohol) or potassium hydrogen phthalate ($KHC_8H_4O_4$). In all cases the indicator used is phenolphthalein.

Example 1

How much anhydrous sodium carbonate would you weigh out to make up 500 mL of a 0.01 M solution?

Step 1. Find the molar mass of Na_2CO_3 , which is 106 g.

Step 2. Find the no. of moles in 500 mL of a 0.01 M solution.

$$\begin{aligned}\text{No. of moles} &= M \times \frac{V \text{ mL}}{1000} \\ &= 0.01 \times \frac{500}{1000} \\ &= 0.005\end{aligned}$$

Step 3. Find the no. of grams.

$$\begin{aligned}\text{No. of grams} &= \text{no. of moles} \times \text{molar mass} \\ &= 0.005 \times 106 \\ &= 0.53 \text{ g}\end{aligned}$$

Example 2

How many (a) moles and (b) grams are there in 100 mL of a 0.01 M solution of sodium hydroxide?

Step 1. Find the molar mass of NaOH. It is 40 g.

Step 2. Find the no. of moles present.

$$\begin{aligned}\text{No. of moles} &= M \times \frac{V \text{ mL}}{1000} \\ &= 0.01 \times \frac{100}{1000} \\ &= 0.001\end{aligned}$$

Step 3. Find the no. of grams.

$$\begin{aligned}\text{No. of grams} &= \text{no. of moles} \times \text{molar mass} \\ &= 0.001 \times 40 \text{ g}\end{aligned}$$

In each of the following problems, find
(a) the moles, and (b) the grams present

Problem 1

500 mL of a 2 M solution of anhydrous sodium hydrogen carbonate.

Answer: (a) 1 mole, (b) 84.01 g.

Problem 2

500 mL of a 0.01 M solution of anhydrous sodium carbonate.

Answer: (a) 0.005 mole, (b) 5.3 g.

Problem 3

Problem 3

100 mL of a 0.2 M solution of anhydrous calcium hydroxide.

Answer: (a) 0.02 mole, (b) 1.48 g.

Example 3

Dilution

How many mL of water must be added to dilute 300 mL of a 0.2 M solution of HCl to a 0.01 M

$M_1 V_1 = M_2 V_2$, where M is molarity,

$0.2 \times 100 = 0.01 V_2$, where V is volume (mL)

$$V_2 = 2000 \text{ mL}$$

Amount of water added = $V_2 - V_1$

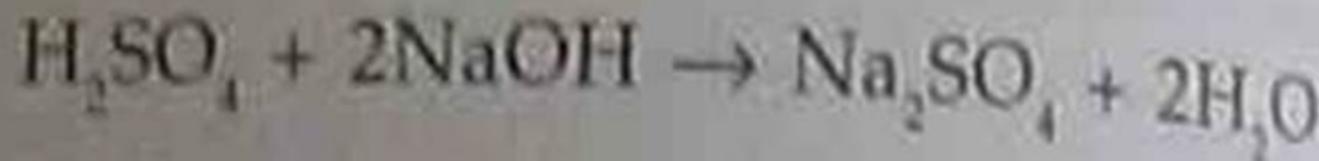
$$= 2000 - 100 = 1900 \text{ mL} = 1.9 \text{ L}$$

Example 4

Neutralisation

What volume of 0.1 M NaOH will just neutralise 25 mL of 0.08 M H₂SO₄?

Step 1. Write word equation



Step 2. Find mole ratio.

$$\frac{\text{H}_2\text{SO}_4}{\text{NaOH}} = \frac{1}{2}$$

Step 3. Find the no. of moles of H_2SO_4 .

$$= 0.08 \times \frac{25}{1000} \quad (\text{a})$$

Step 4. Find the no. of moles of NaOH .

$$= 0.1 \times \frac{x}{1000} \quad (\text{b})$$

Step 5. Divide (a) by (b). i.e. $\frac{1}{2} = \frac{0.08 \times 25}{0.1 \times x}$

Step 6. Solve for x . i.e. $x = \frac{0.08 \times 25 \times 2}{0.1} = 40 \text{ mL}$

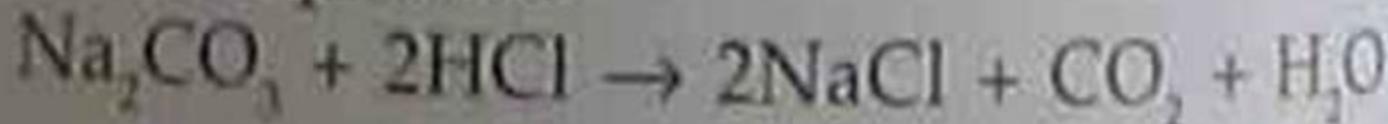
Volume of 0.1 M NaOH needed is 40 mL

Example 5

When one reagent is a solid

Find the molarity of HCl if 24 mL reacts completely with 0.207 g of sodium carbonate.

Step 1. Write equation.



Step 2. The number of moles of solid = $\frac{0.207}{106}$

Step 3. Find the mole ratio.

1 mole of Na_2CO_3 uses 2 moles HCl.

$$\text{Step 4. No. of moles of HCl} = 2 \times \frac{0.207}{106}$$

Step 5. Find molarity of HCl.

$$\text{No. of moles} = M \times \frac{V \text{ mL}}{1000}$$

$$\begin{aligned}\text{Molarity of HCl} &= 2 \times \frac{0.207}{106} \times \frac{1000}{24} \\ &= 0.163 \text{ M}\end{aligned}$$

Calculations

Example 1

Find the molarity of a 20.00 mL HCl solution that needs 25.00 mL of a 0.05 M Na_2CO_3 for neutralisation using methyl orange as indicator.

Step 1. Write equation.



$$\text{Step 2. Mole ratio} = \frac{\text{Na}_2\text{CO}_3}{\text{HCl}} = \frac{1}{2}$$

Step 3. No. of moles = molarity (M) $\times \frac{\text{vol. in mL (N)}}{1000}$

$$\text{No. of moles of Na}_2\text{CO}_3 = 0.050 \times \frac{25.00}{1000}$$

$$\text{No. of moles of HCl} = X \times \frac{20.00}{1000}$$

Step 4. Mole ratio = $\frac{1}{2} = \frac{0.050 \times 25.00}{X \times 20.00}$

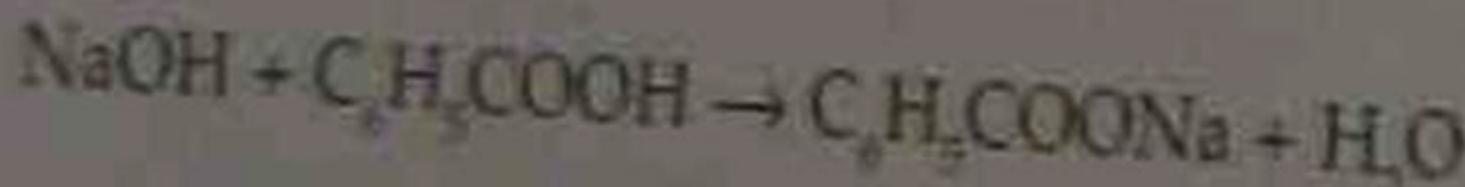
Step 5. $X = \frac{2 \times 0.050 \times 25.00}{20.00} = 0.125 \text{ M}$

So the molarity of HCl is 0.125 M.

Example 2

Find the molarity of a solution of NaOH if 20.00 mL of it reacts completely with 0.122 g of benzoic acid (C_6H_5COOH) dissolved in ethanol using phenolphthalein as indicator.

Step 1. Equations:



Step 2. Mole ratio = $\frac{NaOH}{C_6H_5COOH} = \frac{1}{1}$

Step 3. Molar mass of acid = 122

Step 4. No. of moles of benzoic acid

$$= \frac{\text{mass}}{\text{molar mass}} = \frac{0.122}{122}$$

Step 5. From the mole ratio

$$\text{No. of moles of NaOH} = \frac{0.122}{122}$$

Step 6. No. of moles = molarity \times vol. in mL

$$\frac{0.122}{122} = M \times \frac{20.00}{1000} = 0.05\text{M}$$

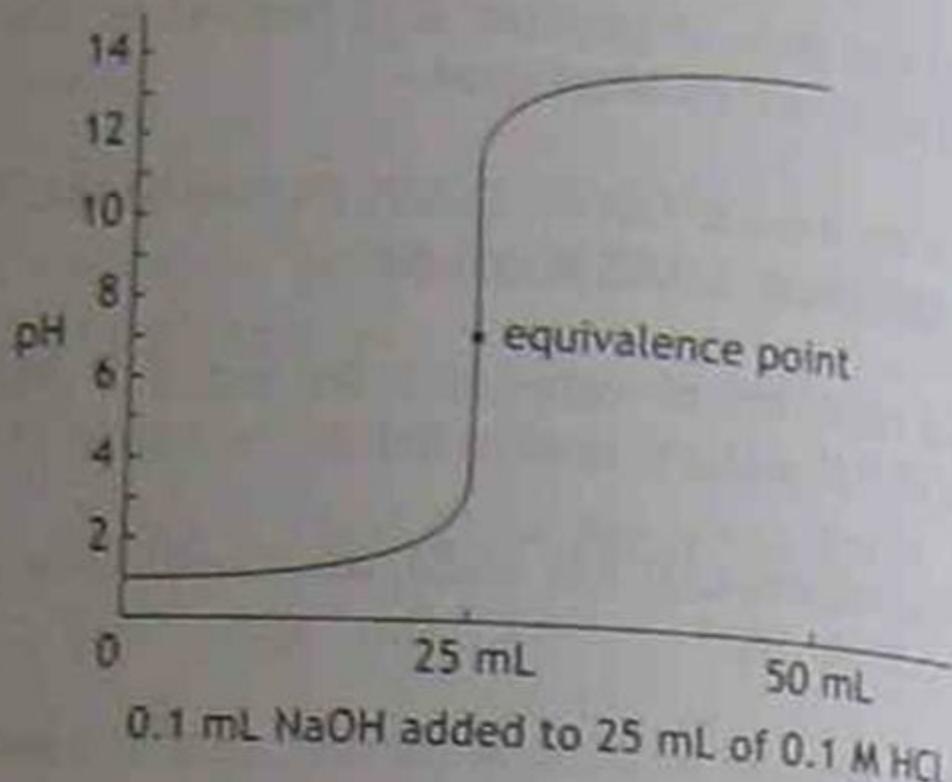
So molarity of NaOH = 0.050 M.

2.24

Titration curves

Accurate acid/base titration curves can be obtained using a pH meter (see Figures 2.9–2.12).

Strong acid/strong base titrations



From the graphs of titrations involving a strong acid/strong base (Figures 2.9 and 2.10) it can be seen that any indicator in Table 2.6 could be used.

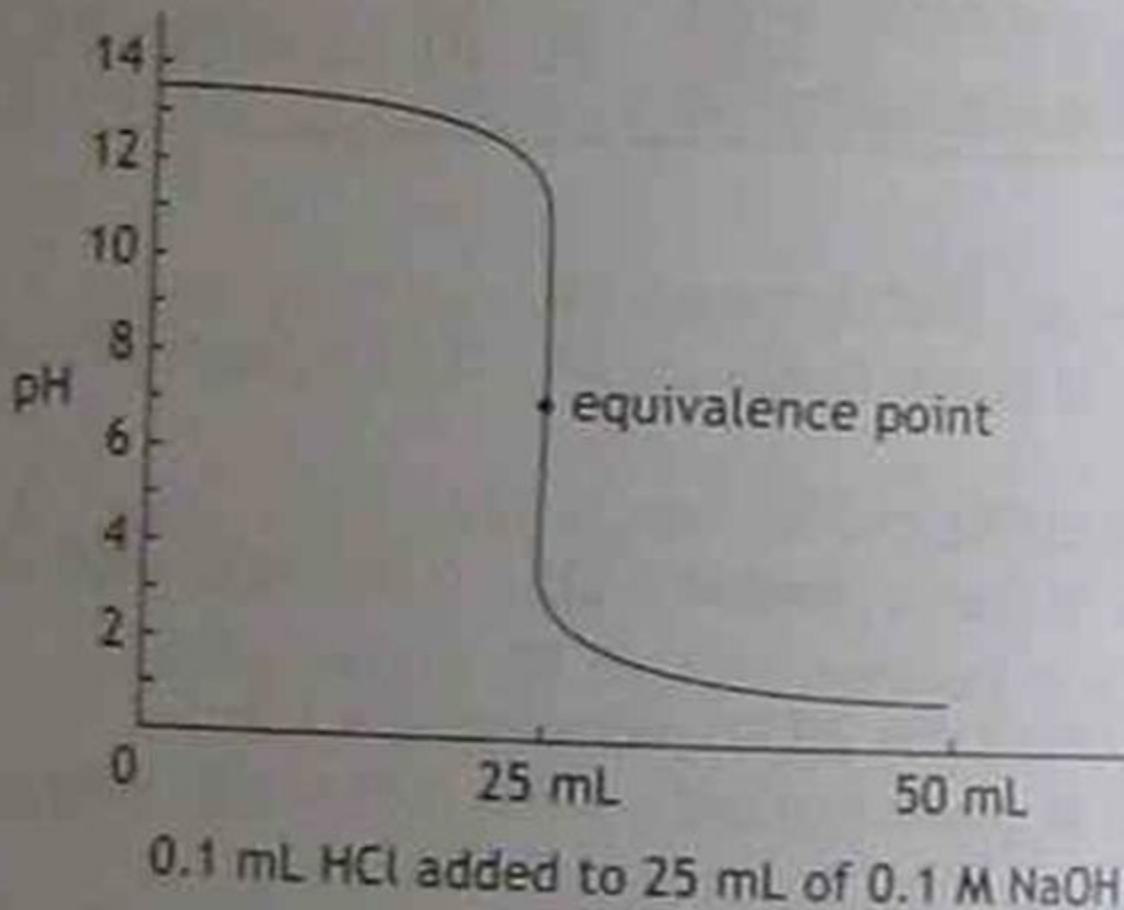


Figure 2.10 Titration of strong base by strong acid

Strong acid/weak base

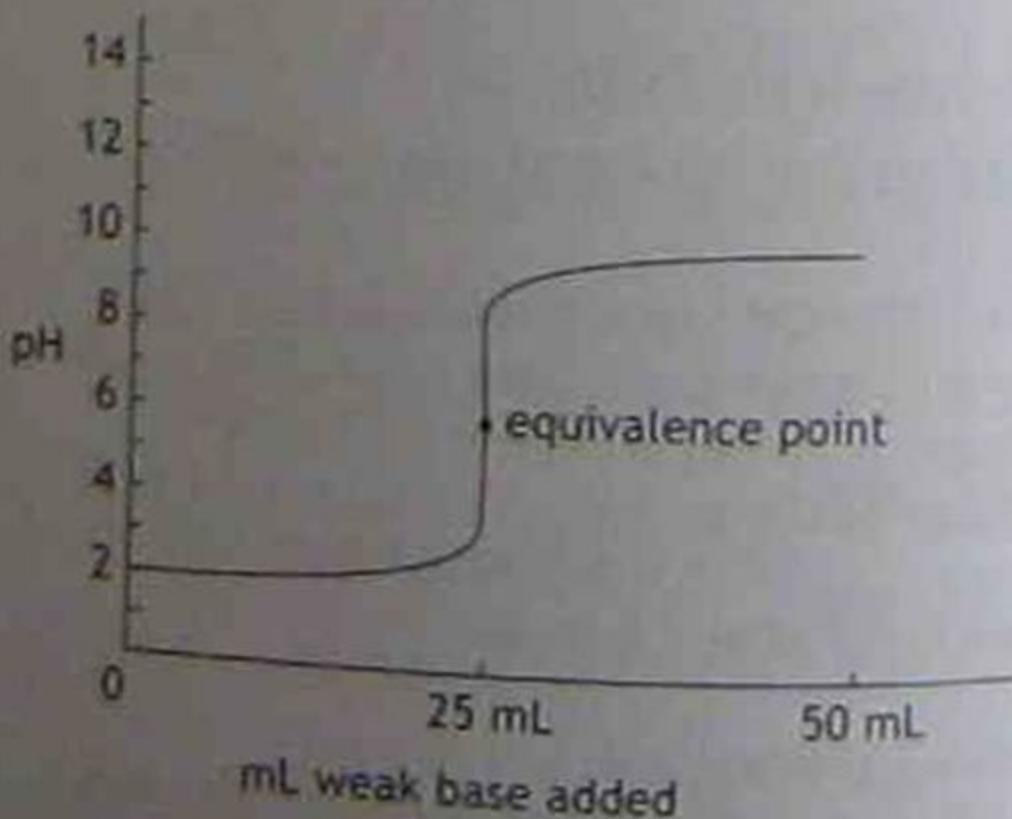


Figure 2.11 Titration of strong acid by weak base

pH range 4.5–8.0, so only methyl red or bromothymol blue are suitable

Weak acid/strong base

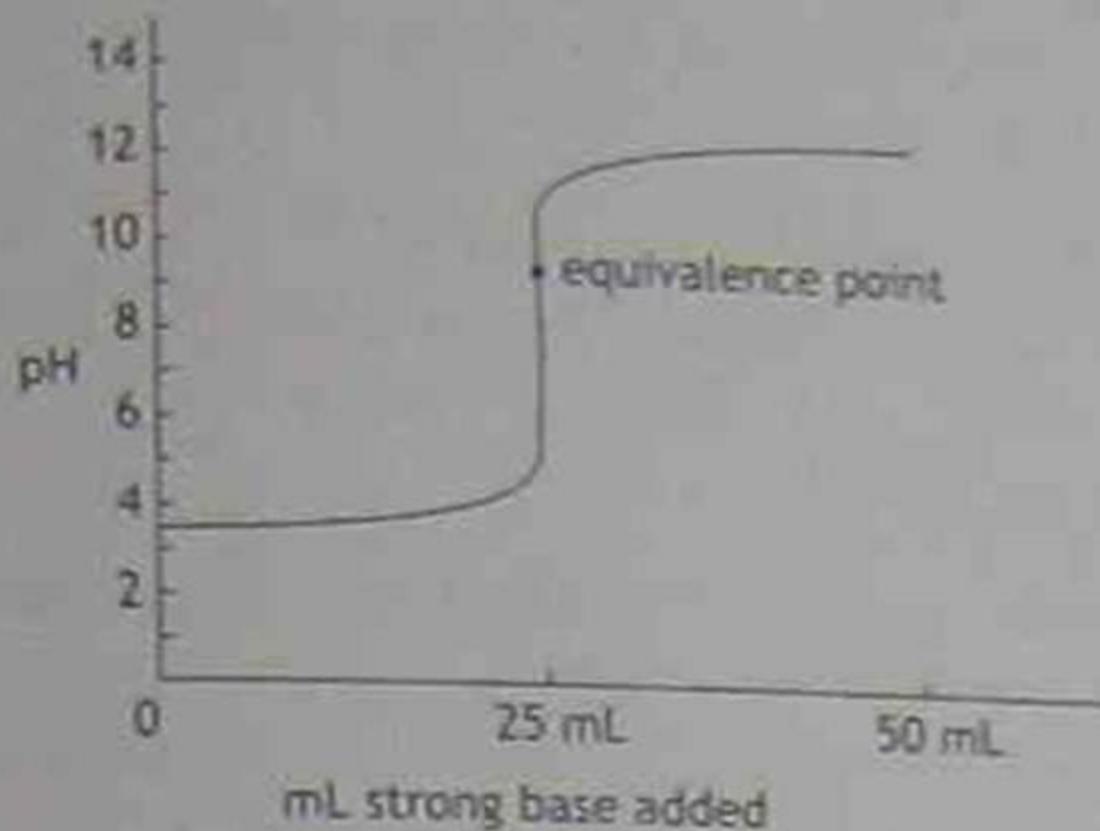


Figure 2.12 Titration of weak acid by strong base

pH range 7–11, so only phenolphthalein can be used.

2.26

The effect of buffers in a natural system – blood

Many aqueous solutions resist a change in pH on addition of small amounts of an acid or a base. Such solutions are called buffer solutions.

A buffer is a mixture of a weak acid and its conjugate base. Human blood is a complex aqueous medium which is buffered at about 7.4. Death results if the pH falls below 7.0 or rises above 7.8. The blood contains several buffers, including H_2CO_3 , $-\text{HCO}_3^-$, H_2PO_4^- – HPO_4^{2-} and the complex buffering system involving haemoglobin, a protein present in red blood cells.

Haemoglobin and oxyhaemoglobin (both bases) form their conjugate acids. Oxygen in the blood is carried by the large haemoglobin molecule and our oxygen fixing system depends on the chemical equilibrium



Haemoglobin (Hb) is involved in a series of equilibria whose overall result is



Acidosis (pH of blood < 7.4) and alkalosis (pH of blood > 7.4) cause the mechanisms by which haemoglobin transports oxygen in the blood to be disrupted. In acidosis, the equilibrium shifts to the left and the ability to form oxyhaemoglobin (HbO_2) is decreased. The reduced supply of oxygen to body

Fatigue and headaches. Acidosis is the more common tendency, because ordinary metabolism produces several acids. Temporary acidosis occurs during strenuous exercise, when energy demands exceed the oxygen available for the complete oxidation of glucose to CO_2 . The glucose product lactic acid.

Note 1: The natural buffer system involves haemoglobin and oxyhaemoglobin, which are both bases, with their conjugate acids. An interplay between these acid-base pairs enables CO₂ to be transported in venous blood and released in the lungs.

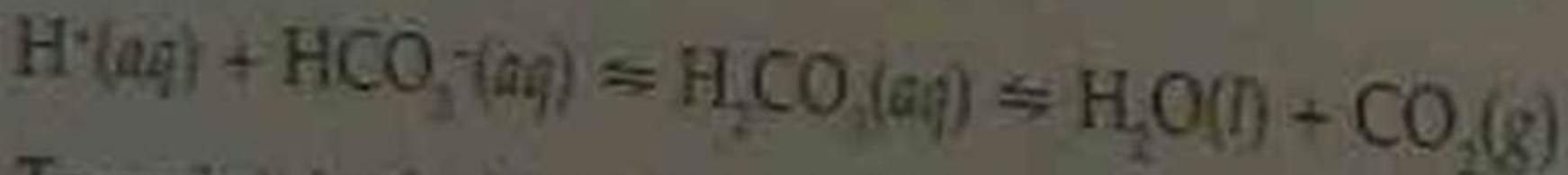
Note 2: Arterial blood coming from the left ventricle is bright red and loaded with oxygen. About 86% of the oxhaemoglobin is in its 'basic' form and 14% of its 'acidic' form. Venous blood, returning to the right atrium of the heart, is dark blue deoxygenated blood; only about 14% of the haemoglobin is in its 'basic' form and 86% is in its 'acidic' form.

The haemoglobin buffer system can be represented as $\frac{\text{haemoglobinate}}{\text{H-haemoglobin}}$

The oxyhaemoglobin buffer system can be represented as $\frac{\text{oxyhaemoglobinate}}{\text{H-oxyhaemoglobin}}$

The major extracellular system in the blood is the bicarbonate system ($\text{H}_2\text{CO}_3/\text{HCO}_3^-$).

Equilibria

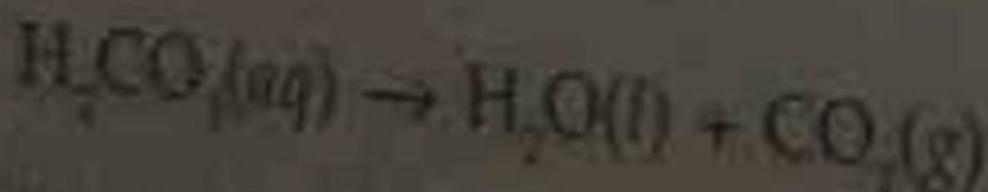


To maintain the blood pH at 7.4 requires the HCO_3^- / HCO_3^- ratio to be 1.20. HCO_3^- is an important base in the blood.

When acid is added to the blood



and the ratio will rise. As this happens, CO_2 is expelled more rapidly from the lungs from the decomposition of



so that as more acid is added to the blood, more of the blood acid H_2CO_3 is decomposed and excreted through the lung as $\text{CO}_2(\text{g})$. In this way, relatively

large amounts of acid can be added to the blood without changing appreciably the 1:20 ratio of $\text{H}_2\text{CO}_3 : \text{HCO}_3^-$.

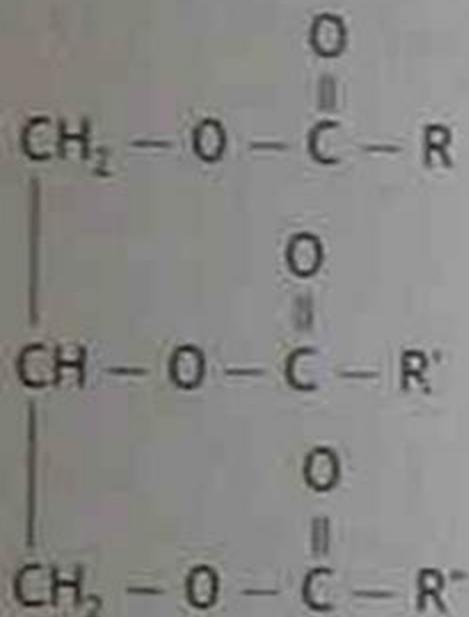
2.27

The naturally-occurring esters

Esters are used widely as artificial flavourings, for example, in jellies and in cosmetics. Esters are excellent solvents and are used in nail-polish removers and in lacquers.

Animal fats and vegetable oils are naturally occurring esters. They are formed from glycerol (1,2,3-propanetriol) and a single fatty acid or a mixture of fatty acids. These esters are called triglycerides.

General formula for triglycerides



2.28

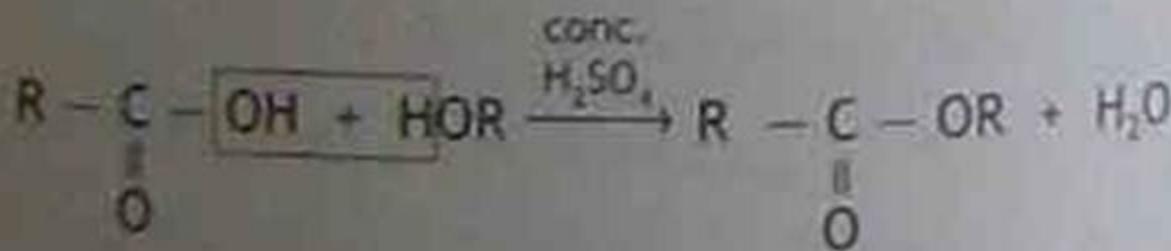
Artificially produced esters

Esters can also be made in the laboratory by the reaction of an alkanol and an alkanoic acid.

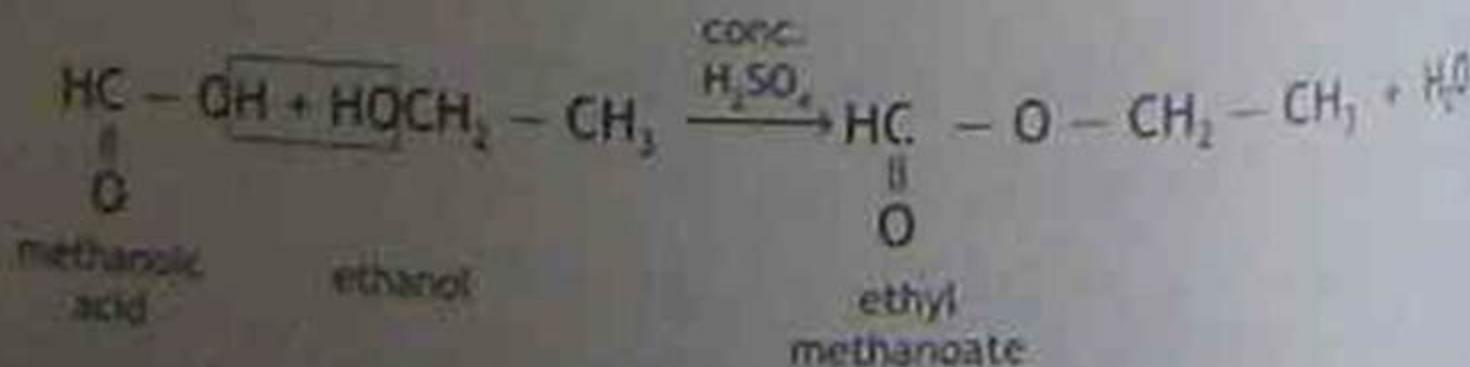
Preparation of artificial esters

Esters are prepared by the reaction of an alkanoic acid and an alkanol in the presence of concentrated H_2SO_4 , which acts as a dehydrating agent and removes water formed.

General equation



Example

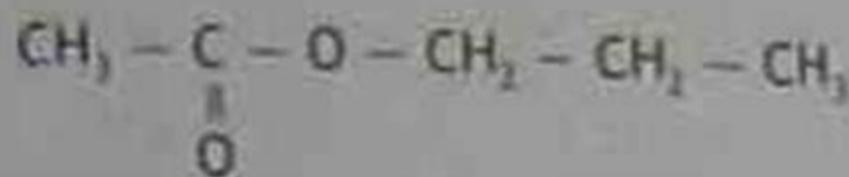


Naming

The 'surname' ending in -oate comes from the acid

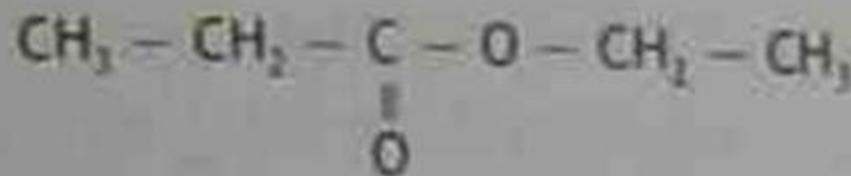
The 'first name' is the alkyl group which comes from the alkanol. The acid part of the formula is, however, written first and is followed by the alkyl group.

Example 1



is called 1-propyl ethanoate.

Example 2



is called ethyl propanoate.

Distillation and refluxing methods

An esterification reaction is an example of an equilibrium reaction. If the amount of water present is minimised (by use of conc. H_2SO_4) and if an excess of one reactant (alkanol or carboxylic acid) is used, then the reaction will favour the formation of the ester. (In manufacturing esters, the cheaper reactant is used in excess.)

The reaction mixture is often heated in a vessel with a cooling condenser attached to prevent loss of any volatile reactant or product. This process is called refluxing (see Figure 2.13).

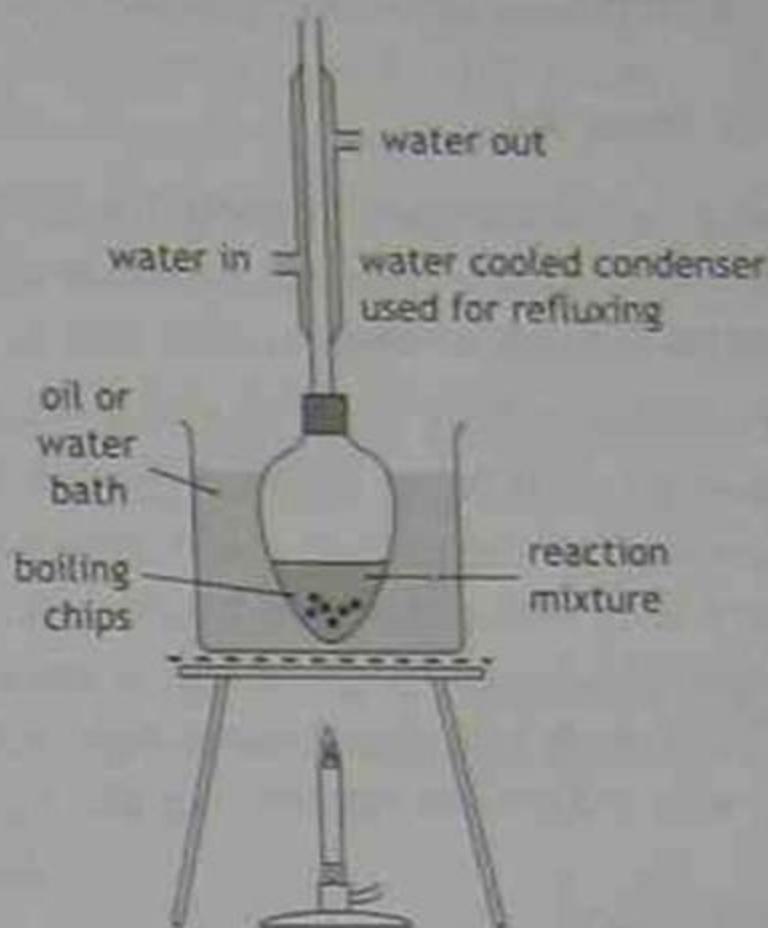
The process used to collect the ester varies with the boiling points of the reactants and products (Table 2.7).

Table 2.7 Boiling points

Alkanoic acids	BP (°C)	Alkanols	BP (°C)	Esters	BP (°C)
methanoic acid	100	methanol	65	methyl methanoate	32
ethanoic acid	118	ethanol	78	methyl ethanoate	57
propanoic acid	141	1-propanol	97	ethyl ethanoate	77
butanoic acid	164	1-butanol	117	ethyl propanoate	99
pentanoic acid	186	1-pentanol	138	propyl ethanoate	102
				butyl ethanoate	126.5

When the boiling point of the ester formed is lower than that of the reactants, distillation can follow refluxing, e.g. methyl ethanoate. If the boiling point of the ester is relatively high then, after refluxing,

the contents of the flask may be transferred to a separating funnel and Na_2CO_3 soln is gradually added to remove excess acid. After the layers have separated, the lower (aqueous layer) is discarded. The layer containing the ester is then distilled (see Figure 2.14), e.g. ethyl propanoate (B.P. 99°C).



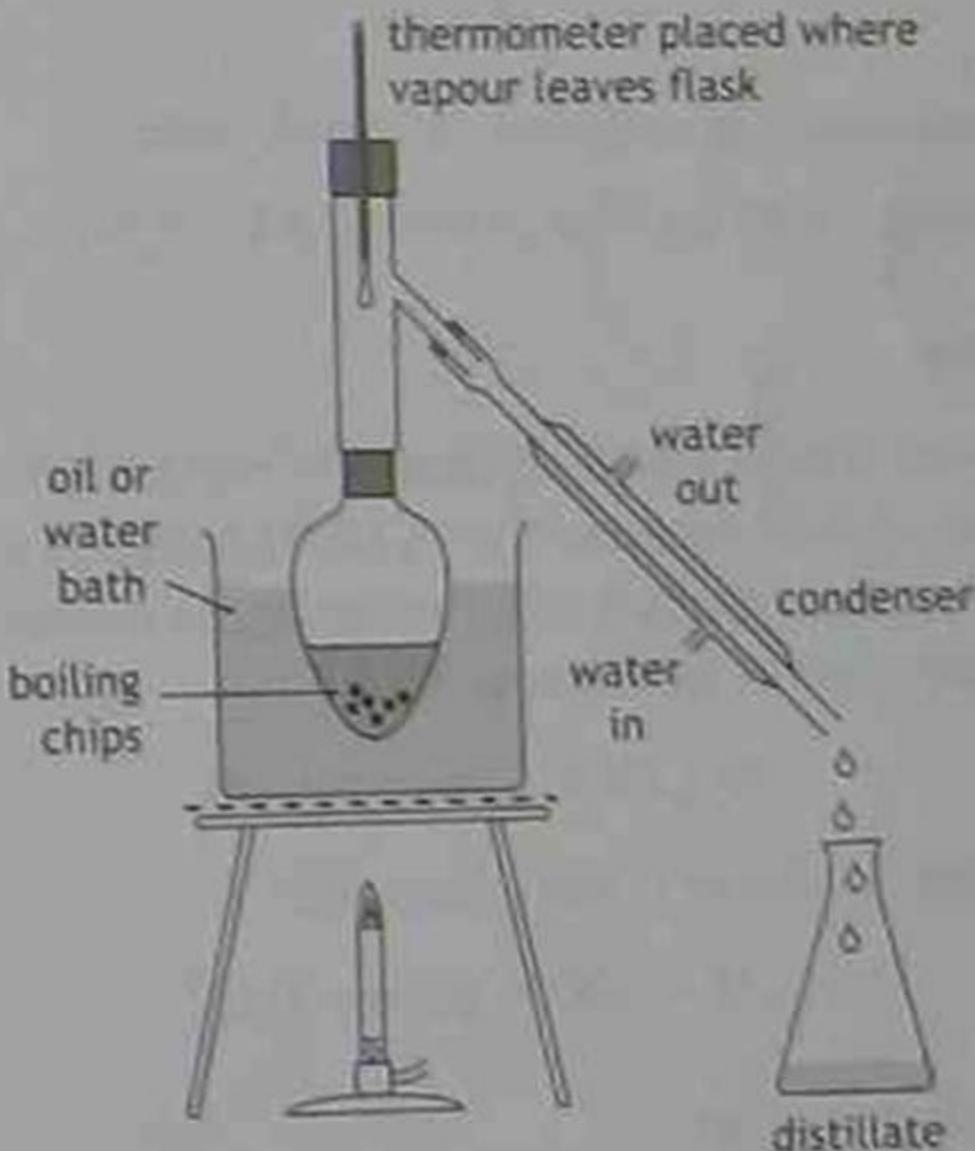


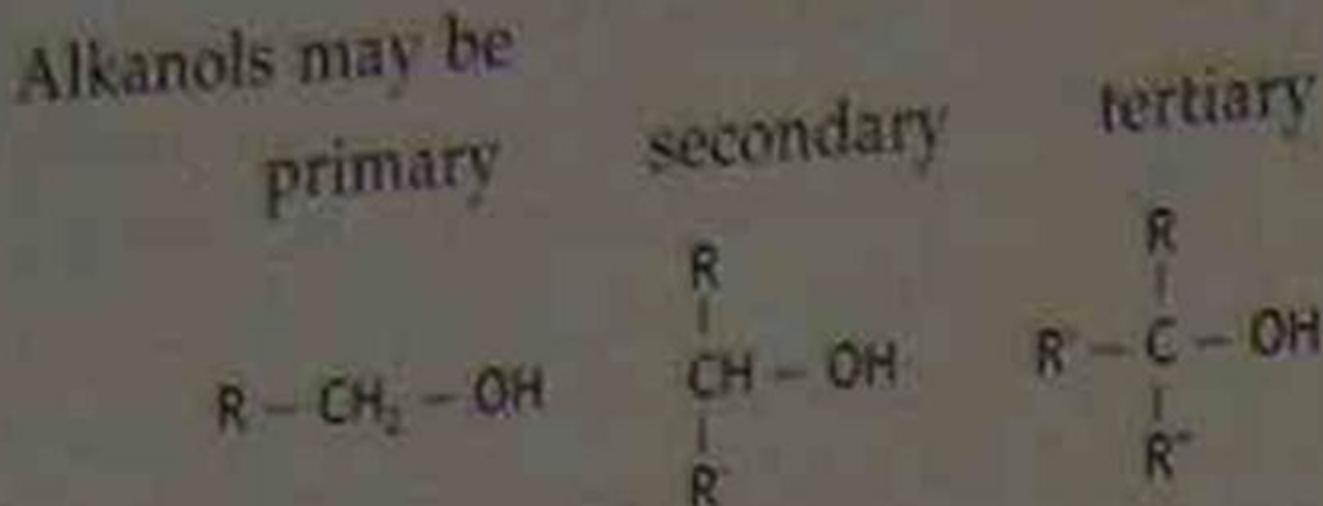
Figure 2.14 Distilling mixtures

Alkanols (alcohols)

General molecular formula

$C_nH_{2n+2}O$; first member CH_3OH methanol

Alkanols are alcohols which are formed from alkanes. Alcohols refer to a wider group of compounds which all contain an $-OH$ group. For example, cholesterol is an alcohol.



where R- is any alkyl group.

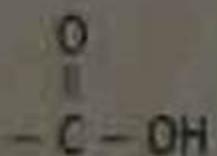
Physical properties

- Because of hydrogen bonding, the alkanols have much higher boiling points than the corresponding alkanes.

2. The molecules are polar and this results in the lower alkanols being soluble (miscible) in water. However, as the carbon chain becomes longer, since it is non-polar, the higher alkanols are insoluble in water. Ethanol is an excellent solvent since it is miscible not only with water, but also with some organic liquids, e.g. ethers.

Alkanoic acids

If any alkyl group is attached to the functional group

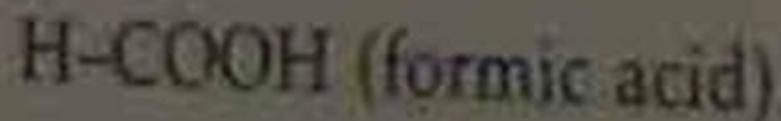


the substance is called an alkanoic acid.

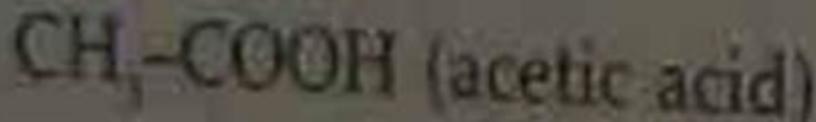
The general molecular formula is $\text{C}_n\text{H}_{2n}\text{O}_2$.

Naming

The -e of the alkane is replaced by -oic and the word acid is added. Because the -COOH group is always on a terminal carbon, no numbering is needed. The first member is methanoic acid:



The next member is ethanoic acid:



Physical properties

1. The first four members are water soluble.
2. Because of their hydrogen bonding they have relatively high boiling points.

Relationships between functional groups of alkanols and alkanolic acids

- (a) Oxygen has a greater attraction for bonding electrons than carbon or hydrogen do, so C–O bonds of alkanols are polar.

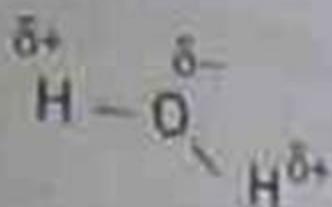
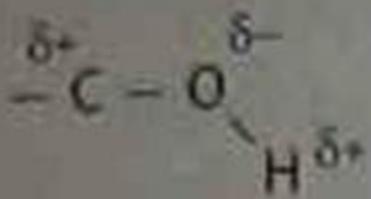
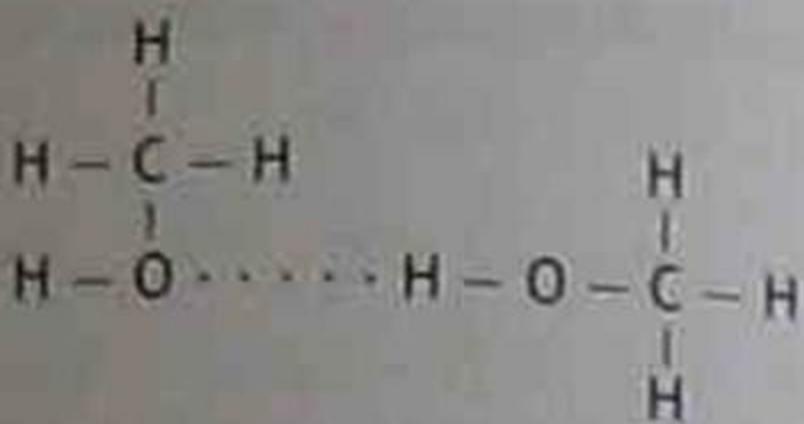
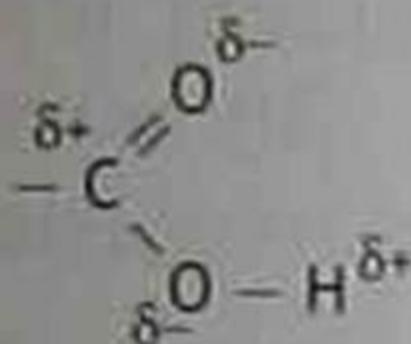


Figure 2.15 Comparison of polar $-COH$ group with water

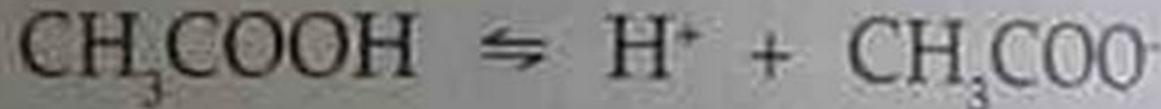
Hydrogen bonding also occurs with alkanols to a lesser extent than with water.



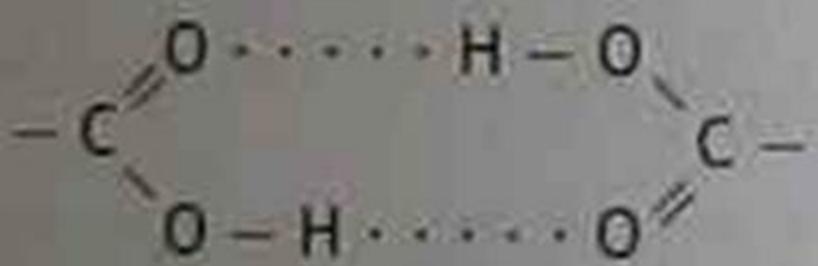
- (b) The carboxylic acid group is a planar group with a 120° bond angle separating bonds. The presence of two oxygen atoms on the one carbon atom leads to a polar carbonyl group.



The high polarity of the $-\text{COOH}$ group makes the carboxyl group weakly acidic in water,



The presence of a hydrogen atom on one of the oxygen atoms enables hydrogen bonding to occur.



Because of the polar nature of the functional groups of alkanols and alkanoic acids and because of hydrogen bonding, both groups have much higher melting and boiling points than hydrocarbons of comparable molecular mass.

Table 2.8 Formulae and some physical properties of alkanols

Name	BP (°C)	Formula	Solubility in water
methanol	65	CH ₃ OH	miscible
ethanol	78	CH ₃ CH ₂ OH	miscible
1-propanol	97	CH ₃ CH ₂ CH ₂ OH	miscible
1-butanol	117	CH ₃ CH ₂ CH ₂ CH ₂ OH	slightly soluble
<hr/>			
methanoic acid	100	HCOOH	miscible
ethanoic acid	118	CH ₃ COOH	miscible
propanoic acid	141	CH ₃ CH ₂ COOH	miscible
butanoic acid	164	CH ₃ CH ₂ CH ₂ COOH	miscible

Note: Higher numbers = higher bp.

Some commercial uses of esters

Food flavouring

Esters are usually sweet-smelling substances and many are responsible for the flavour and odour of fruits. Even though there are usually several compounds contributing to the odour and aroma, it is often one ester which is mainly responsible, e.g. 1-pentyl ethanoate has the aroma of bananas.

Many esters used in the commercial manufacture of perfumes and flavourings are made from petroleum.

Table 2.9 Examples of esters and their uses as food flavouring

methyl butanoate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$	rum
ethyl butanoate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_3$	pineapple peach apricot
1-pentyl butanoate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	apricot
1-pentyl ethanoate	$\text{CH}_3\text{C}(=\text{O})\text{O}(\text{CH}_2)_4\text{CH}_3$	banana
1-octyl ethanoate	$\text{CH}_3\text{C}(=\text{O})\text{O}(\text{CH}_2)_7\text{CH}_3$	orange

Food

The main use of glycerol esters (i.e. natural fats and oils) is food, e.g. margarine, fats.

Solvents

Another major use of esters is as solvents, since they dissolve both polar and non-polar organic compounds.

Ethyl and pentyl ethanoate are used, for example, in the manufacture of cellulose lacquers. Ethyl ethanoate is also used as a solvent in the preparation of paints, varnishes (including nail varnish, model aeroplane glue and plastic cement).

Soaps

Soaps are produced by the hydrolysis of long-chain esters found in vegetable oils and fats.

Other uses

Some glycerol esters are used for cosmetics, commercial oils and for making linoleum.

The work of chemists in monitoring and managing reactions

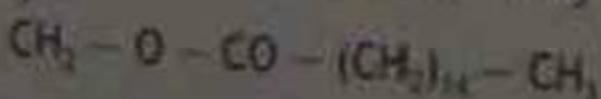
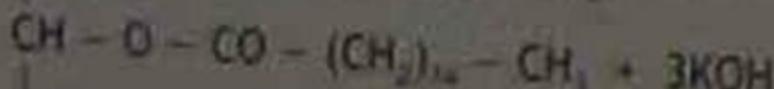
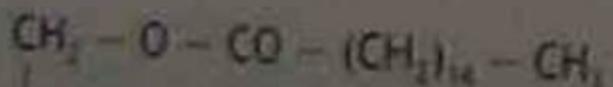
Chemistry and the needs of human society are strongly linked as the processes of quality control on everyday products are carried out by chemists and laboratory staff. The quality of products may be assessed by knowing

- (a) what chemicals are present (*qualitative analysis*), and
- (b) how much of each chemical is present (*quantitative analysis*).

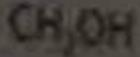
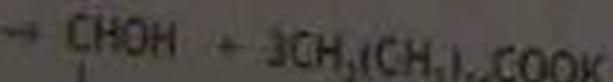
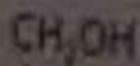
- Packaging materials are tested for weight, thickness and size.
- Raw materials, such as fatty acid blends, are carefully checked since the ratio of palm oil, palm stearin and palm kernel oil determines the type of lather produced when the soap is used. Three checks are carried out:
 - (a) The *free fatty acid test* which is defined as the volume in mL of standardised 0.1 M KOH needed to neutralise a 5.0 g sample of the fat or oil.

(b) Saponification value which gives a measure of the average molar mass of fats and oils used to make the soap and is the number of moles of KOH needed to saponify one gram of the fat or oil.

Example



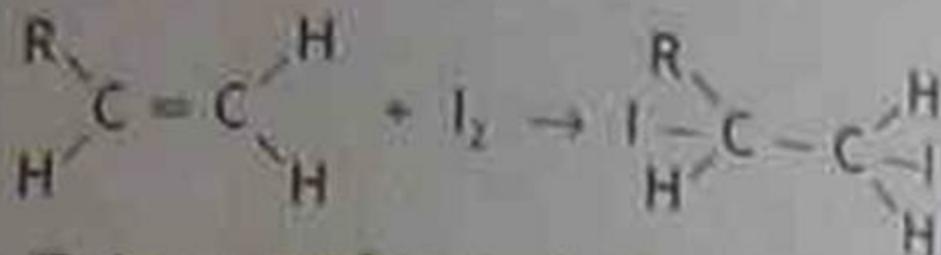
glyceryl tripalmitate



glycerol soap

(c) The iodine number which is the mass in grams of iodine which reacts with 100 g of oil or fat. This is a measure of the degree of unsaturation of the fat or oil.

Example



where R is a carbon chain of 8 to 18 carbon atoms.

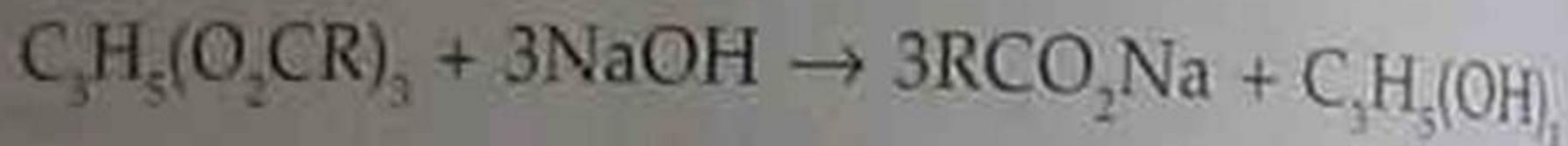
Palmolive soaps are made by a two-step process

Step 1. The initial neutralisation of fatty acids by soda ash.

Step 2. The final saponification of unreacted acids by caustic soda.

Soda ash (Na_2CO_3) is used in the first step because of its low price and minor level of metallic impurities which could have a long-term effect on the soap's perfume and colour stability.

The basic reaction in soap manufacture is that between a fat or oil and an alkali which results in soap and glycerol:



where R is the carbon chain which can consist of between 8 and 18 carbon atoms.

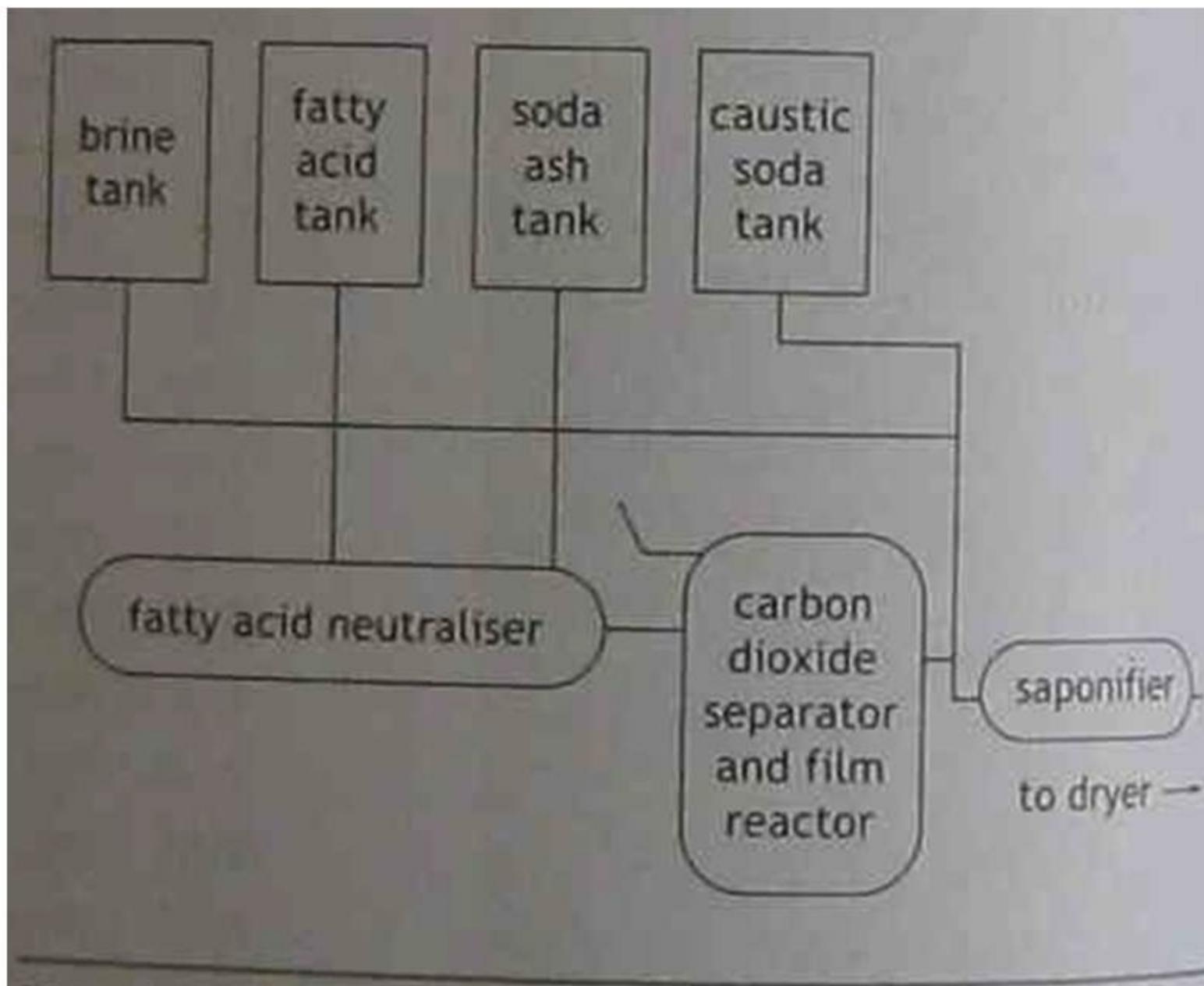


Figure 3.1 Soap manufacture

Intermediate products

Soap is tested to ensure that correct amounts of NaOH are used in the final saponification process. This soap is called 'neat' soap and contains about 65% soap and 35% water with minor levels of impurities. After the soap has been neutralised, it is vacuum-dried to reduce the level of moisture to below 17%. Moisture levels must be tested. Preservatives are added and lastly fragrances, colour and a deodorant ingredient complete the production.

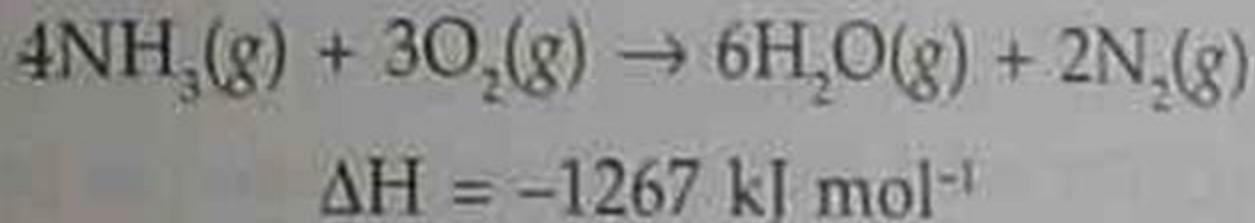
Final product is examined by a quality inspector who checks weights, odour and appearance of wrapped and unwrapped soap before it goes to the warehouse. Chemists and other laboratory staff check the product throughout manufacture to ensure that the final product meets the Australian Standard for personal soap.

3.2

A chemical process for managing reaction conditions

The viability of the *Ostwald process* used to manufacture nitric acid from ammonia needs monitoring since reactants can form different products under different conditions. The production of nitric acid depends on the control of kinetic and equilibrium factors and the choice of a suitable catalyst.

At high temperature, NH₃ burns in air to produce mainly nitrogen but not NO.

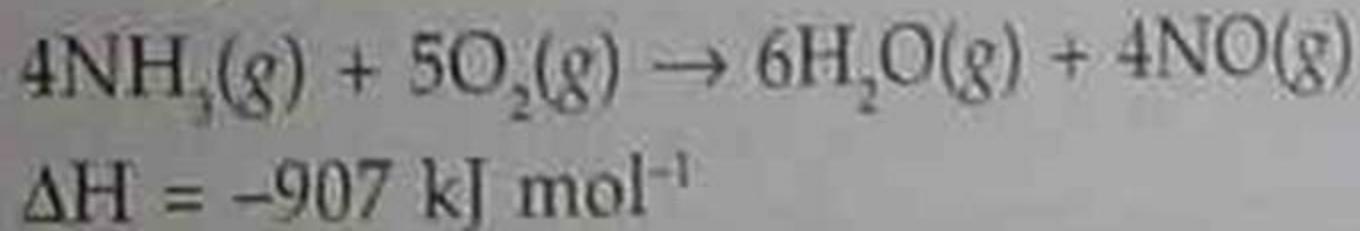


However, if conditions are carefully controlled so that

- the optimum temperature is in the range of 820–930°C (depending on pressure),
- a fine wire gauze pad of a 90% platinum/10% rhodium alloy is used as a catalyst for a contact time of below 0.003 seconds, and

- the level of $\text{NH}_3(g)$ /air mixture is 9–12% (to keep the fraction of NH_3 well below the explosive limit),
then the required high yield of NO can be obtained.

Step 1. Catalytic oxidation of ammonia:



3.3 Ammonia and its applications

Table 3.1 Applications of ammonia in industry

Industry	Application of ammonia
Fertiliser	production of $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{PO}_4$, NH_4NO_3 , where ammonia acts as a base; urea $(\text{NH}_2)_2\text{CO}$ is made by reaction with CO_2
Chemicals	synthesis of HNO_3 , NaHCO_3 , Na_2CO_3 , HCN , N_2H_4
Explosives (5%)	NH_4NO_3
Fibres and plastics (10%)	nylon and other polyamides
Refrigeration (5%)	used for making ice, large scale refrigeration plants, air-conditioning in buildings and plants

Pharmaceuticals

manufacture of drugs, e.g. sulfonamide, anti-malarials, vitamins

Pulp and paper

ammonium hydrogen sulfite enables some hardwoods to be used

Mining and metallurgy (5%)

used in nitriding (bright annealing) steel; in zinc and nickel extraction

Cleaning

in solution as a cleaning agent, e.g. 'cloudy ammonia'

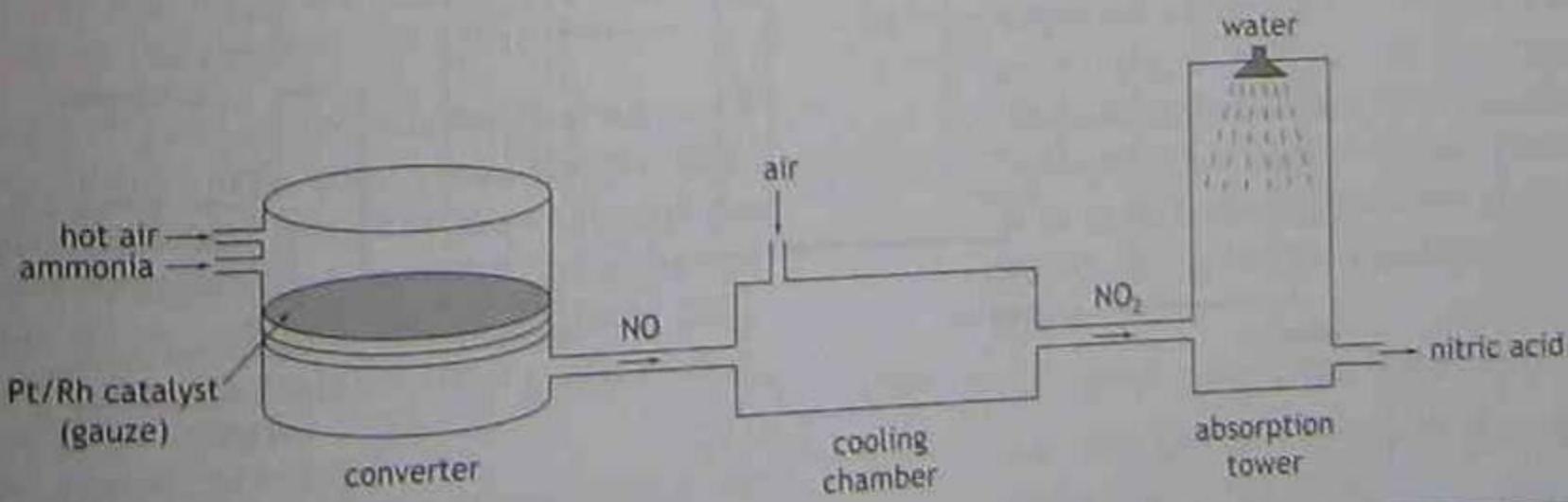
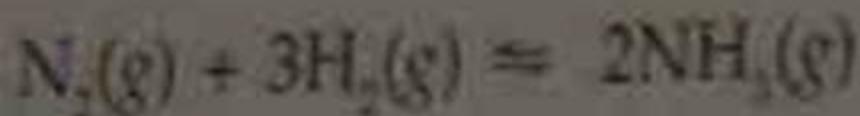


Figure 3.2 A flow diagram of the Ostwald process

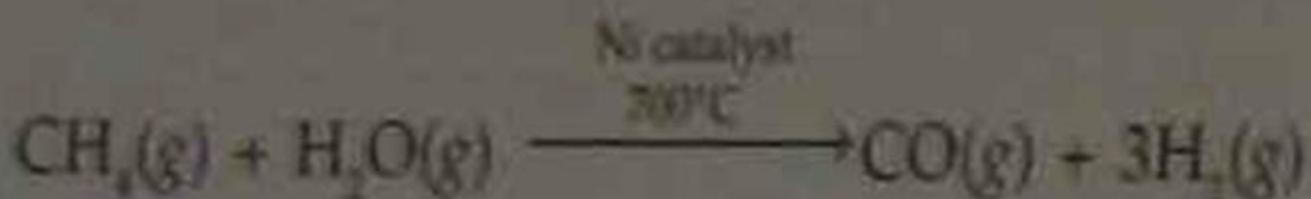
Production of ammonia by the Haber process

Haber was a German chemist who investigated the reaction

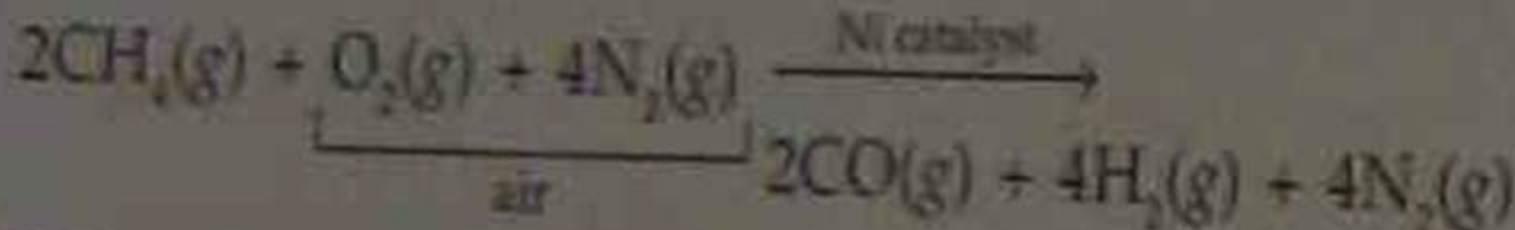


Haber's research was of great interest to the German chemical industry. Germany was preparing for World War I and nitrogen compounds were needed for explosives. By 1913, Haber had produced ammonia in a large scale from atmospheric nitrogen.

Hydrogen must be of high purity and low cost. The catalyst used must not be poisoned. Hydrogen is now obtained by reforming light petroleum fractions or natural gas (methane) by adding steam.



Only enough steam is added to react with about 45% of the methane as shown in the above equation. The rest of the methane is reacted with air over another nickel catalyst:



This reaction removes all the O₂ from the air leaving N₂ and some H₂. All the CO in the mixture is oxidised to CO₂ by adding steam and using an iron oxide catalyst.



CO₂(g) is removed using a suitable base and the N₂ and H₂, which are in the ratio of 1:3 after compression, enter the converter where they combine to form ammonia:

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

Since the reaction is exothermic.

Since the reaction is exothermic and involves a decrease in the number of total gaseous molecules, the position of equilibrium could be forced to the right by lowering the temperature and increasing the pressure (Le Chatelier's Principle).

A suitable catalyst is used so that it is possible to achieve acceptable reaction rates at temperatures which give acceptable equilibrium yields. The optimum operating conditions in terms of cost and yield in the reactors of modern ammonia plants are as follows:

- (a) The N_2 and H_2 gases enter in a 1:3 ratio.
- (b) Temperatures used range from 400 to $500^\circ C$.
- (c) Pressures of 250 atmospheres are used, so the converter must have very thick walls to withstand such pressures.
- (d) A porous iron catalyst made from iron oxide (Fe_3O_4) is used (better catalysts such as osmium are too costly) to reduce the activation energy needed to break N_2 and H_2 bonds.

The yield of ammonia is about 10–20%. During commercial production, the gas mixture does not reach equilibrium. The gas mixture leaving the reactor is cooled to liquefy and remove the ammonia formed. The remaining mixture of gases is recycled to improve the yield. Heat released by the initial reaction between nitrogen and hydrogen must be removed to keep the temperature within the desired limits.

The 'waste heat' is used to heat the incoming gas mixture.

Note: A control system is vital for this process. Automatic controls are used to adjust, for example, the rate of feed of the incoming gases according to the pressure of the recycled gases.

Under normal atmospheric conditions, the reaction basically does not occur (K is very small). The reaction, in fact, needs a *catalyst* (an added substance which allows the reaction to occur). In the presence of a catalyst, it has been found that reaction is most efficient when subjected to high pressures — several hundred times atmospheric pressure — but that increasing the temperature in fact causes a decrease in ammonia production. Figure 3.4 shows the effect of temperature and pressure on the process.

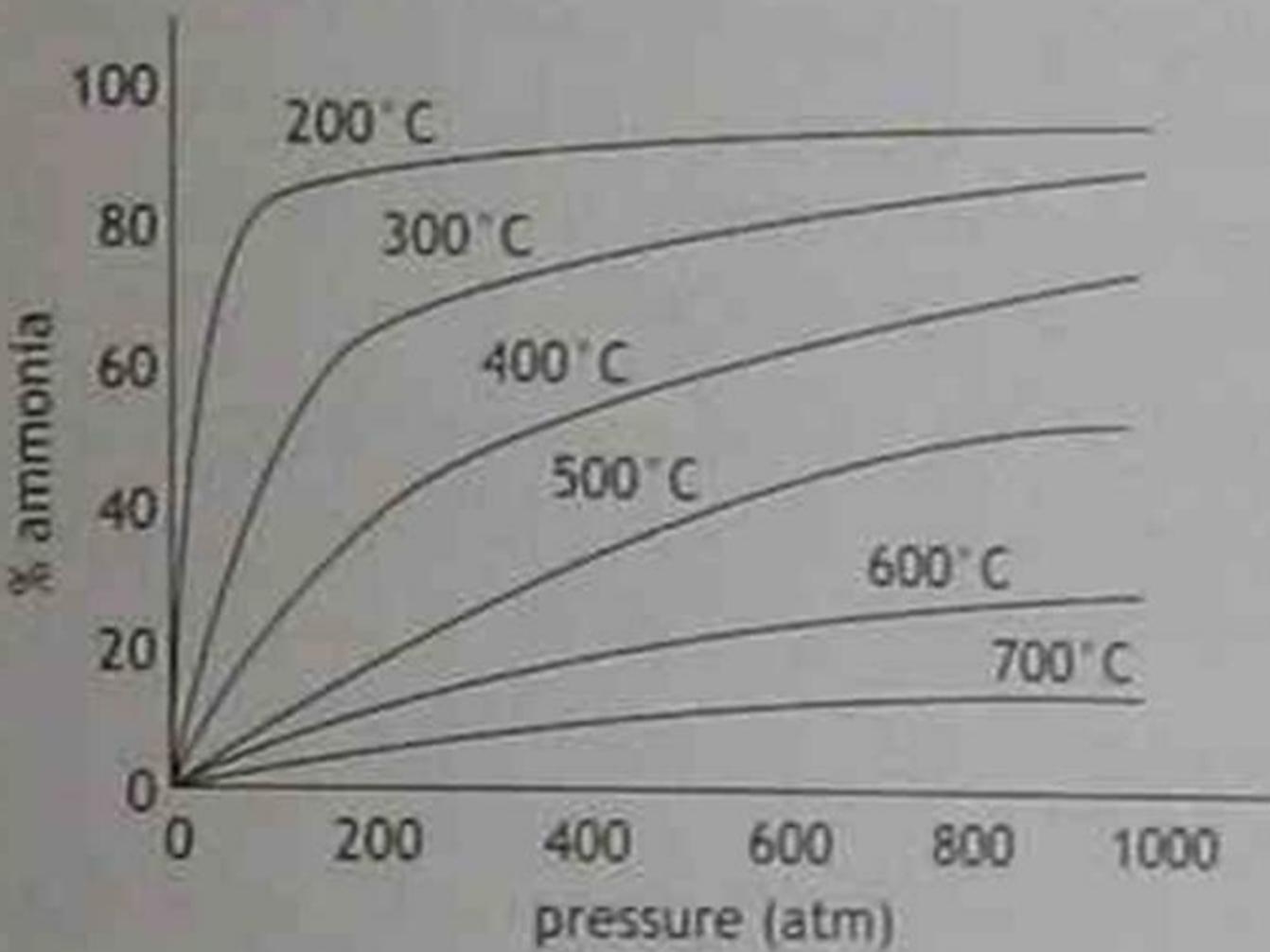


Figure 3.4 Effect of temperature and pressure on the Haber process

At 200°C, it is evident that an almost 100% conversion of reactants is obtained at pressures above 750 times atmospheric. In practice, most production systems use significantly lower pressures (around 200 atmospheres) because of the difficulties of containing large amounts of materials at the high pressures. This, of course, reduces the yield of ammonia. The temperature used is around 500°C, which also limits the percentage conversion, but speeds up the process.

According to Figure 3.4, the percentage of ammonia obtained under these conditions is only 20%. Although this seems low, it is the choice of the engineers who design the plant to maximise the rate of producing the ammonia and to minimise costs and safety concerns in the building and during operation of the plant.

Note 1: The Haber process is an industrial procedure which is not done under equilibrium conditions. Instead, moderately high temperatures

and pressures are used and the liquefied ammonia is drawn off constantly. The high temperature is used because reactions (including exothermic reactions) will proceed more rapidly when molecules have more energy.

According to the equilibrium system (where $\Delta H = -92 \text{ kJ}$), high temperature would reduce the concentration of ammonia but the reaction would be extremely slow at room temperature.

Note 2: A catalyst is used in the Haber process to lower the activation energy so that the N_2 bonds and H_2 bonds may be broken more readily.

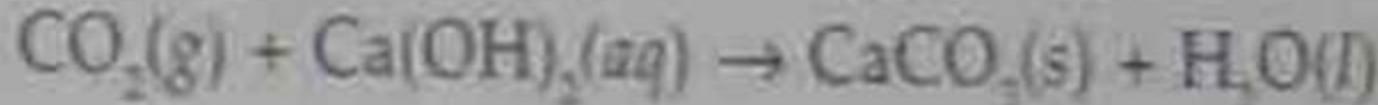
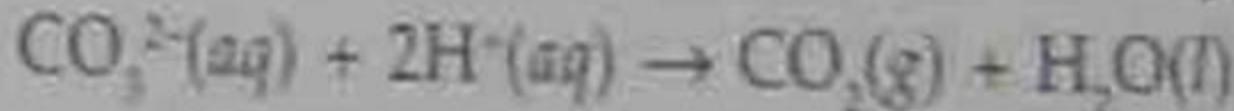
3.5

Tests to identify specific ions

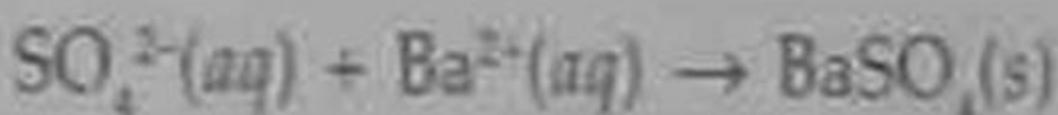
The following tests can be carried out to identify the ions below:

Anions

CO_3^{2-} Add a dilute inorganic acid, e.g. HCl. Bubble any gas evolved into a test-tube containing limewater. If a carbonate is present, the limewater will turn milky.

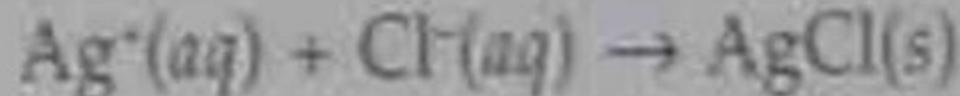


SO_4^{2-} Add $\text{Ba}(\text{NO}_3)_2$ solution. A white precipitate indicates the presence of a sulfate.



Note: Ensure that a carbonate is absent by testing with dilute acid

Cl^- Add a solution of AgNO_3 . A white precipitate which turns purple on exposure to light indicates the presence of a chloride.

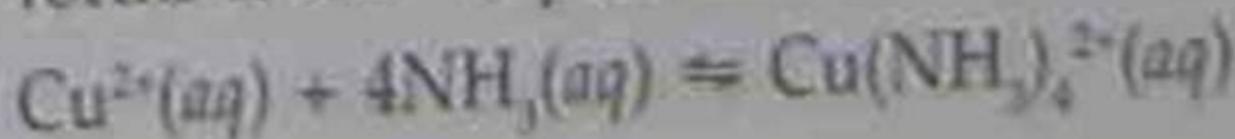


PO_4^{2-} Yellow precipitate is formed on warming with a solution of ammonium molybdate and nitric acid.

Cations

Ba^{2+} Carry out a flame test. A Pt wire is mounted in a glass holder. It is dipped in concentrated HCl and then cleaned in the non-luminous Bunsen flame. The clean Pt wire is then dipped into the sample to be tested. Ba^{2+} gives an apple-green colour to the flame.

- Ca^{2+} Ca^{2+} gives a brick-red colour to the flame.
- Cu^{2+} Add NH_3OH and a deep blue complex ion forms if Cu^{2+} is present.



2. Add excess HCl. A white precipitate of PbCl_2 forms which dissolves in hot water.



3. Add KI and a yellow precipitate of PbI_2 forms.



Fe^{2+}

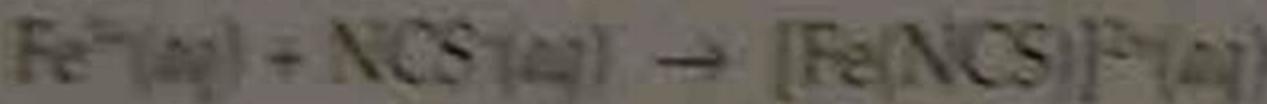
- 1. Forms a white precipitate when NaOH is added. The precipitate rapidly turns brown.

- 2. Forms a deep blue precipitate with potassium ferricyanide.

Fe^{3+}

- 1. Forms a red-brown precipitate of Fe_2O_3 , when NaOH is added.

- 2. Forms a blood-red complex ion when potassium thiocyanate solution is added to the Fe^{3+} ion.



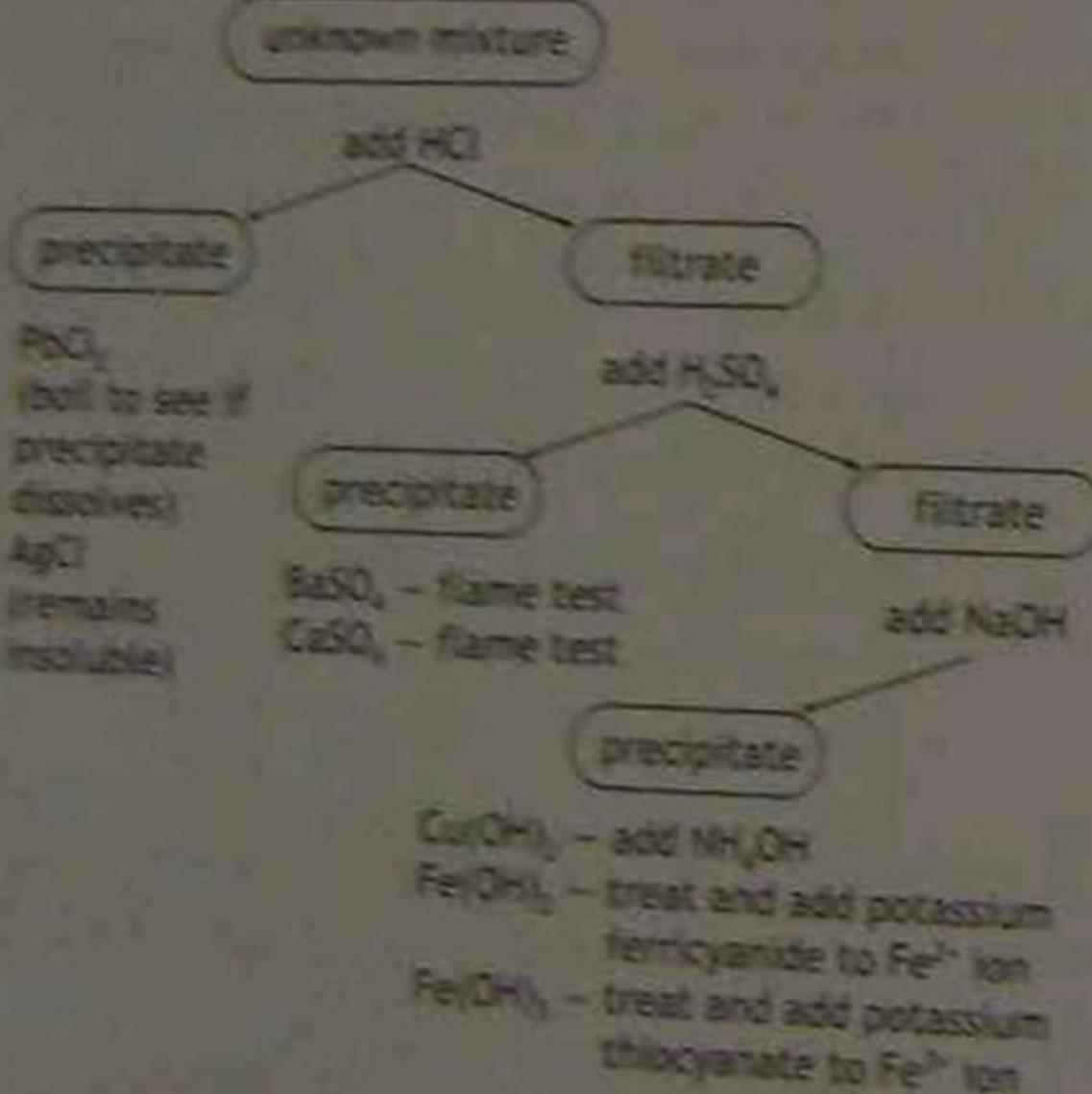


Figure 1.5 Scheme to deduce the above cations present in an unknown mixture of their solutions.

Gravimetric analysis is used to determine the percentage by weight of an element or group in a compound or mixture.

Example experiment:

To find the sulfate content of a fertiliser. Ammonium sulfate is the main constituent in 'salt ammonia' which is a common lawn fertiliser.

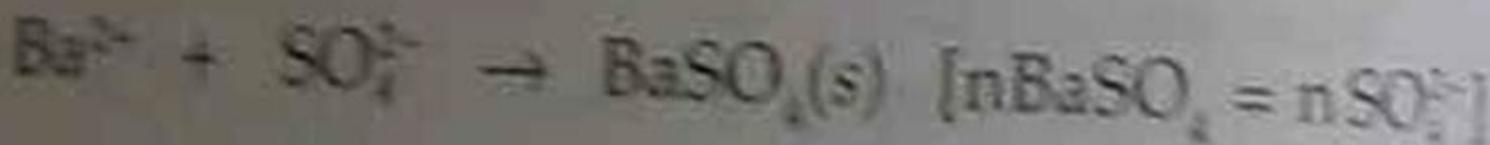
Method:

Method:

1. Accurately weigh a small sample (about 1 g) of the fertiliser into a clean, dry beaker.
2. Dissolve in 100 mL of hot, distilled water.
3. Add a slight excess of saturated barium chloride solution.
4. Heat with stirring to coagulate the white barium sulfate precipitate.

5. Filter quantitatively through a pre-weighed sintered glass crucible and wash with small amounts of hot water, using a wash bottle, to remove any soluble salts.
6. Dry crucible in an oven at 120°C. Cool in desiccator and weigh. Difference in mass of crucible masses = mass of barium sulfate.

Calculation:



Step 1: Convert the mass of BaSO_4 to moles [$n(\text{BaSO}_4)$].

Step 2: Convert the moles of sulfate [$n(\text{SO}_4^{2-})$] to grams ($m = nM$).

Step 3: Express this as a percentage of the weight of the fertiliser sample.

Note: A suitable filter paper may be used to replace the crucible.

The use of atomic absorption spectrophotograph to determine metal ion concentrations

The atomic absorption spectrophotograph (AAS) was invented by the Australian Alan Walsh in 1953. It is a special lamp (a hollow-cathode lamp) used to produce a sharp-line emission spectrum of the metal to be determined. The radiation from the lamp of a chosen wavelength passes through a flame (usually an air-acetylene flame) into which a solution of the metal of interest is sprayed using a nebuliser to obtain a fine mist.

Atoms of the element being analysed are converted to an atomic vapour and then absorb some of the radiation.

The light beam passes through a filter (monochromator) to separate light of the chosen wavelength from other light. The intensity of the light is measured by an electronic detector (photomultiplier tube).

The amount of light absorbed by the sample is proportional to the concentration of the metal in the solution being tested. Atoms of each metal absorb light at characteristic wavelengths in proportion to the amount present.

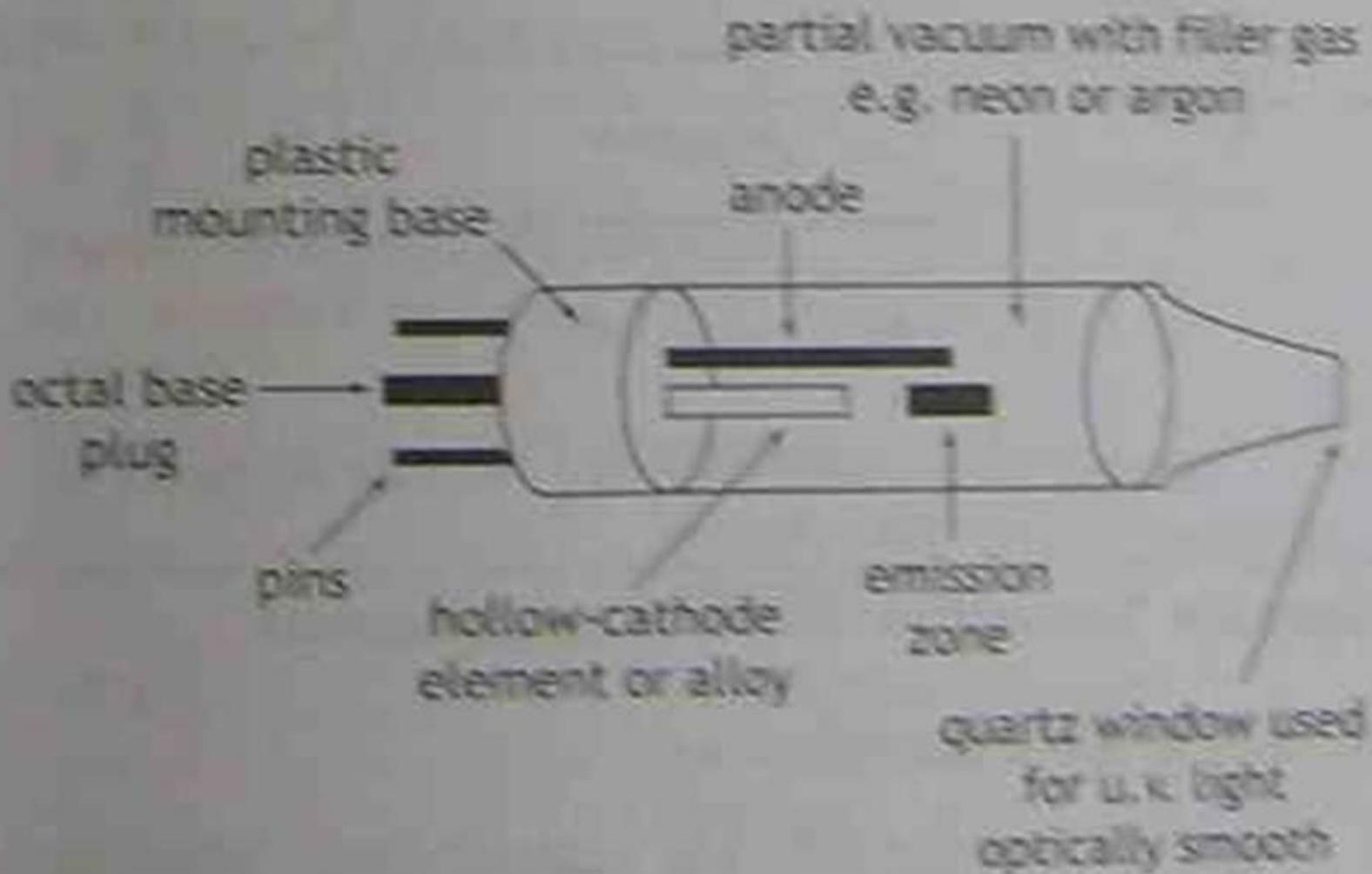


Figure 3.7 Hollow-cathode lamp

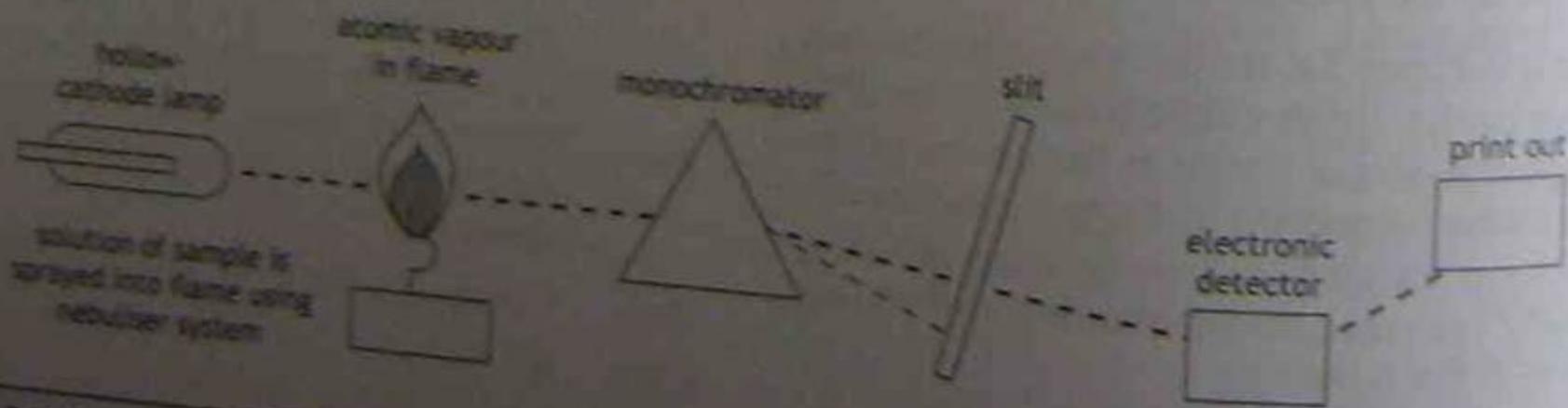


Figure 1.6 Schematic diagram of an atomic absorption spectrometer.

The determination of concentrations of metal ions in solutions

Principle

Flame atomic absorption spectroscopy (AAS) relies on the following:

- (a) Heating a sample sufficiently to produce free atoms.
- (b) Free atoms of an element being able to absorb energy only at certain discrete wavelengths.

Such a wavelength is called a resonance wavelength and corresponds to the transfer of an electron between the ground state and a higher energy level in a specified atom.

- (c) The energy absorbed being a function of the concentration of the absorbing atoms.

Techniques

- A solution of the metal is nebulised into a flame.
- The absorption of energy is measured at a specified wavelength.
- The absorption measurement is independent of any radiation emitted by the flame.
- In calibrating solutions, use Analytical grade reagents (AR).
- Use high purity water.

- Make up
 - a blank set solution,
 - a set of suitable standard solutions, and
 - duplicate sample solutions.
- Calibration graphs should be linear.

Use

The atomic absorption spectroscopy is one of the most widely used instrumental techniques and is capable of detecting 68 metals in the range of parts per million to pure metal. In the metals industry, volumetric and gravimetric analysis is outdated.

The mining industry uses AAS for the analysis of geological samples, testing the purity of products such as copper, silver and gold and monitoring pollution levels in effluents. It is used for quality control of alloys and in the detection of dangerous metal particles in the air.

An example of the use of AAS analysis in determining the concentration of an M^{2+} ion in parts per million is given below. Parts per million are used for very small concentrations (1 part to 10^6 parts of solvent by mass).

Question

The level of iron in two brands of multivitamin tablets was determined by AAS. One tablet from each brand was crushed and separately dissolved in 1 L of pure water. Standard solutions of Fe^{2+} were made up using ARs; a 'blank' solution was also made up. Their absorbances were tested followed by those of samples of the multivitamin solutions.

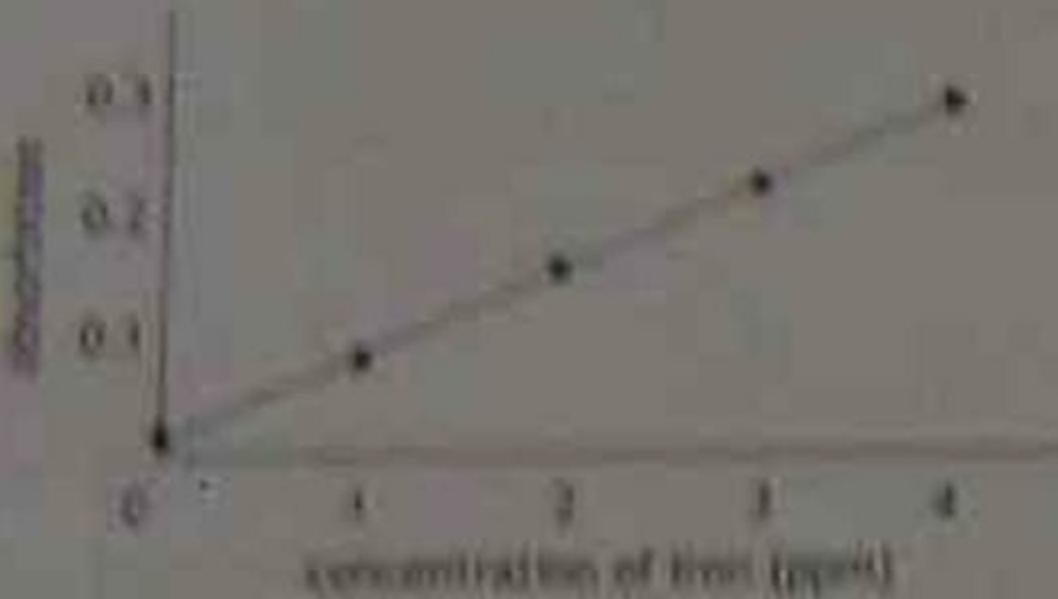
The following data were recorded:

Solution concentration (ppm)	Absorption
0.00	0.010
1.00	0.080
2.00	0.150
3.00	0.220
4.00	0.290
Sample 1	0.190
Sample 2	0.250

- (a) Plot a graph of absorption against concentration of iron in ppm. State the concentration of iron (ppm) for each sample.
- (b) Why did the standard containing no added iron give a small absorption reading?
- (c) Most multivitamins contain other metal ions such as Cu^{2+} , Zn^{2+} and Ca^{2+} as well as Fe^{2+} . How can Fe^{2+} be selectively analysed?

Solution

(a)



Sample 1 — Iron concentration is 2.5 ppm

Sample 2 — Iron concentration is 3.8 ppm

- (b) Very small amounts of iron could be present in the water used to make up the blank.

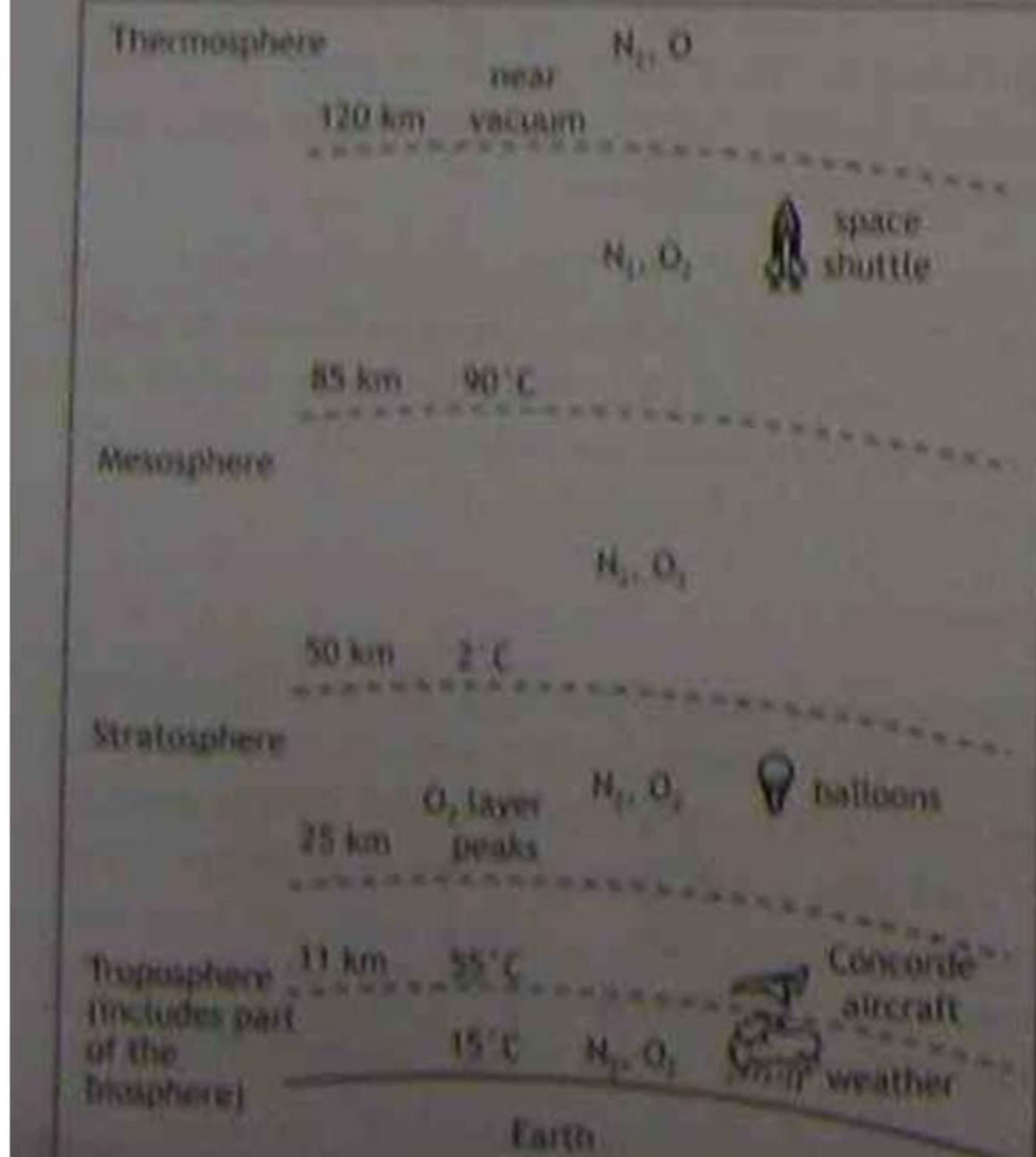


Figure 3.8 Regions of the atmosphere (not to scale)

- (c) The hollow-cathode lamp is changed for each element, being specific for the element being analysed.

The main regions of the atmosphere

The layers of the atmosphere are defined by temperature changes. They are, however, distinct in other ways, e.g. the weather systems are confined to the troposphere because the warmer stratosphere acts as a lid. The stratosphere is the region of the atmosphere containing the ozone layer.

Atmospheric pollution problems include the following.

(a) Photochemical smog

Produced in the tropospheric ozone from burning of fossil fuels, e.g. nitric oxide (NO) from car exhausts, NO(g) interacts with sunlight to produce NO_2 (nitrogen dioxide) which not only contributes to urban haze, but also produces oxygen atoms which combine with O_2 in the air to produce toxic ozone (O_3).

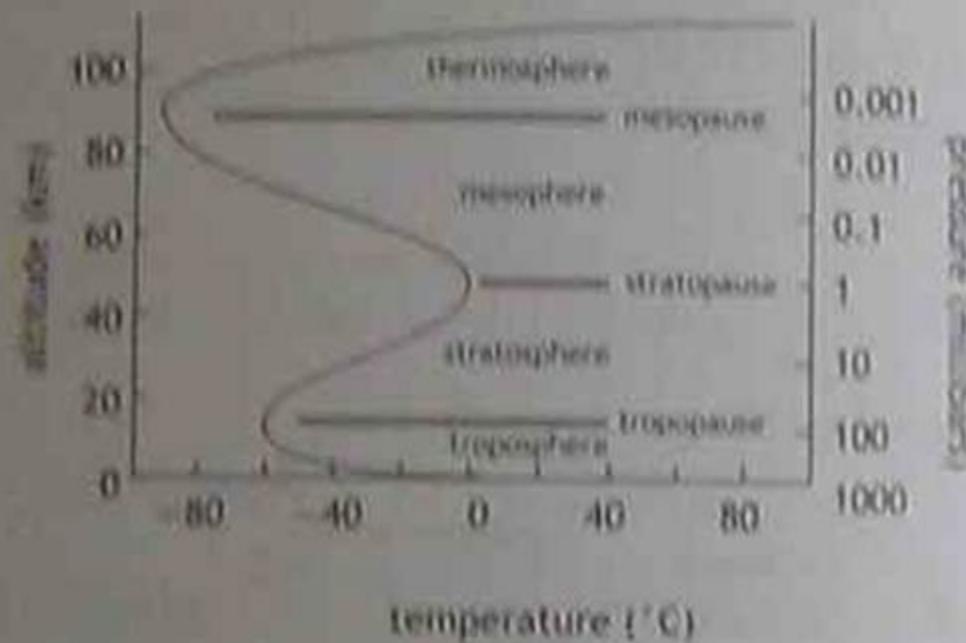


Figure 3.9 Temperature variation in the atmosphere

(b) The greenhouse effect

Light rays penetrate the atmospheric boundary and are absorbed by the plants, animals and soil. They are then re-radiated as longer-wave infrared heat rays from the Earth's surface. The atmospheric boundary reflects these rays back to earth. Greenhouse gases absorb some of these infrared rays.

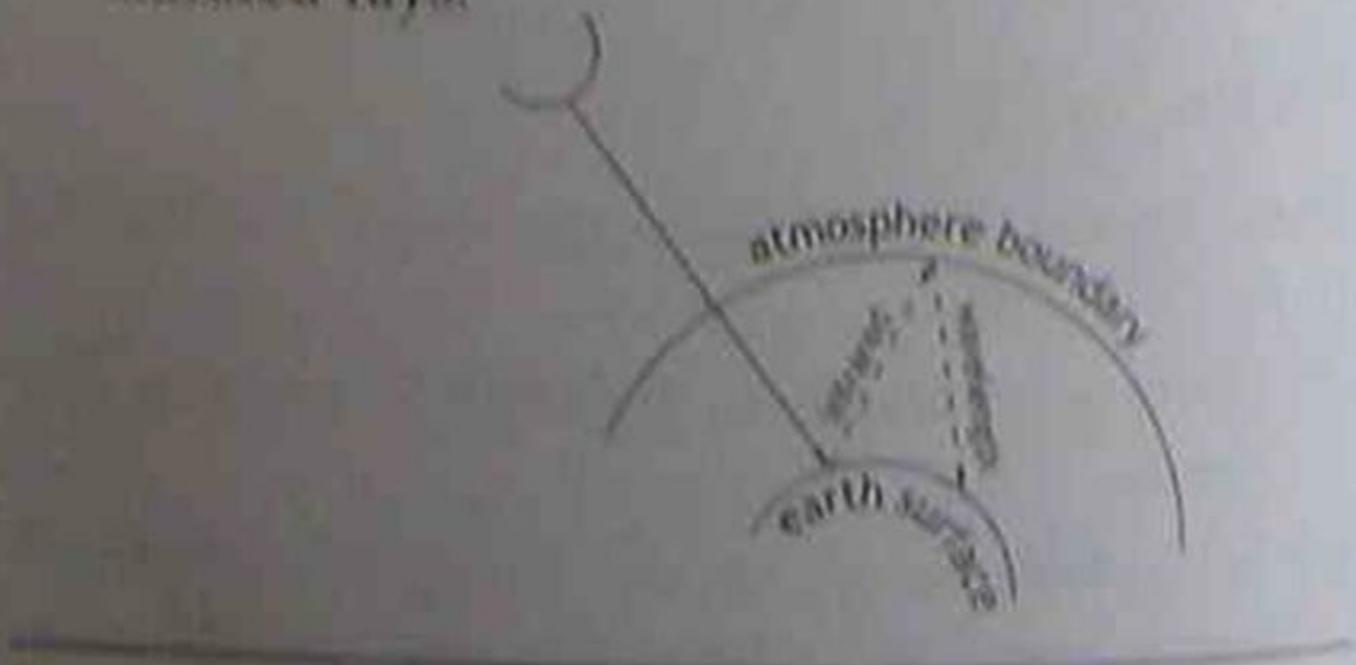


Figure 3.10 The greenhouse effect

The enhanced greenhouse effect is brought about by human activity. The atmosphere's ability to absorb infrared radiation has increased. Greenhouse gases such as water vapour, carbon dioxide, methane, nitrogen oxides and chlorofluorocarbons (CFCs) all absorb some of the infrared radiation emitted by the Earth without absorbing energy from the sun's radiation. Some of them are natural components of the atmosphere, so Earth has always had a greenhouse effect which maintains the average temperature of the planet at about 16°C.

Table 3.2 Main gases in the enhanced greenhouse effect

Gas	% effect	Warming potential ranking
Carbon dioxide	57	1
Methane	12	11 (11 times that of CO ₂)
CFC-11, CFC-12	15–25	~5000
N ₂ O	6	270

3.3

Lower atmospheric pollutants

The most disturbing consequences of atmospheric modification are

- the enhanced greenhouse effect,
- the depletion of ozone in the stratosphere, and
- pollution in the troposphere due to acid rain and photochemical smog.

Table 3.3 Lower atmospheric pollutants and their sources

Gas	Source
Troposphere pollutants	
(a) Enhanced greenhouse gases:	
(i) increased CO ₂	decomposition of organic matter, fossil fuel combustion, deforestation
(ii) CH ₄	mainly from anaerobic decomposition of organic matter, ruminants, landfill, rice paddies
(iii) CFCs	manufactured chemicals used in aerosols, foams, refrigerants, air conditioners

(iv) oxides of nitrogen	motor car engines, combustion of organic matter
(v) ozone	mostly by diffusion from the stratosphere, photochemical smog
(b) Particulates (especially in cities)	increases are due to soot, smoke, oil and salt spray
(e) SO_2	volcanic gases, fossil fuels, industrial processes

Stratosphere pollutants

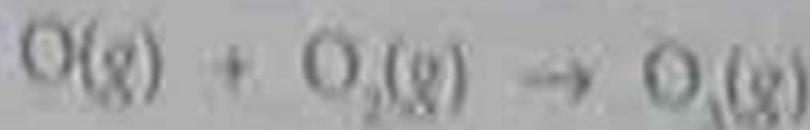
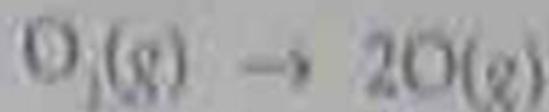
CFCs	aerosols, foams, refrigerants, air conditioners
oxides of nitrogen	vehicle exhausts, burning of fossil fuels, volcanic gases

Role of ozone in the troposphere and stratosphere

Ozone

Ozone reacts readily with other gases in the atmosphere and so it remains in the lower atmosphere (troposphere) for a relatively short time. Ozone is a greenhouse gas formed throughout the atmosphere. In the troposphere it contributes to the greenhouse effect, coming from two sources:

- (a) Mostly from the stratosphere. Ozone in the stratosphere is formed largely by the impact of light on oxygen molecules.



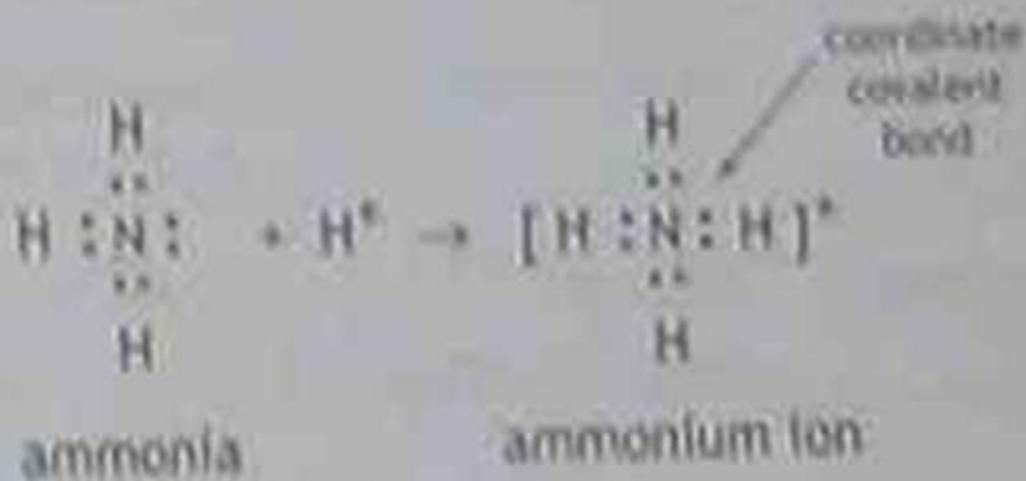
- (b) Some ozone forms in the troposphere as a result of chemical reactions between a number of gases such as oxides of nitrogen and volatile hydrocarbons.

In the lower atmosphere, ozone is both a pollutant and an irritant. Ninety per cent of ozone is found in the stratosphere where it shields the planet from damaging solar ultraviolet radiation.

Structure of ozone

A covalent bond between two atoms consists of a pair of shared electrons. Each atom may contribute an electron to the pair. However, one atom may provide both electrons and is called a donor atom. The bond formed is called a coordinate covalent bond.

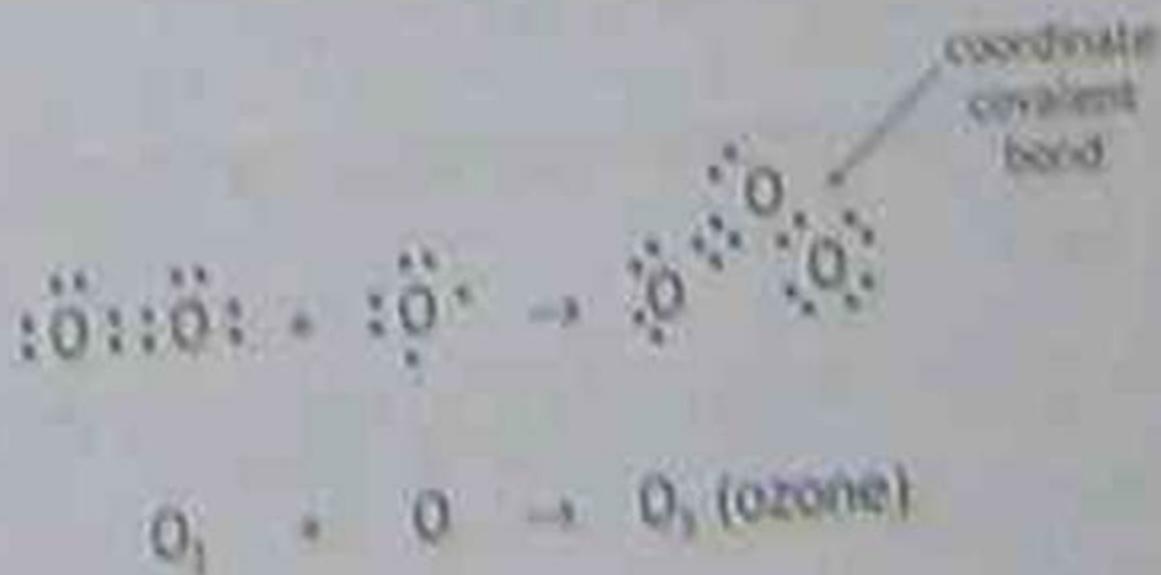
Exemplo



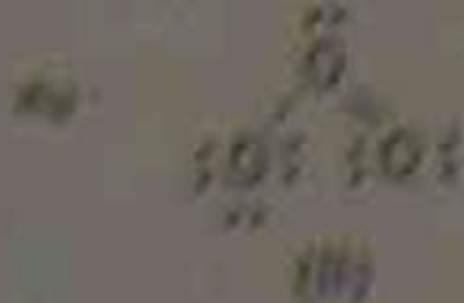
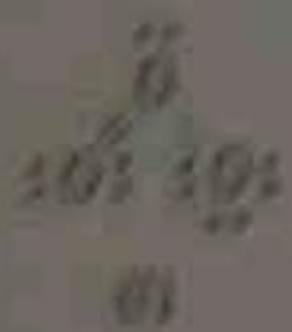
Electrons cannot be distinguished once bonds are formed.

QUESTION

Ozone and O_3 are allotropes of the element oxygen. *Allotropes* are different forms of the same element in the same state (both gases). Below is a theoretical example of the formation of a coordinate covalent bond:



The Lewis Structure representing ozone shows that one double and one single bond is present. From bond length measurements, however, both bonds are of equal length and are intermediate between a double and single bond. The ozone molecule can be represented by the following resonance forms:



If the structure of the ozone molecule can be represented by a structure intermediate between formulas I and II, then bond lengths and bond energies can be accounted for. The structures differ only in the position of the electrons.

Oxygen occurs as a diatomic molecule and the short bond distance and high bond energy suggest that O₂ has a double bond. The following Lewis structure is consistent with this:



But according to the Lewis structure, all valence electrons are paired. In fact, the O₂ molecule is paramagnetic and contains two unpaired electrons. This can only be resolved using the more complex molecular orbital theory.

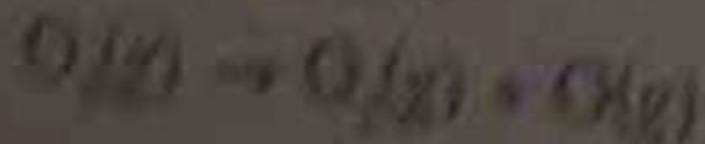
B10 The structure and properties of O₂, O₃ and O₄

Table 7.4 Properties of O₂ and O₃

Property	O ₂	O ₃
Odour	slightly musty	slightly pungent
Molecular size	large size	large, temporary and very problematic
Reactions with flammables	reactive, oxidising agent	more reactive at lower temperatures, strong oxidising agent

Ozone can be used to aerate water supplies (more soluble in water than O₂).

Ozone is less stable than oxygen and more reactive.
This leads directly to energy of



1017 kJ mol⁻¹ activation for O(2), the bond energy
is 495 kJ mol⁻¹.

The lower bond energy of O(2) explains its greater

Properties of O₂(g)

Oxygen is a covalent molecular gas at room temperature. Oxygen consists of small diatomic molecules with low melting and boiling points. Sharing of electrons occurs.

Structure of the oxygen radical $\cdot\text{O}_2$.

At high altitudes, oxygen molecules decompose to atoms by the high energy ultraviolet radiation of the sun. Some of the oxygen atoms react with oxygen molecules to form ozone O₃.

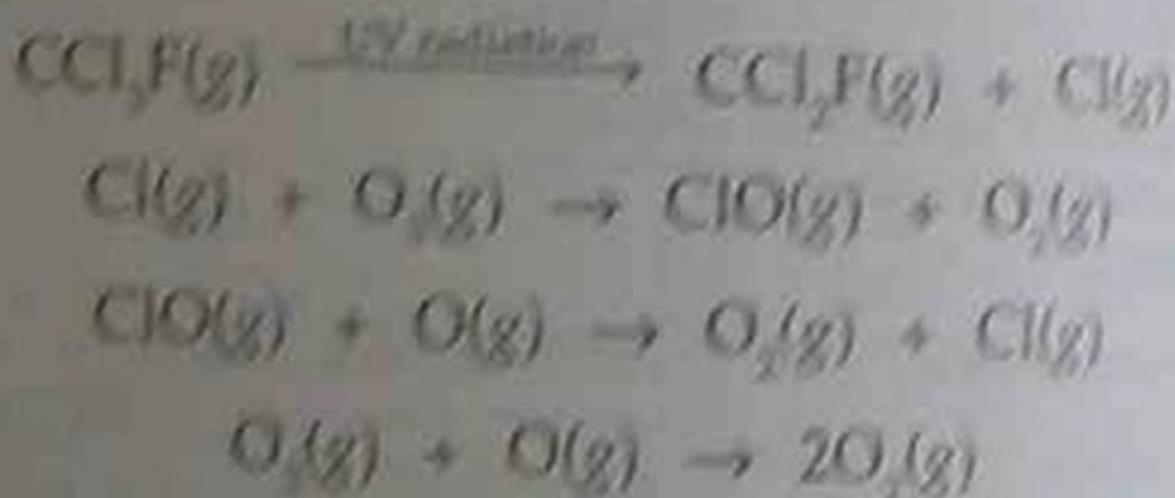
A possible reaction is $\text{O}_2 + \text{O} \rightarrow \text{O}_3$
(See equation on previous page.)

3.11 The origins of CFCs and halogens in the atmosphere

Chlorofluorocarbons are synthetic chlorine containing compounds. They were originally chosen because of their inertness and because they are non-toxic and safe to use. Eventually they move into the stratosphere where they can be broken down by ultraviolet light releasing free halogen atoms, e.g. chlorine,

Example

CFC-11 has the formula CCl_3F

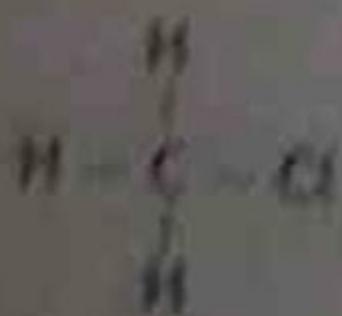


Since chlorine atoms are not permanently used up in the reaction, they can attack more ozone molecules. The O_3 molecule is not being replaced in the above cycle of reactions.

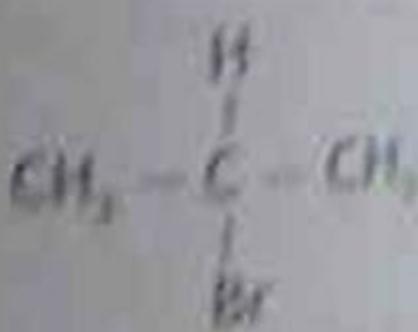
Increasingly HCFCs are replacing CFCs since they have much less ozone-destroying potential.

12.2 Naming straight chain haloalkanes

These derivatives are formed when a hydrogen atom is replaced by a halogen atom (Br, Cl, F and I).



chloromethane



2-bromopropane

Q13 Identifying and naming isomers of haloalkanes

Isomers are two or more different compounds having the same molecular formula.

Examples of isomers of haloalkanes



Table 3.5 Main commercial CFCs of the 1980s

Coded compound	Formula	Name	Uses
CFC-11	CCl ₃ F	trichlorofluoromethane	refrigeration, aerosols, foams
CFC-12	CCl ₂ F ₂	dichlorofluoromethane	refrigeration, aerosols, air conditioning, foams
CFC-13	CCl ₂ FCClF ₂	1,1,2-trichloro-1,2,2-trifluoroethane	electronics, dry cleaning, fire extinguishers
CFC-14	CClF ₂ CClF ₃	1,2-dichloro-1,1,2,2-tetrafluoroethane	aerosols

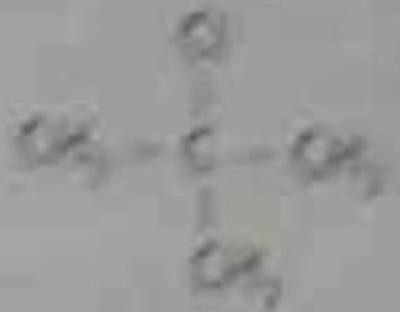
Table 3.6 Substitutes used for CFCs to reduce ozone depletion

Coded compound	Formula	Name	Uses
HCFC-22	CHClF_2	chlorodifluoromethane	air conditioning, refrigeration, foams
HCFC-142b	CH_2CClF_2	1-chloro-1,1-difluoroethane	aerosols
HFC-152a	CH_2CHF_2	1,1-difluoroethane	aerosols, refrigerant

3-chloro-2-methylpropane



2-chloro-2-methylpropane



3.14

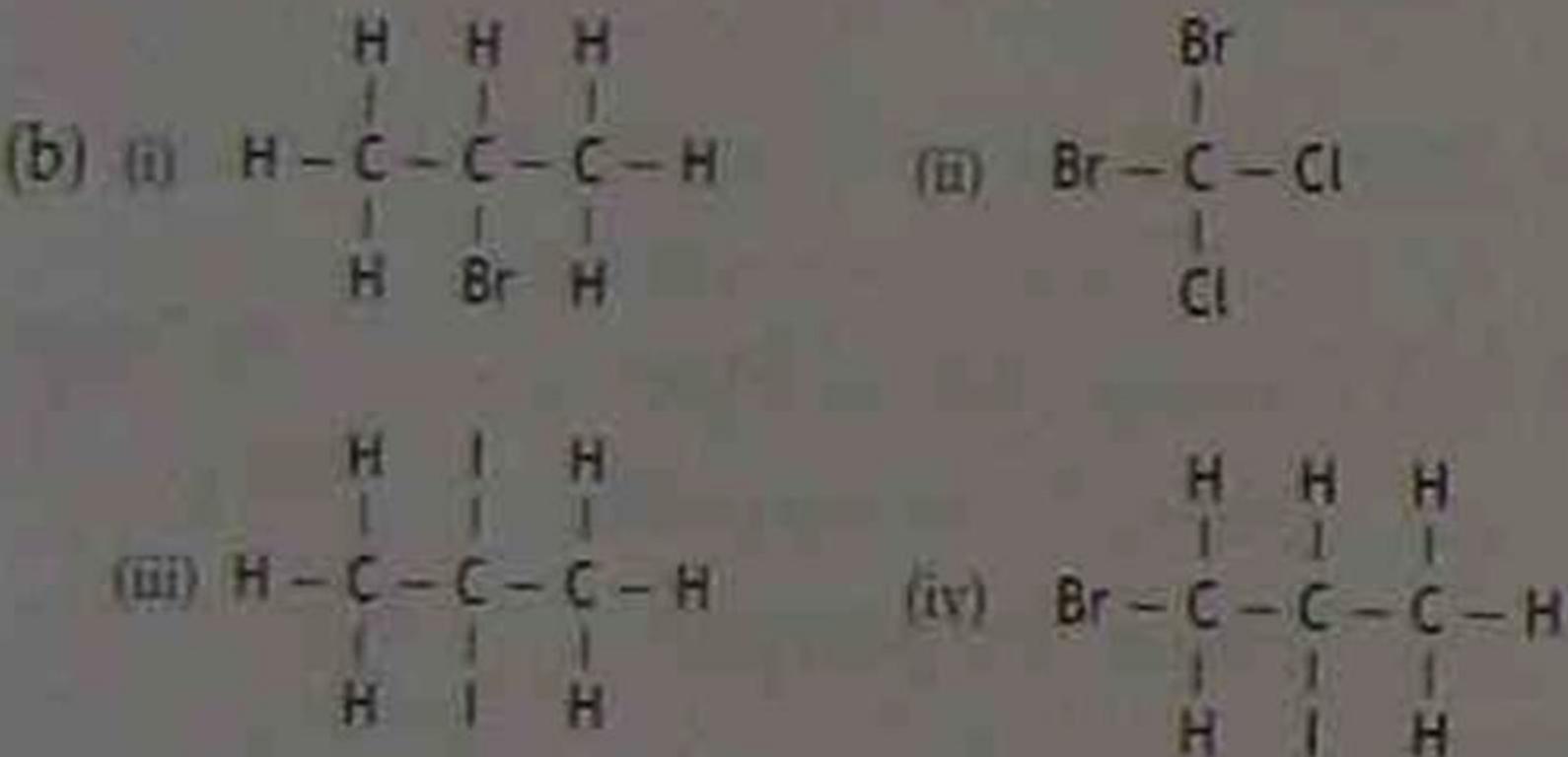
Rules for naming haloalkanes

Haloalkanes

1. Bromo-, chloro-, fluoro-, and iodo- are used as prefixes to the hydrocarbon name.
2. The position of the halogen (halo) atom is denoted by a number if more than one of a particular type of halo atom is present, di-, tri-, tetra- are used and a location number is given for each such atom.

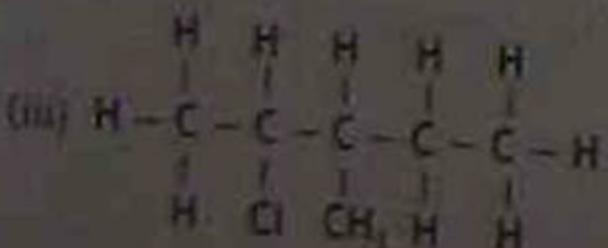
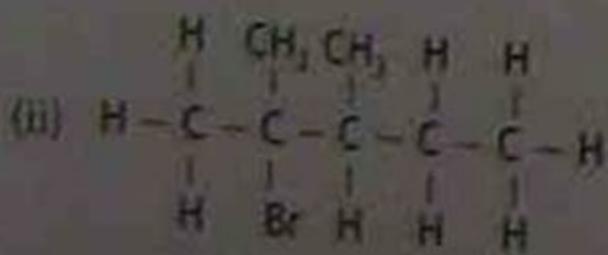
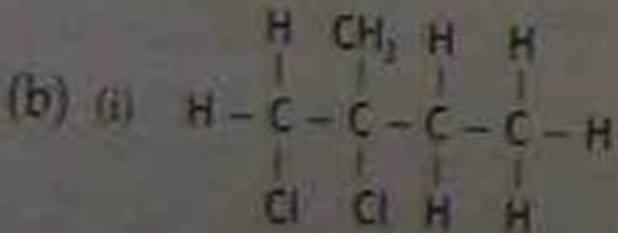
3. If more than one type of halo atom is present, they are listed alphabetically with any di-, tri-, tetra- being ignored in deciding this order.
4. Halo atoms are given before alkyl side chains.

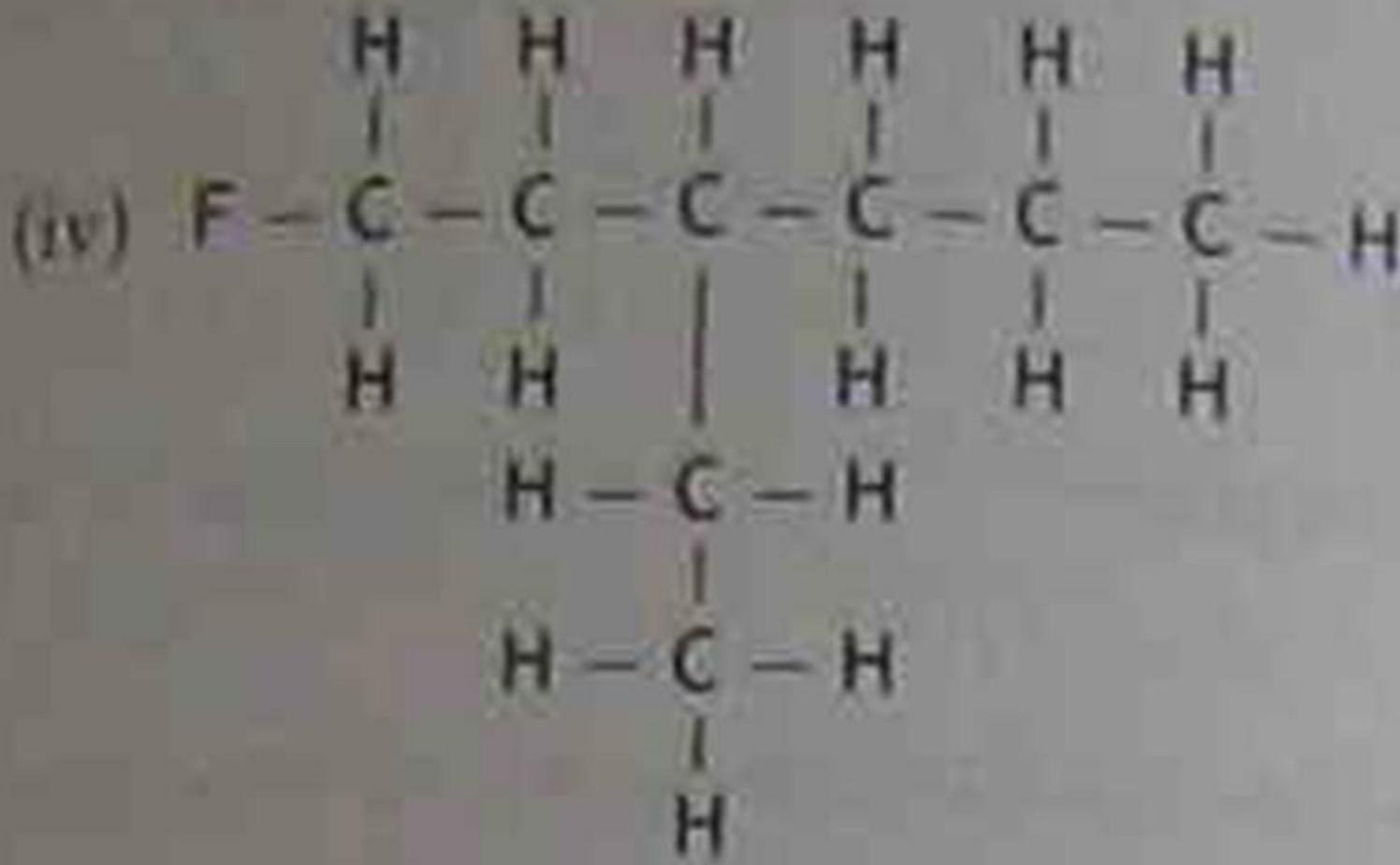
- (a) (i) 2-bromo-3-chlorobutane
 (ii) 1,1-dibromo-2-chloroethane
 (iii) 1-chloro-4-iodobutane
 (iv) 2-bromo-4-chloro-3-iodopentane



Exercise 2

- (a) (i) 1-chloro-2-methylpropane.
(ii) 2-bromo-2-methylpropane.
(iii) 1-chloro-3-methylbutane.
(iv) 2-iodo-4-methylhexane.





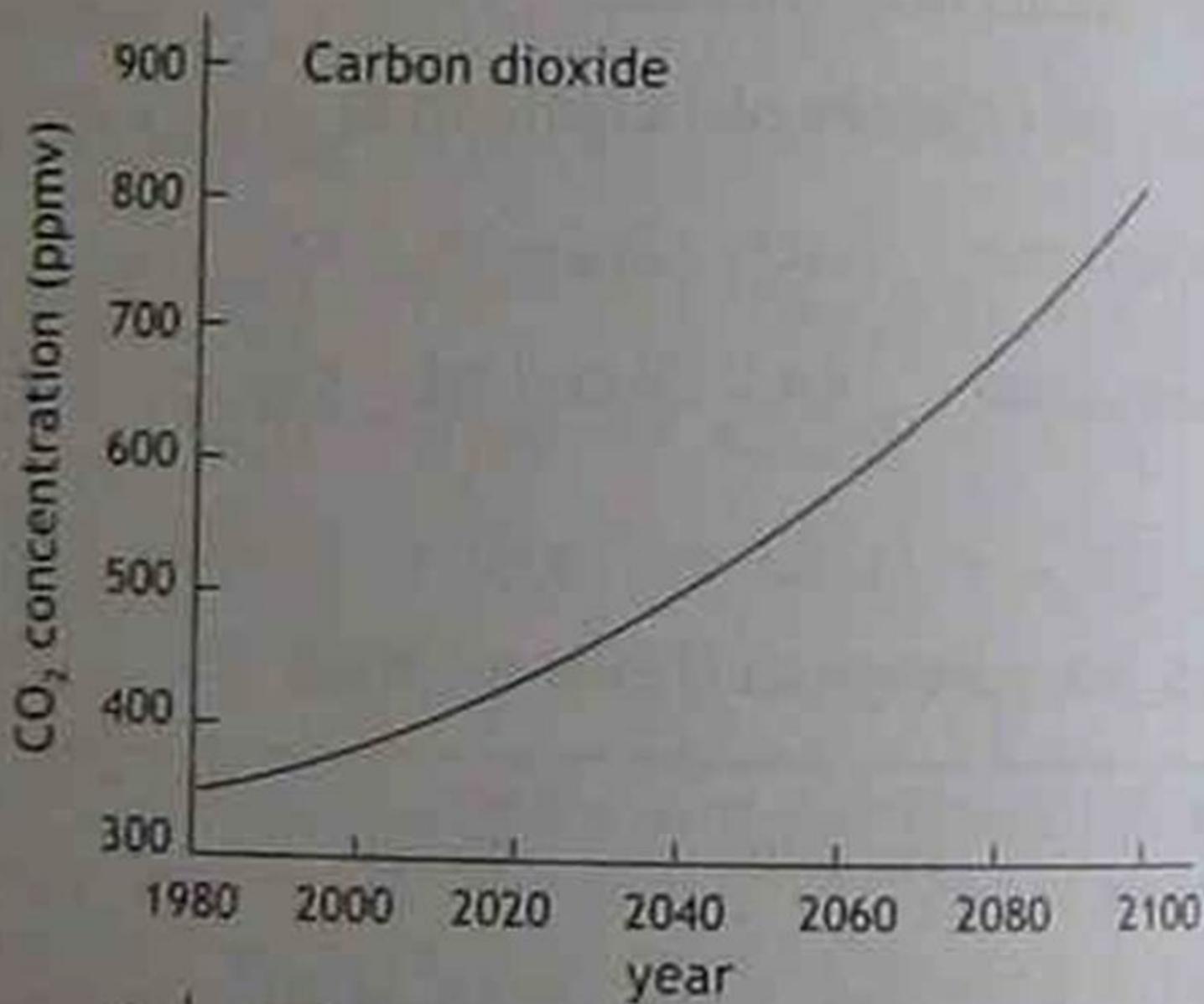
3.15

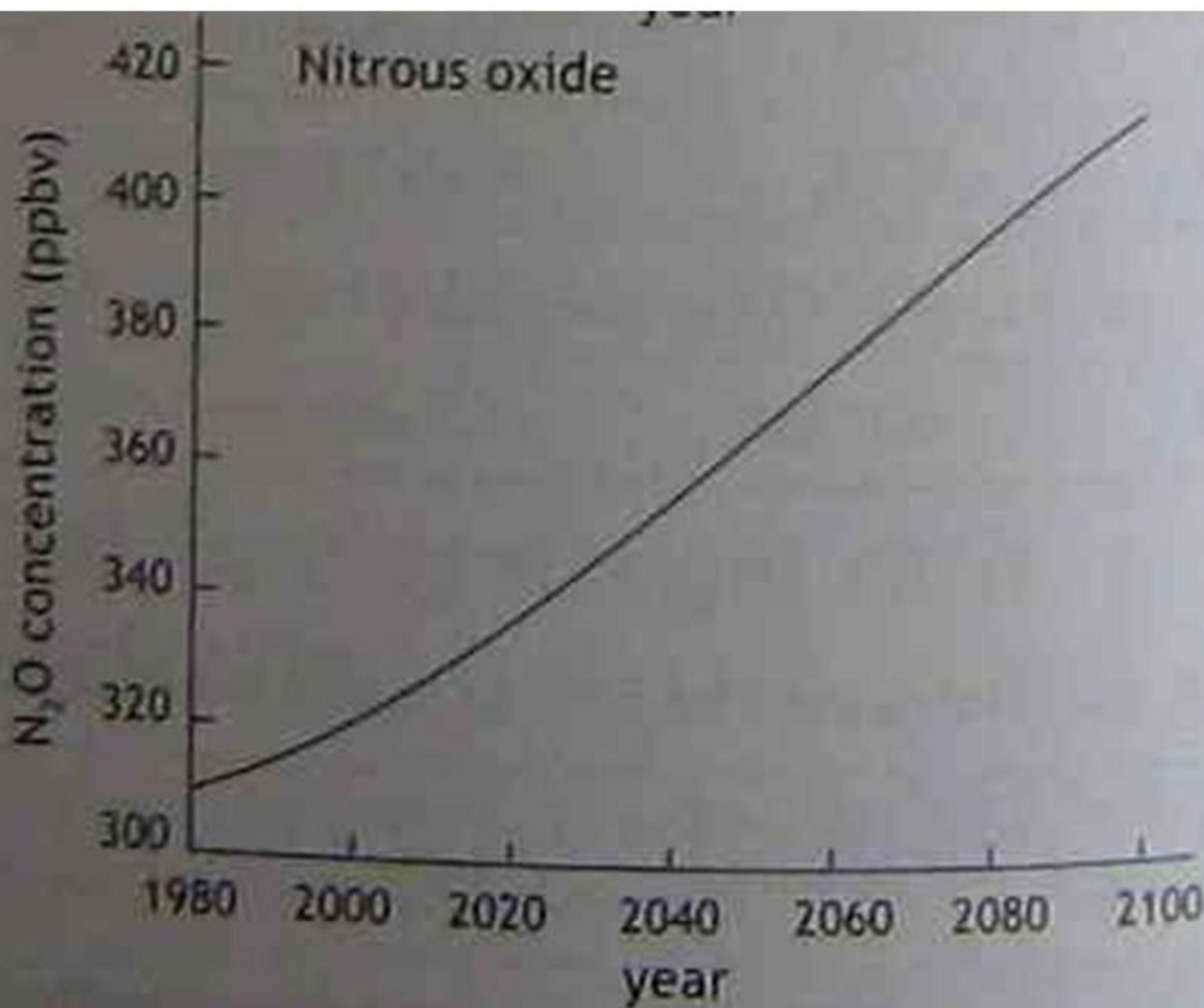
The enhanced greenhouse effect

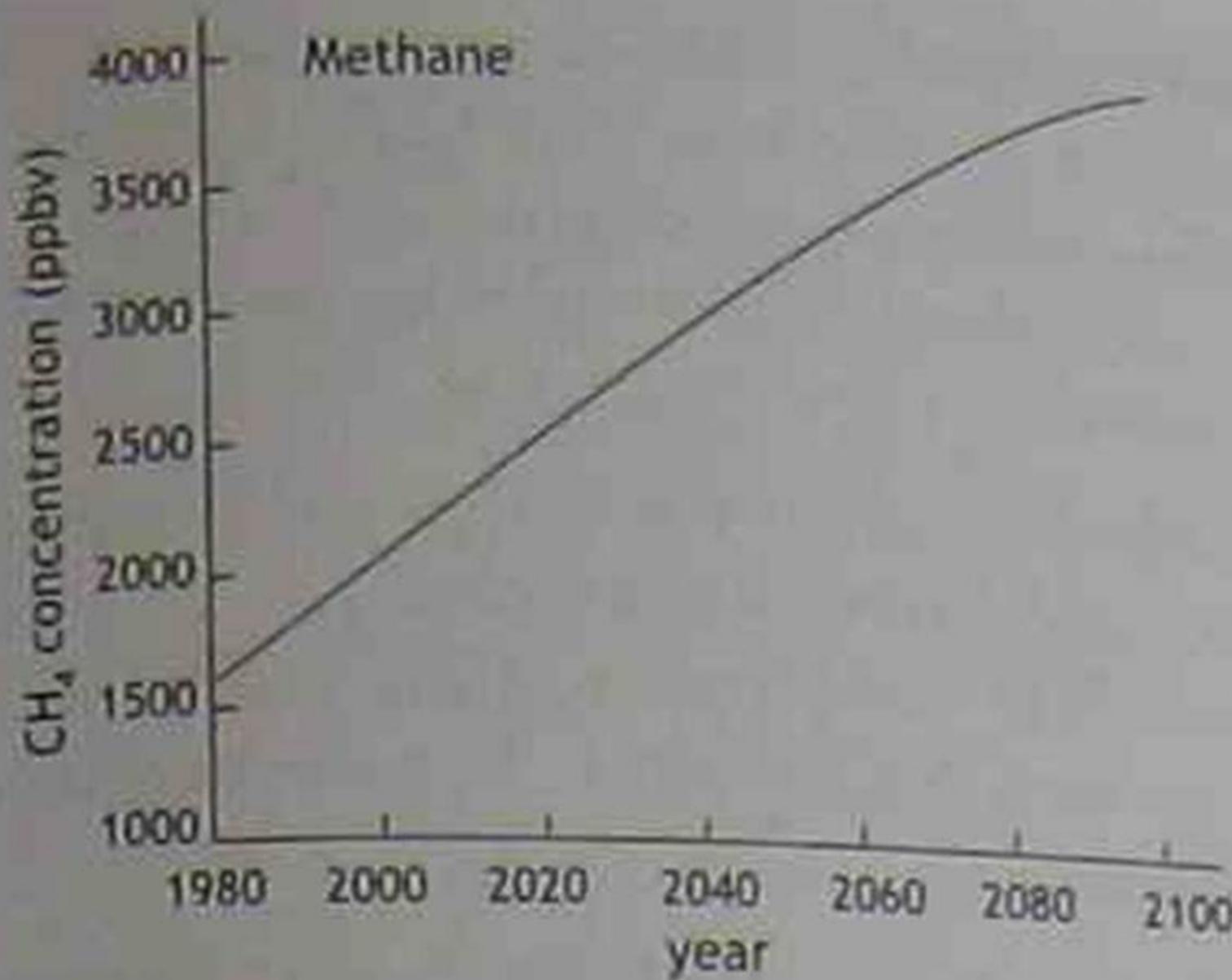
The following graphs are a result of the following assumptions put forward by the Intergovernmental Panel on Climate Change (IPCC):

- Global population reaches 9.5 billion by 2050.
- Economic growth in OECD countries is 2–3% per year, and 3–6% in Eastern European and developing countries.

- Energy supply is coal-intensive.
- Carbon dioxide controls are modest.
- Deforestation continues until the tropical forests are depleted.
- The Montreal Protocol governing the release of CFCs is implemented, but with partial compliance only.







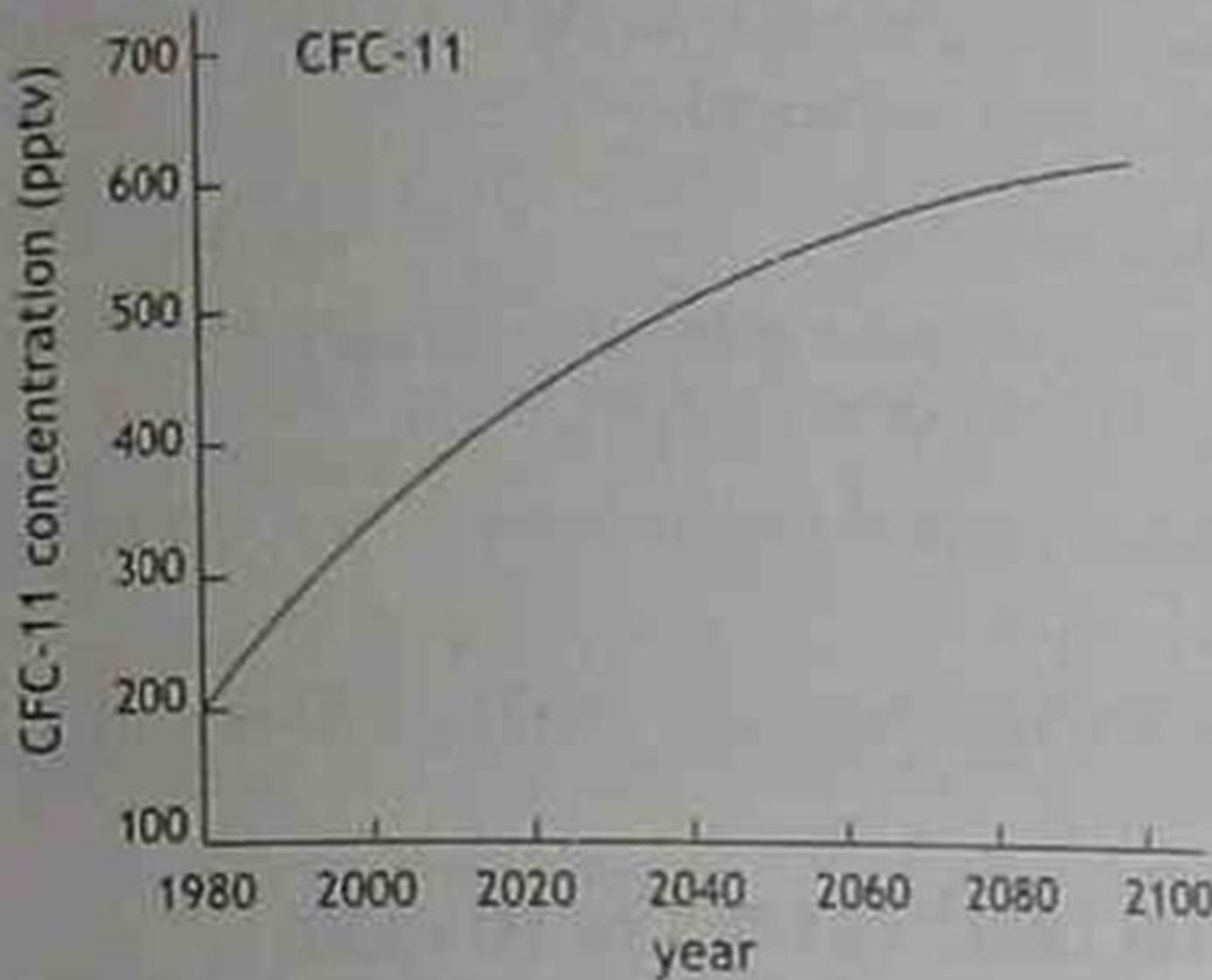


Figure 3.11 Atmospheric concentrations of greenhouse gases

Predictions of future global changes in climate

These predictions include

- a rise in sea level (20–50 cm);
- tropical cyclones may become more intense;
- temperature rises (1– 4°C) may occur; and
- there may be major shifts in the Earth's climatic zones.

To limit the impact of the enhanced greenhouse effect

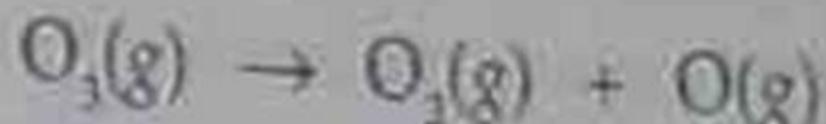
- alternatives to fossil fuels should be developed;
- energy conservation should be encouraged;
- tree plantings should be promoted; and
- the use of CFCs must be phased out.

3.16

Depletion of the ozone layer

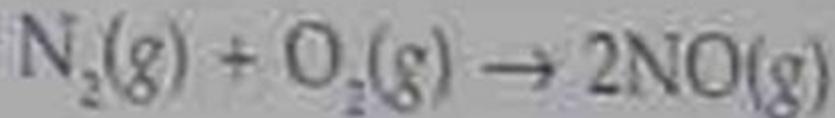
Changes caused by human activity are not confined to the troposphere but extend into the stratosphere. Ultraviolet radiation in the stratosphere releases the chlorine in manufactured CFCs with the consequence that ozone is destroyed. The ozone layer absorbs high energy ultraviolet radiation.

which could be damaging to life if it reaches the Earth's surface. Ozone in the stratosphere is constantly being formed and decomposed by natural effects. The ozone formed strongly absorbs ultraviolet radiation (230–290 nm band) and undergoes photochemical decomposition to form O_2 and oxygen atoms. The ozone then reforms releasing heat energy:

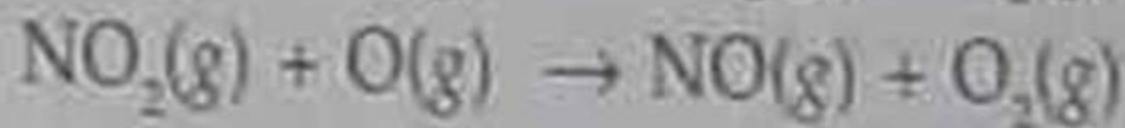
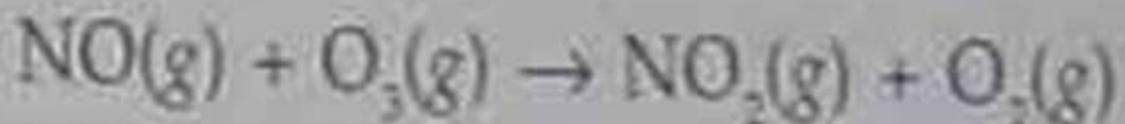


When supersonic aircraft destined to fly at very high altitudes were on the drawing board, warning was given that the jet engines could produce nitrogen oxide (NO) which could act as a catalyst in the decomposition of ozone (O_3).

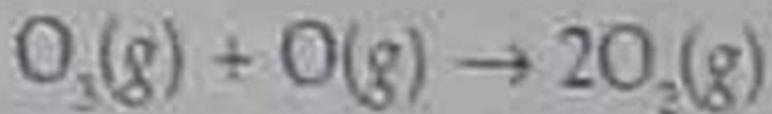
In the engines



In the stratosphere



The net effect is



The high flying aircraft fleets were never developed as a result of commercial decisions. The Concorde (a prototype) is still flying. As explained earlier, the CFCs have seriously depleted the ozone layer by releasing free chlorine atoms (one chlorine atom could remove almost 100 000 ozone molecules). Halons, which are similar to CFCs, where chloride atoms are replaced with bromine atoms and which were used in fire extinguishers, have an even greater damaging effect on the ozone layer, e.g. CBrF_3 and CBr_2F_2 .

Ozone loss is greatest over Antarctica, the decline being most significant at the beginning of spring. In 1982, specially equipped aircraft flew at a height of 18.5 km across the boundary of ozone destruction and found ClO (free radicals) at least 100 times the normal level. The chlorine atoms were from CFCs. Ozone loss is worst in the World's coldest region because of polar stratospheric clouds (PSCs) which form when temperatures fall below -80°C . In 1986,

it was suggested that these clouds are necessary for the chemical reactions to occur late in the Antarctic winter. Once spring appears and light shines on the PSCs, rapid destruction of ozone occurs.

With a continuing rise in temperature, the PSCs are reduced and the ozone destruction levels off. The ozone depleted air eventually disperses to areas farther from the South Pole. The greater the loss of

stratospheric ozone, the more UV-B reaches ground level. Assuming that global CFC release is soon halted (in line with the revised Montreal Protocol of 1990) the area of the ozone 'hole' is likely to increase since Antarctic stratosphere ozone levels will take several decades to recover. Peak ozone depletion levels are expected in 2002.

Ozone concentrations are measured in Dobson units. One unit represents one molecule of ozone to every billion molecules of air. The 'hole' in the ozone layer is a region where the concentration of ozone has been reduced.

Water analysis

- Before you start designing and planning your sampling program, look at your local catchment area and determine the factors which may be polluting the waterway.
- When collecting samples, for safety reasons
 - (i) work in pairs,
 - (ii) always wear gloves and safety glasses, and
 - (iii) place all rubbish in a plastic bag for removal from the site.
- Take water samples as far away from the bank and as close to midstream as possible.

Chemical reactions in the Winkler determination of dissolved oxygen

1. $\text{O}_2(\text{dissolved}) + 4\text{Mn}^{2+} + 8\text{OH}^- \rightarrow 2\text{Mn}_2\text{O}_3(\text{s}) + 4\text{H}_2\text{O}$
2. $\text{Mn}_2\text{O}_3(\text{s}) + 6\text{H}^+ \rightarrow 2\text{Mn}^{3+} + 3\text{H}_2\text{O}$
3. $2\text{Mn}^{3+} + 2\text{I}^- \rightarrow 2\text{Mn}^{2+} + \text{I}_2$
4. $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$
thiosulfate tetrathionate

Thus 1 mole of $\text{S}_2\text{O}_3^{2-}$ is equivalent to 0.5 mole of I^- , which is equivalent to 0.25 mole (8.00 g) of O_2 .

Significance

The concentration of dissolved oxygen (DO) in water is an important parameter in the assessment of water quality. The survival of plants and animals in any body of water depends on the ability of the water to maintain a minimal concentration of dissolved oxygen. Oxygen in the water is replenished by absorbency from the atmosphere and from photosynthesis. The primary causes of oxygen

from photosynthesis. The primary causes of oxygen depletion are the presence of biodegradable wastes and the excessive growth of plant life. This latter effect, called eutrophication, follows a build-up in the levels of plant nutrients such as ammonium nitrate or phosphates. In a river or lake with a low DO concentration (less than 10–20% saturation) only anaerobic bacteria survive. The metabolic products include NH_3 and H_2S .

Table 3.7 Tests for some metals found in water (all metals except Group I must be absent)

Ion	Reagent (or test)	Positive result (colour)
Al^{3+}	aluminon	pink-red
Mg^{2+}	magneson I	light blue
Na^+	(flame test)	yellow
K^+	(flame test)	lilac (through cobalt glass)
Ca^{2+}	(flame test)	brick-red
NH_4^+ and NH_3	Nessler's reagent	yellow-brown

Table 3.8 Tests for some ions

Anion	Reagent	Positive result
PO_4^{3-}	acidify with HNO_3 , then add excess ammonium molybdate solution	a yellow crystalline precipitate of ammonium phosphomolybdate
Cl^-	silver nitrate solution	white turbidity which darkens on exposure to light
S^{2-}	lead acetate solution or paper	a black deposit of PbS is formed
SO_4^{2-}	boil with HCl (to expel CO_2) and add barium chloride solution	a white precipitate of BaSO_4 forms

Heavy metal pollution of water

Detection

This can be carried out by precipitation with the sulfide ion. For qualitative testing to be carried out, the water sample must be concentrated by boiling (500 mL to 50 mL).

Trace amounts of Zn, Cu and Mn (0.05 mg L^{-1}) are usually present in natural waters. Zinc and copper may be present at higher levels in irrigation water, due to extensive use of galvanised iron, copper and

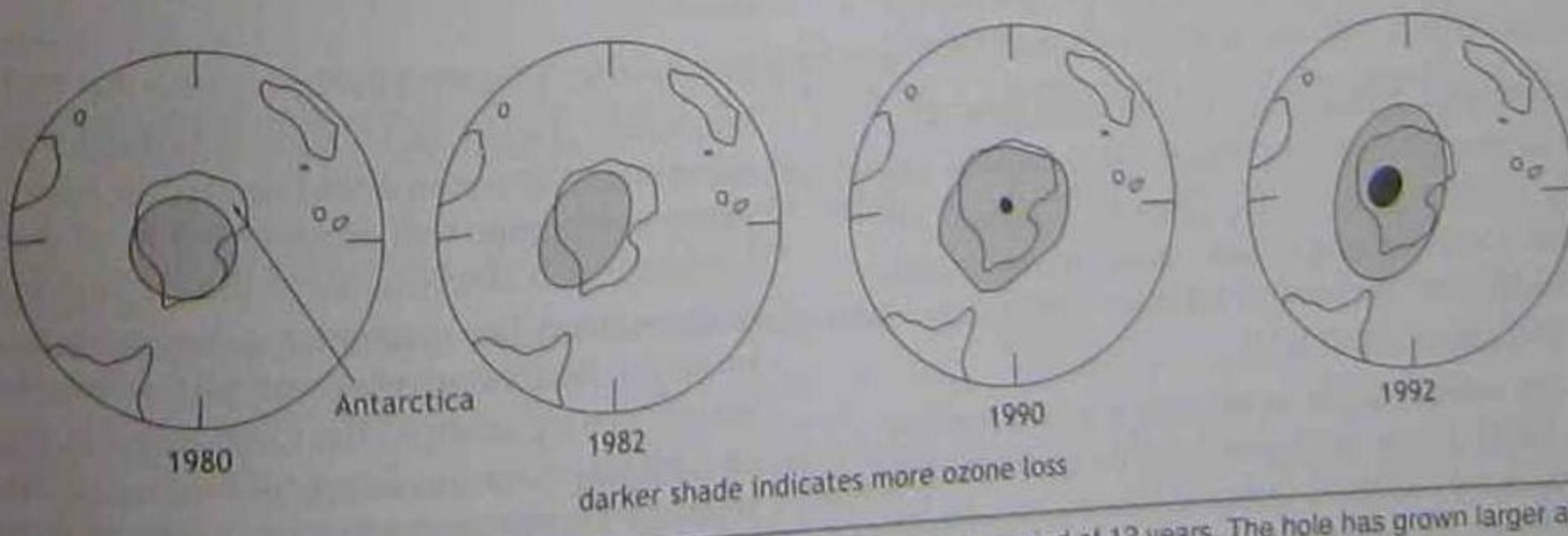


Figure 3.12 Antarctic zone. The development of the Antarctic ozone hole over a period of 12 years. The hole has grown larger and ozone loss become more severe in the centre.

brass in plumbing fixtures and for water storage. For irrigation, acceptable levels are 0.2 mg L^{-1} for Cu and 2.0 mg L^{-1} for Zn and Mn. Concentrations are measured by AAS using direct aspiration.

Table 3.9 Spot testing

Ion	Reagent	Positive result (colour)
Fe^{2+}	ammonium thiocyanate	blood-red
Cu^{2+}	* dithizone in 1,1,1-trichloroethane	yellow-brown
Pb^{2+}	* dithizone in 1,1,1-trichloroethane	brick-red
Zn^{2+}	* dithizone in 1,1,1-trichloroethane	pink

* Paper chromatography can be used. Ions are in 2 M HCl. Solvent is acetone, HCl and H_2O in ratio of 8:1:1. Dithizone solution is sprayed onto the paper after the movement of the solvent front to identify the cations.

3.18 Factors affecting concentrations of ions in natural water systems

Rivers

- Groundwater which has increased concentrations of Ca^{2+} and Mg^{2+} is a result of water passing through limestone areas, e.g. area around the Jenolan Caves in New South Wales.
- Increased salinity in river systems where, due to the clearing of native forest, the recharge rates for groundwater have increased and, with rising groundwater, dissolved salts are brought to the surface, e.g. the Murray-Darling catchment. Sodium concentrations in the Murray River near Adelaide are as high as 60 mg L^{-1} .
- An increase in the use of fertilisers containing phosphates and nitrates raises the amount of

nitrogen and phosphorus in water run-off. At the same time there is a reduction of the flow of water in inland rivers due to the removal of water for irrigation, industry and domestic supply. Nitrogen and phosphorus are also carried into rivers from sewage treatment plants, irrigation drains and extensive animal industries. As a result, algal blooms can form. Levels at Swan Hill in Victoria can reach 0.8 mg/L of nitrogen and 1.0 mg/L of phosphorus.

Oceans

The disposal of sewage and other aqueous effluents from large coastal cities in a way that does not compromise the use of the coastal environment is an ongoing problem. To define the dispersion and subsequent ecological impact of the released waste waters, radiotracers are used to monitor sewage releases to the ocean. Marine pollution is worst near the shore.

Sewage can over-fertilise areas of the sea, especially in late summer when, due to high light intensity, eutrophication can occur. The death and decay of such plankton blooms can prove fatal to fish. Another pollutant in ocean waters which can affect shellfish, e.g. oysters, is lead. Ninety-eight per cent of lead in ocean waters is estimated to come from the atmosphere, that is, from motor car emissions.

Treatment of waste water

Until 1991, millions of tonnes of raw sewage were dumped close to Sydney's popular beaches. Ocean outfalls were opened in 1991 to pump sewage through pipelines 4 kilometres out to sea and release it 80 m under the surface. At the Malabar waste treatment plant near Sydney, radiotracers are used near the deep ocean outfall to validate the plant's computer models. The two radioisotopes used are gamma-emitting gold-198 to provide accurate information about the dispersing plume, and tritium which is used for accurate dilution measurements.

Modern sewage treatment involves

Modern sewage treatment is a four-stage process:

- **Preliminary treatment** by screening to remove the larger floating and coarser suspended solids. Air is bubbled through the mixture to cause turbulence and to remove odours. Total solids in raw sewage is about 0.1%.

- **Primary sedimentation** where settling tanks allow about 60% of the suspended solids to settle out. The primary sludge is pumped into heated sludge digesters. At Malabar, the clarified liquid is

treated with chlorine and released into the sea.

- During secondary treatment, bacteria already present act on the effluent from the primary treatment process which has been pumped into aeration tanks where air is bubbled through the mixture. This is called the 'activated sludge' method, which can remove up to 90% of the suspended solids.

- The final stage is *chlorination* which removes most of the remaining bacteria. The resulting effluent is released into rivers, lakes or the Pacific Ocean and is used for irrigation.

Note: Chemically, the objective of the 'activated sludge' method is the complete conversion of the wastes to inorganic materials. This is dependent on the ability of the micro-

- (i) the ability of micro-organisms to form aggregates (flocs) which absorb colloidal materials and allow oxidation and settling.
- (ii) the chemical hydrolysis and oxidation of the soluble carbohydrates and proteins to form, for example, CO_2 , H_2O , NH_3 , NH_4^+ , as well as nitrate, sulfate and phosphate ions.

In this process, active micro-organisms are continually recycled.

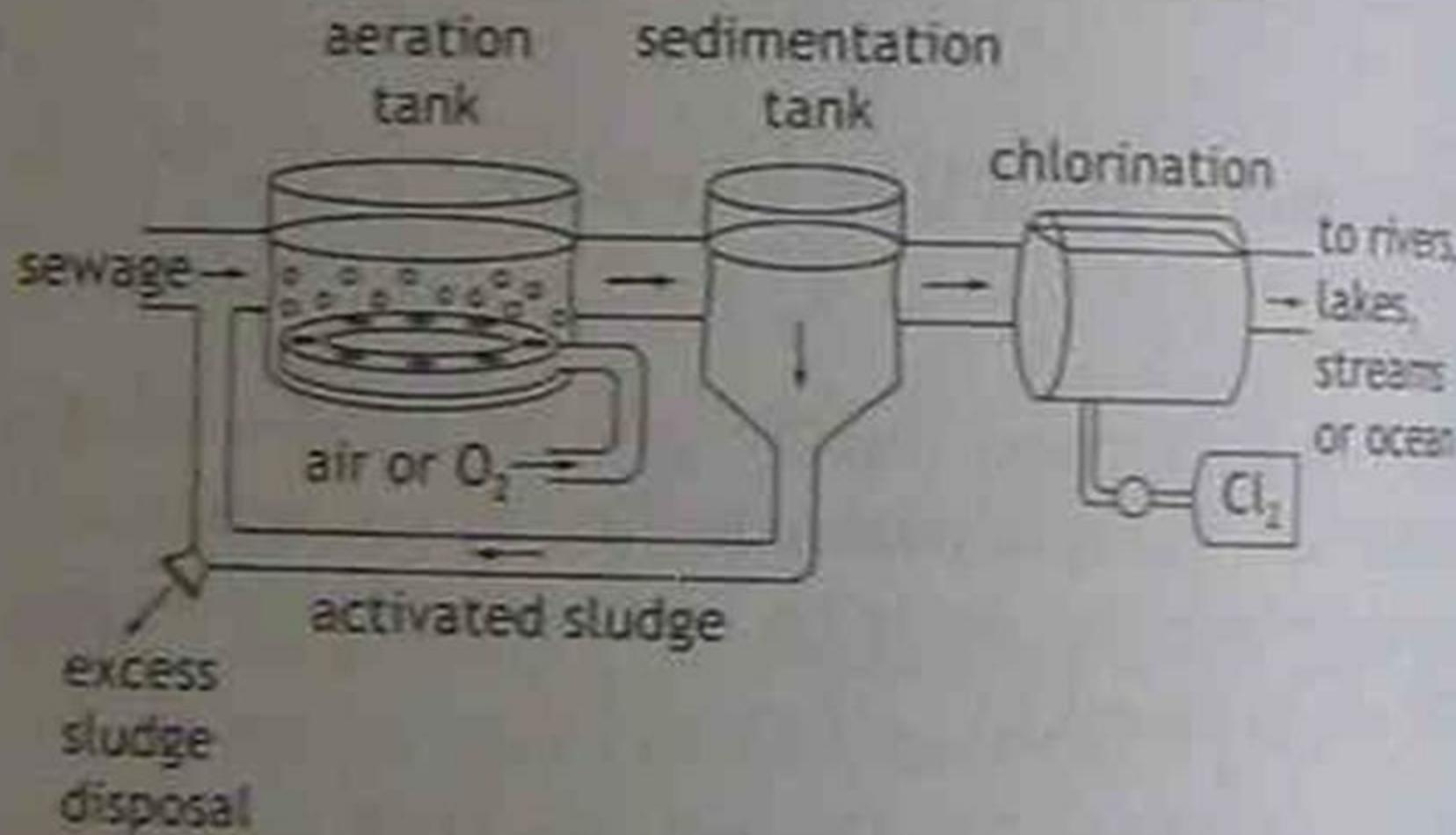


Figure 3.13 Secondary sewage treatment by the 'activated sludge' method

Other methods for secondary treatment include the following:

- *The Sirofloc process* developed by the CSIRO. Magnetite (Fe_3O_4) in an unmagnetised state is stirred into the water. Acid is added to adjust the pH of the solution to a range of 5–7.5, so that the magnetite will absorb most of the organic matter in the sewage. The magnetite is then passed close to large permanent magnets and forms large rapidly setting clumps. The clear water is run off and the magnetite can be reactivated using NaOH solution. This process needs only 10% of the land area and is much faster than other techniques.

- *Trickle filter method.* Effluent from primary treatment flows over a bed of rocks on the surface of which aerobic bacteria grow. These bacteria break down the organic matter in the sewage. Gaps in the rocks allow circulation of the air which the bacteria require to function.
- *Lagooning.* Most of Melbourne's sewage is treated at Werribee Farm by this method. Raw sewage is treated by lagooning and by soil and grass filtration. Lagooning is a less popular method because of the large amounts of land required.

Treatment of drinking water

In Australian cities, water is treated before being supplied to consumer. The following steps are involved:

- *Flocculation* is the addition of electrolytes to force colloidal particles to aggregate and form filterable precipitates. The electrolytes neutralise the surface charge on the colloidal particles and allow flocculation to occur. The higher the charge on the electrolyte ions, the more efficient the electrolyte is as a floccing agent. Aluminium ions (Al^{3+}) are effective at floccing negatively charged colloids.

...⁻⁶ g/g very charged colloids,

Table 3.10 Water analysis – some tests

Test	Reason
Temperature Use an alcohol thermometer in a hard plastic cover.	Temperature influences the amount of dissolved oxygen hence the survival of aquatic organisms.
pH Use a pH meter in a hard plastic cover, pH paper or Universal Indicator solution.	pH is a measure of acidity or alkalinity of the water. pH of rain water = 5.5–6. pH will rise during photosynthesis (CO_2 drops). Acidic water ($\text{pH} < 5$) is most damaging to eggs and larvae of aquatic organisms.
Turbidity Use a Secchi disc  (you can make one from a tin lid and string), or use a 500 mL measuring cylinder standing on paper marked with a cross.	Turbidity is a measure of water clarity. Suspended solids can stop light reaching submerged plants and also raise water temperature.

Total dissolved solids

Use an appropriate TDS meter. Freshwater meters (0–1990 ppm). Dual range brackish water meters (0–19 900 ppm). Saltwater meters – higher range to above 35 000 ppm.

This is a conductivity test of available ions in the water. Most important ions include Ca^{2+} , Na^+ , K^+ , Fe^{2+} , Fe^{3+} and HCO_3^- as well as ions containing phosphorus, sulfur and nitrogen.

Dissolved oxygen (DO)

1. Use the Winkler titration method (see Experiment 3.1).
2. Use a colorimetric method ('Smart' colorimeter for field work).

Sample must be collected under water to ensure that there are no trapped air bubbles. Collect two samples, one for a DO and one for a BOD determination.

The dissolved oxygen test measures the current oxygen status of a stream or river. DO levels vary with temperature. DO levels are highest in the afternoon (due to photosynthesis) and lowest just before dawn.

Biochemical oxygen demand (BOD)

The sample is kept in a dark cupboard at collection temperature for 5 days, then the dissolved oxygen is determined.

The BOD measures the rate of consumption of oxygen by organisms in the water over a 5-day period.

Salinity in water

A determination of the chloride content using AgNO_3 soln. (2.73 g/100 mL) and K_2CrO_4 as the indicator. The end point of the titration is given by the reddening of the AgCl precipitate. The volume of the AgNO_3 used = chloride content in g L^{-1} .

Hardness

Calcium ions are usually determined by complexometric titration using EDTA (ethylenediaminetetraacetic acid) at a pH of 12–13. At this pH, Mg^{2+} ions are precipitated and not complexed with EDTA.

Magnesium ions also contribute to total hardness of water. They can be titrated by EDTA at a pH = 10. The titration measures both Ca^{2+} and Mg^{2+} so a correction must be supplied using the result of the first Ca^{2+} determination.

Potentiometric techniques using ion selective electrodes can be used. Soluble Ca^{2+} and Mg^{2+} can be measured by AAS.

Many species can only survive in a very narrow range of salt concentrations since salts control osmotic pressure.

Ca^{2+} is a major contributor to the hardness of water. Temporary hardness is due to $\text{Ca}(\text{HCO}_3)_2$, which, on boiling, deposits CaCO_3 as a scale. Industries involving low pressure boilers use water softened by an ion exchange process. Mg^{2+} levels are often high in irrigation water and can cause scouring in stock. Soil structure can also be affected. Ca^{2+} and Mg^{2+} , when combined with Cl^- and/or SO_4^{2-} ions, cause permanent hardness which is not removed by boiling.

Gravimetric method

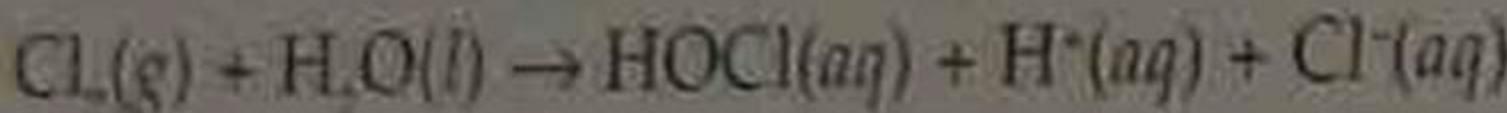
This is sometimes used to detect and/or determine the amount of CaCO_3 , precipitated from a measured volume of hard water by the addition of a standard Na_2CO_3 solution (usually about 0.02 M). Flame testing can also be used to detect Ca^{2+} ions (brick-red colour in a non-luminous Bunsen flame).

e.g. clay colloids. Aluminium ions are used in preference to iron (III) ions as the iron ions impart a metallic taste to the water. Calcium hydroxide is added to adjust the pH of the water.

- **Settling.** In Sydney, under the present system, primary settling tanks are located with filtration systems, e.g. at Woronora dam, Prospect reservoir, Pott's Hill and Pipe Head. The 'floc' is allowed to settle in the tanks until a sludge forms. The clear water is then moved to the filtration stage and the sludge is removed from the bottom of the settling tank.

- **Filtration.** Water from the settling tank is filtered through a bed of sand over gravel to remove other suspended solids, including mineral particles.
- **Chemical additives** to water include the following:

- (i) Gaseous chlorine which is used after filtration to destroy bacteria.



It is the hypochlorite ion (OCl^-) that removes biological contaminants, such as bacteria, so that the water becomes fit for human consumption.

(ii) Many water supplies also have fluoride ions added to them in the final stages. Certain levels of fluoride will reduce dental decay in children by being incorporated into tooth enamel (and also into bones). Excess fluoride can cause mottling in teeth. Fluoride is added as sodium fluoride (NaF), sodium silicofluoride (Na_2SiF_6) or calcium fluoride (CaF_2).

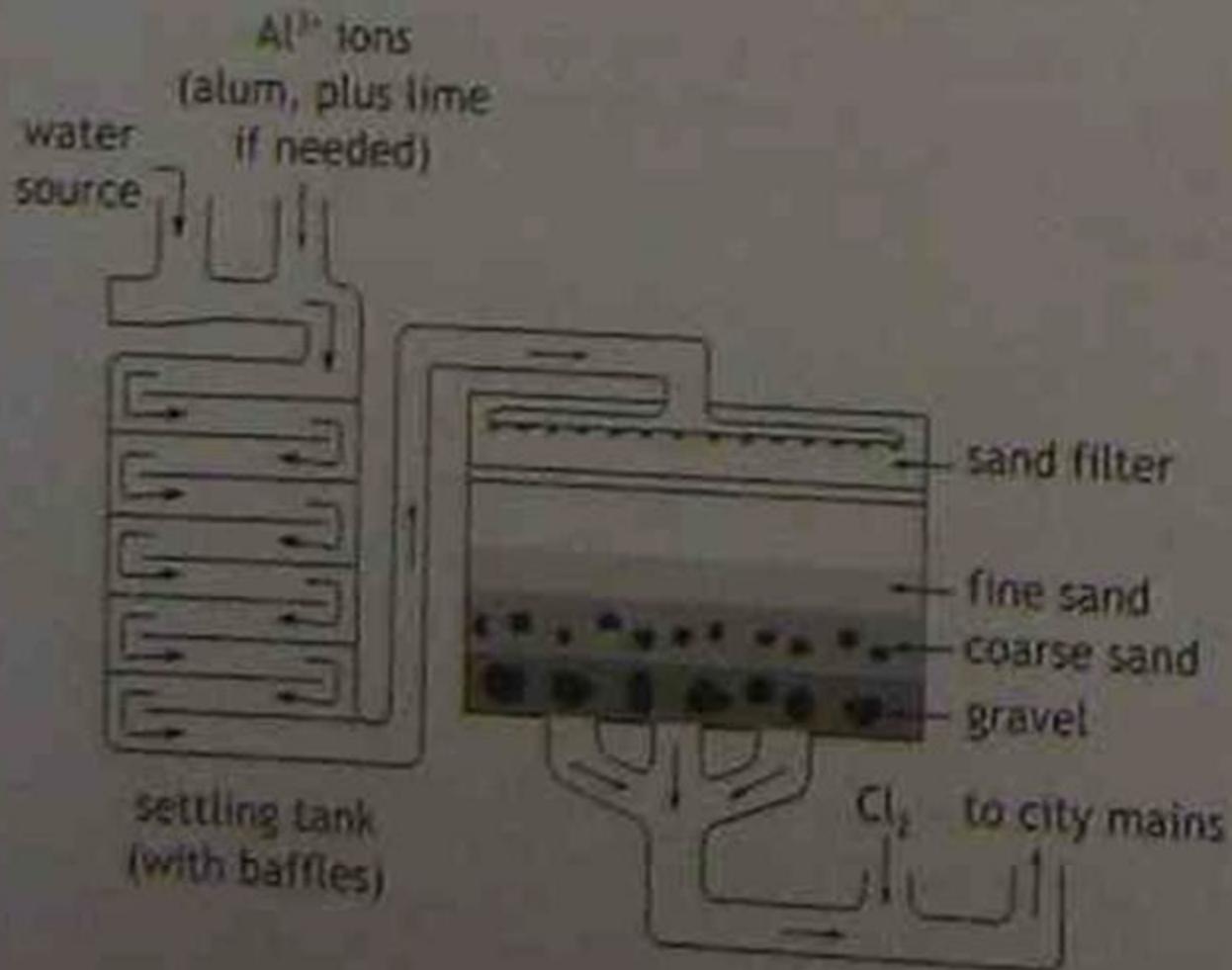


Figure 3.14 Treatment of city water supplies

3.21

Desalination of water

Desalination can be carried out by several techniques:

- *Multistage flash distillation* from seawater is used in countries where the energy costs are relatively low, e.g. Saudi Arabia.

The Commonwealth Scientific & Industrial Research Organisation (CSIRO) has developed a *Sirotherm* process where the ion exchange resin removes Na^+ and Cl^- ions from the water with a high saline level, replacing them with H_3O^+ and OH^- ions. Beads of this ion exchange resin can reduce salt levels from 3000 ppm to acceptable levels of 500 ppm for human consumption. The resin is regenerated by flushing it with hot water.

- The *reverse osmosis process* required the use of a semi-permeable membrane which allows the passage of water molecules but not dissolved solids. The salinity can be lowered from 35 000 to 500 ppm. In an industrial plant, pressure is used to reverse the natural direction of the flow of water into salt water by osmosis. Membranes are of pliable cellulose triacetate or polyamides. This process is used in many household types of water purifiers where tap water produces sufficient pressure. Many Sydney people now use

pressure. Many Sydney people now use microscopic membrane filters after the protracted cryptosporidium and giardia crisis several years ago. One type of filter with fine pores is used. Water first passes through a pre-filter, then through a pliable cellulose triacetate membrane using a reverse osmosis system, and lastly, through a post-filter containing carbon to remove any odours.

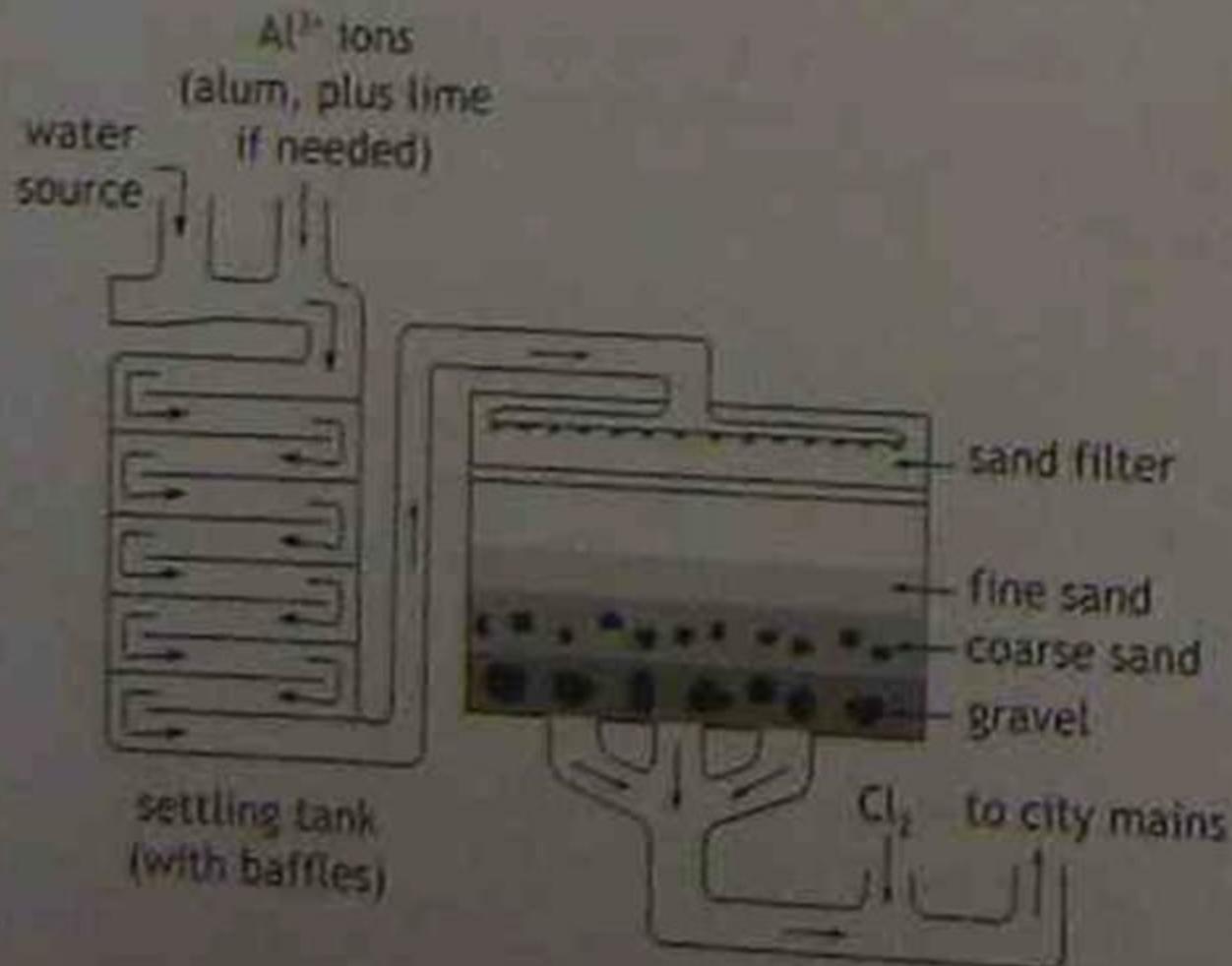


Figure 3.14 Treatment of city water supplies

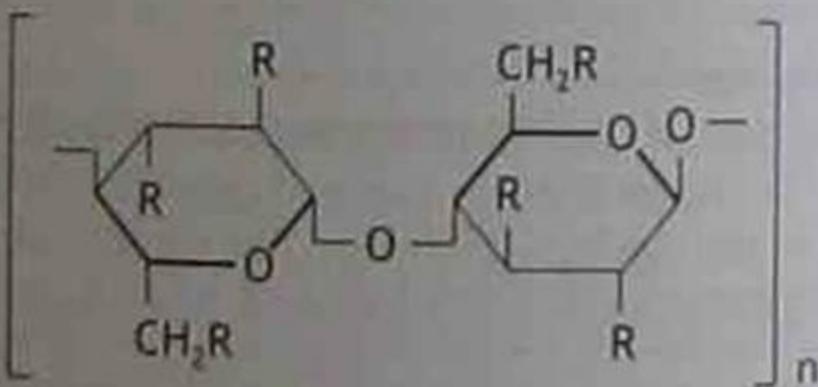


Figure 3.15 Cellulose triacetate

Another type of filter uses a polyamide type of membrane.

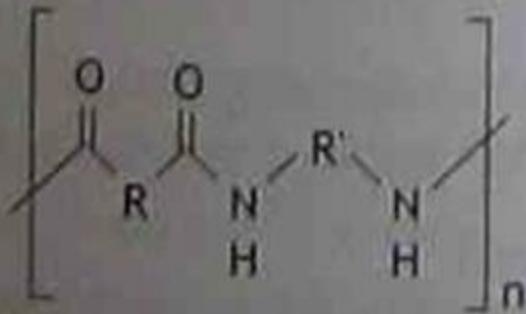


Figure 3.16 Amide link (R and R' are alkyl groups)