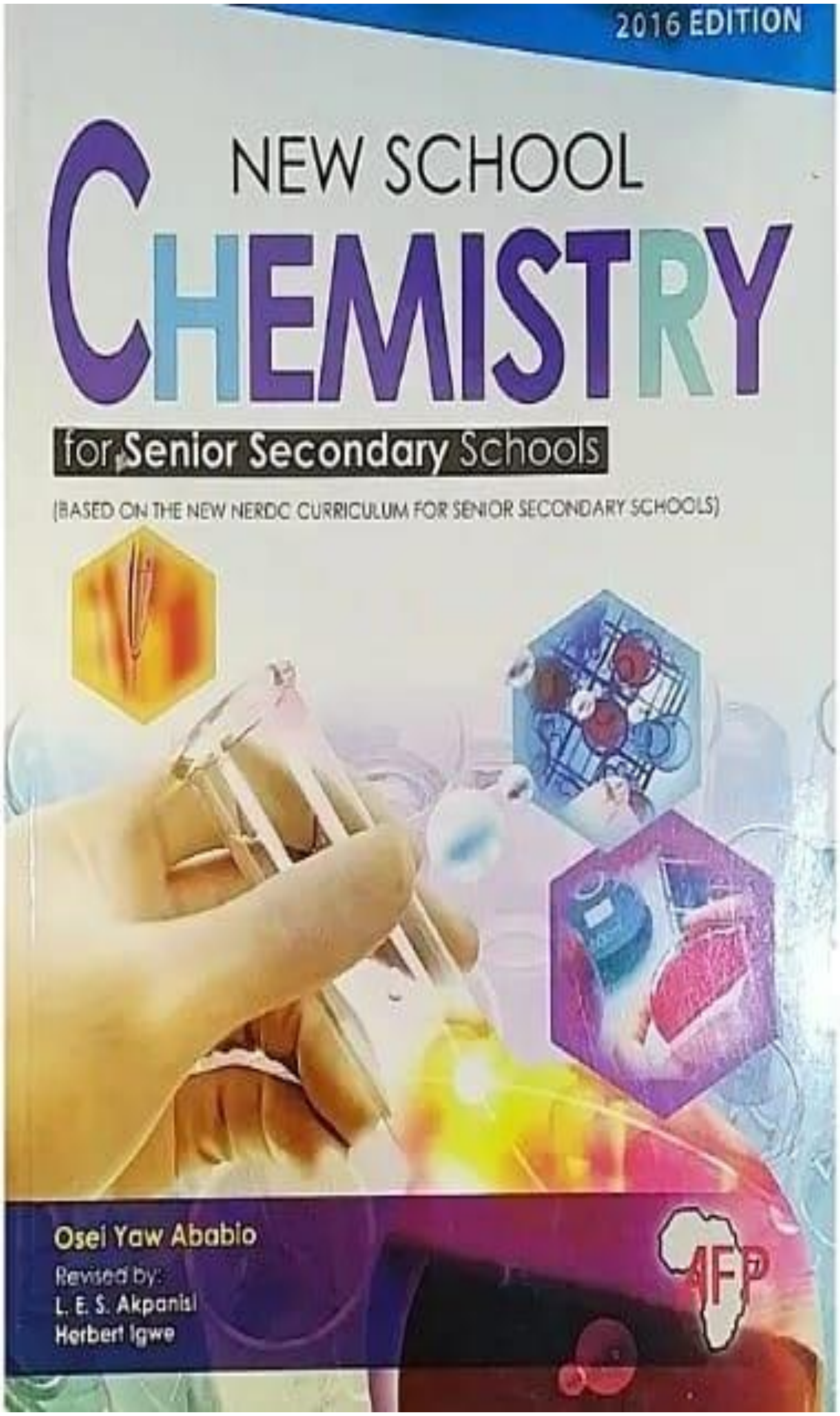

2016 EDITION

NEW SCHOOL
CHEMISTRY

for Senior Secondary Schools

(BASED ON THE NEW NERDC CURRICULUM FOR SENIOR SECONDARY SCHOOLS)

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HEMISTRY IN OUR LIFE

e see chemical changes around us all the time. miliar activities and happenings like

- lighting a match,
- cooking,
- burning firewood,
- making palm wine,
- rusting nails,
- rotting leaves

e examples of chemical reactions.

All the things we use every day such as

- soaps and detergents for cleaning,
- hair cream and perfumes for grooming,
- oil and margarine,
- plastics for a wide variety of uses

e made by chemical processes.

ses of chemistry

hemistry has contributed greatly towards providing r basic needs and improving the quality of our life.

ood Fertilizers and insecticides have helped to crease food production greatly. Chemical processes e designed especially to preserve and store food for ng periods, so that it can be exported to distant untries and is available to more people. To fight alnutrition, many foods are now enriched by the ddition of essential nutrients.

Fertilizers have contributed greatly towards improving the yield of crops

Clothing Man-made textile fibres, produced as a result of intensive chemical research, have made available a wide range of clothing materials, which can be bought cheaply.

Housing Many high-rise buildings are being constructed to overcome the present need for housing, especially in cities. Such buildings need materials like cement, concrete, steel, bricks and tiles which are produced by chemical industries. The mechanical properties of these materials are a result of chemical research.

These are some of the apparatus a chemist uses.

Chemists are doing research all the time to improve the quality of our life.

Medicine The healthy life that many of us enjoy is due to the variety of medicines that are available as a result of chemical research and technology. Financed by big pharmaceutical firms, research to find new and better drugs is going on all the time.

Transportation Modern transportation is an essential feature of today's world. This rapid development from carts pulled by animals to the latest aircraft was made possible by chemists producing suitable fuels and structural materials like alloys which are light, strong and heat-resistant.

Adverse effects of chemistry

Chemical processes and products have also affected our life adversely.

Pollution One of the main disadvantages of chemical industries is the pollution of our environment by

- chemical wastes from factories and oil refineries; and
- radioactive wastes from nuclear plants.

Oil spillage, exhaust from motor vehicles, pesticides, fertilizers and acid rain have made our environment unclean and endangered plant and animal life. Human health is also being threatened by environmental pollution. Presently, chemists are trying to come up with a fuel that will reduce the air pollution problem. They are also modifying chemical processes to recycle chemical wastes or change them to harmless products which can be safely discharged into the surroundings.

Drug abuse Drugs like heroin, cocaine and morphine are addictive. Although many of these drugs are not used in medical treatment, unscrupulous people produce and sell them at huge profits. Drug addiction is a major problem in our society, especially among the younger people.

Many countries have imposed strict laws to control pollution and drug abuse. However, the most effective control measure is education. We must use what we learn to improve our life and help to control these abuses.

The Concorde, which travels at supersonic speed, is made of many special alloys.

Chemical factories and motor vehicles are the main causes of air pollution.

Chemical research has produced materials which make the construction of buildings possible.

The dumping of solid wastes causes land pollution. This is prevented by recycling most of these wastes.

CAREERS IN CHEMISTRY

Nigeria is a rapidly developing nation with an increasing demand for skilled manpower. Many job opportunities are available for students with a knowledge of chemistry. The public and private sectors of the economy which offer such opportunities are given below.

Teaching service Chemistry teachers and lecturers in secondary schools, polyechnics, colleges of education and universities. Laboratory assistants in schools and universities.

Health service Pharmacists, biochemists, chemists, nutritionists, dietitians, doctors, nurses, medical assistants, laboratory assistants and dispensers.

Food processing Food technologists and research chemists.

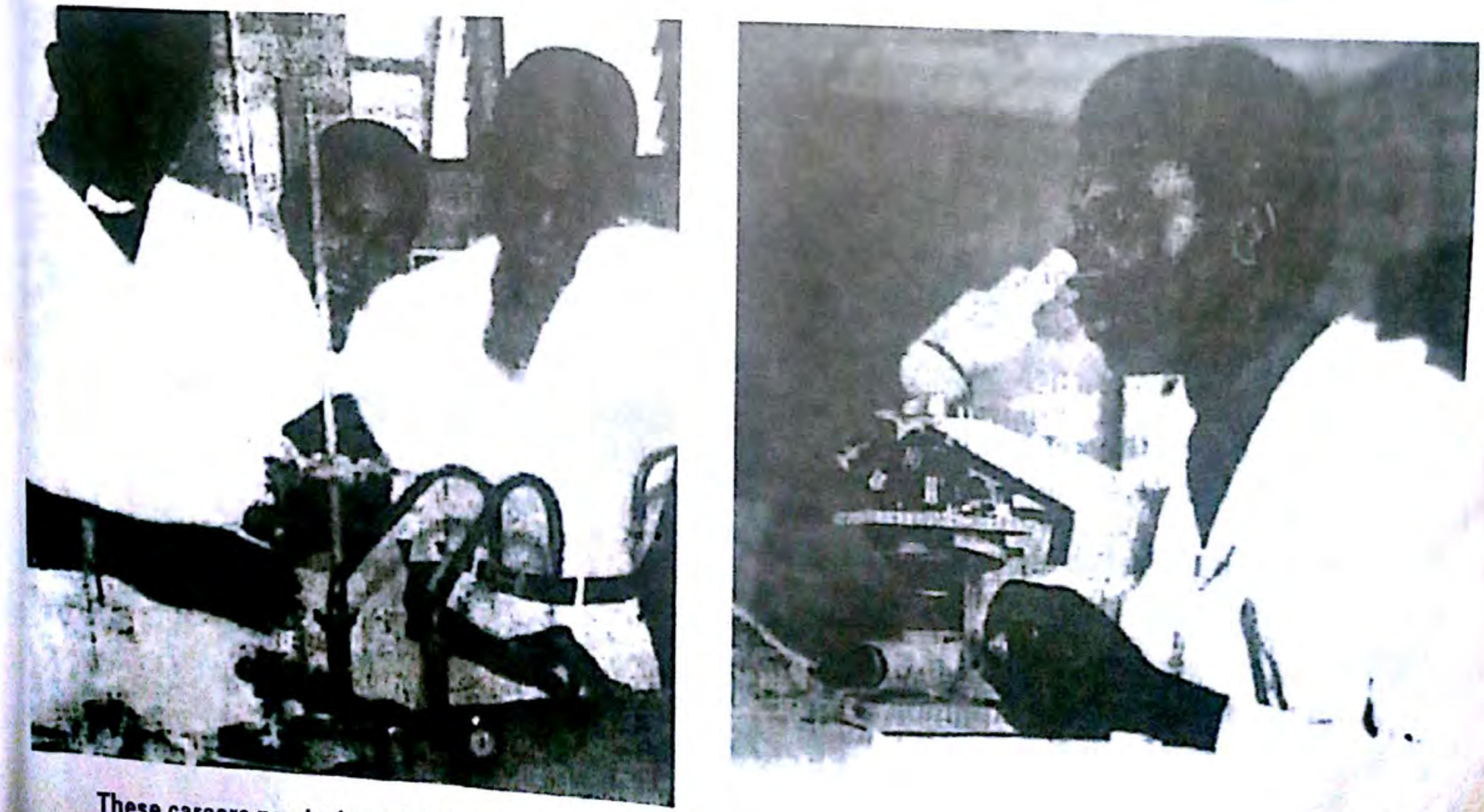
Petroleum and petrochemical industries Application chemists, research chemists, chemical engineers and laboratory assistants.

Manufacturing industry Research chemists and chemical engineers in the wide variety of manufacturing industries such as iron and steel works, and cement factories.

Extractive industry Chemists, mining engineers and geologists.

Agriculture Agricultural scientists, chemists, biochemists and physiologists engaged in research to improve the quality and yield of crops and livestock, and to advise farmers.

Forestry Scientists engaged in research to preserve and improve forests and forestry products.



These careers need a knowledge of chemistry.

EXERCISES

1. Chemistry is defined as
   - A a branch of knowledge which produces chemicals.
   - B a branch of science which makes physics, and biology clearer.
   - C the oldest branch science.
   - D the branch of science which deals with changes in matter.

2. Scientific approach to discoveries follows the order which includes
   - A further experiments and problem solving.
   - B theory, negative and positive results and experiments.
   - C experiments, hypothesis and results.
   - D observation, hypothesis and experiments.

3. Chemical hypothesis is different from chemical law in that
   - A hypothesis is not reasonable while law is reasonable.
   - B hypothesis is a reasonable explanation to observations made while law is a statement from a scientist.
   - C hypothesis is a reasonable explanation to observations while law is a statement which confirms the hypothesis after extensive tests.
   - D none of the above.

4. Chemical changes around us include all except
   - A rusting of iron nails.
   - B fading of coloured cloth.
   - C sieving.
   - D decomposing of green leaves in a compost.

5. One of these professions has no need for chemistry.
   - A miners
   - B engineers
   - C philosophers
   - D geologists

6. One of these is not a chemical change.
   - A rusting
   - B sublimation of solids
   - C slaking of quicklime
   - D fermentation of glucose

7. Which is the odd-one out?
   - A Air
   - B Urine
   - C Brass
   - D Sand

8. Separation of mixtures of solids with various sizes include
   - A magnetic separation.
   - B coarsing.
   - C sublimation.
   - D sieving.

9. Method adopted in the separation of lead II chloride from water is
   - A sieving.
   - B decantation.
   - C crystallization.
   - D distillation.

10. Fractional crystallization is a method of separating

A crude oil.

B liquid – liquid mixture.

C coal.

D solids of different solubilities in a liquid.

11. Separation of different carotenes from carrot root uses a method of

A chromatography.

B carotinization.

C distillation.

D centrifugation.

12. Which of these requires crystallization most?

A drug making

B cement making

C paint making

D perfume making

13. All except one is not a popular criteria for purity.

A melting point

B dielectric constant

C temperature

D centrifugation

14. In paper and gas chromatography respectively, the common feature between them is that they have

A solid phase and moving phase

B stationary phase and moving phase

C long phase and stationary phase

D chromatic phase and stationary phase

2 NATURE OF MATTER • SEPARATION TECHNIQUES

WHAT IS MATTER?

Matter is anything that has mass and occupies space.

By this definition, we see that almost everything in the universe is made up of matter. Examples of matter include the plants and animals around us, the food we eat, the water we drink and even the air we breathe. We ourselves are matter.

The mass of an object is the quantity of matter an object contains and is the same everywhere. The basic S.I. unit for the measurement of mass is the *mole*. For practical purposes, mass is measured in *kilograms* with a weighing balance.

In general, matter is built up of one or more of the following elementary particles: *atoms*, *molecules* and *ions*.

States of matter

Matter can exist in three physical states — solid, liquid and gas. A solid has a definite volume and shape; a liquid has a definite volume but no definite shape (it takes the shape of its container); and a gas has neither a definite volume nor shape (it fills the entire container). Matter can change from one state to another. We see some of these changes around us. The most common example of a substance undergoing a change of state is water.

$$\text{ice} \underset{\text{cool}}{\overset{\text{heat}\ 0\ ^\circ\text{C}}{\rightleftharpoons}} \text{water} \underset{\text{cool}}{\overset{\text{heat}\ 100\ ^\circ\text{C}}{\rightleftharpoons}} \text{steam}$$

Generally, a given substance changes its state when it is heated or cooled. For example, candle wax and margarine liquefy on warming and solidify on cooling. Solid iron melts into a liquid at 1 540 °C. When it is poured into a mould and cooled, it solidifies, taking the shape of the mould.

Properties of matter

Substances can be identified by the characteristics they possess. These characteristics are called *properties*. Sugar is a white solid which dissolves in water and tastes sweet, while iron has a metallic lustre; it may be magnetized and rusts with the formation of a reddish deposit.

Physical properties are properties associated with physical changes. Common physical properties of a substance include its boiling point, melting point, density, hardness, malleability, crystalline form, as well as properties which may be detected by the senses such as colour, odour and taste.

Chemical properties are those properties which are involved when matter undergoes a change to form new substances. The rusting of iron is a chemical property of iron since a new substance, iron rust, is formed.

Everything around us are composed of matter.

Physical and Chemical Changes

Matter undergoes changes. These changes may be temporary and easily reversible or they may be permanent and very difficult to reverse. The former is known as a *physical change* and the latter as a *chemical change*.

Physical changes

> *A physical change is one which is easily reversed and in which no new substances are formed.*

A change in the state of a substance is a physical property of matter. The dissolution of common salt in water is a physical change because no new substances are formed and the salt can easily be recovered from the solution.

Forward reaction

$$\underset{\text{solute}}{\textit{salt}} + \textit{water} \xrightarrow[\text{solvent}]{\text{mixing}} \underset{\text{solution}}{\textit{salt solution}}$$

Reverse reaction

$$\underset{\text{solution}}{\textbf{salt solution}} \xrightarrow[\text{solute}]{\text{evaporation}} \textbf{salt} + \underset{\text{solvent}}{\textbf{water}}$$

A few other examples of physical changes are as follows:

1. Changes in the states of matter such as the melting of solids to liquids, the freezing of liquids to solids, the vaporization of liquids to gases, the liquefaction of gases to liquids and the sublimation of solids to vapours.
2. The separation of mixtures by evaporation, distillation, fractional distillation, sublimation, and crystallization.
3. The magnetization and demagnetization of iron rods.

Chemical changes

> *A chemical change is one which is not easily reversed and in which no new substances are formed.*

A piece of firewood burns with a flame, giving out heat and light. As it burns, the wood slowly disappears until only a little ash is left. This is a chemical change as we cannot reverse the process to get the firewood. Burning of substances is a chemical change.

$$\textbf{wood} \xrightarrow{\text{burning}} \textbf{ash} + \textbf{gases}$$

More examples of chemical changes are as follows:

1. The dissolution of metals and limestone in acids.
2. The rusting of iron.
3. The addition of water to quicklime, i.e. the slaking of lime.
4. Fermentation and decay of substances.
5. The changes in an electrochemical cell.

Elements, Compounds and Mixtures

Matter may be classified into *elements*, *compounds* and *mixtures*. An element or a compound is a pure substance because it cannot be separated into more than one component by physical methods. A mixture consists of more than one element and/or compound. The components of a mixture can be separated by physical methods.

Most elements and compounds are not pure. They contain small amounts of other substances known as impurities. Such impure elements and compounds can also be regarded as mixtures.

Table 2.1 Comparing the characteristics of physical and chemical changes.

Physical change	Chemical change
• It is easily reversible. • No new substances are formed. • There is no change in the mass of a substance involved in such a change. • It does not involve any great heat changes except the latent heat changes which occur during changes of state, e.g. the heat of dissolution and the latent heats of fusion and vaporization.	• It is not easily reversible. • Entirely new substances are always produced. • There is a change in the mass of a substance that undergoes such a change. • A considerable amount of heat change is usually involved.

Experiment 2.1 To show that zinc oxide undergoes a physical change when heated and cooled.

Method Heat some zinc oxide in a boiling-tube. Then remove the tube from a flame and cool it. What do you notice?

Result White zinc oxide turns yellow on heating and changes back to its original white colour on cooling.

Conclusion The colour change of zinc oxide is a physical change because the process is easily reversed without affecting the chemical nature of the substance.

Experiment 2.2 To show that chemical changes take place when (a) magnesium burns; (b) sugar is heated: (c) metallic zinc is added to dilute tetraoxosulphate(VI) acid.

Method

(a) Using a pair of tongs, hold a piece of magnesium ribbon in a Bunsen flame.

(b) Place some sugar in a crucible, cover it with a watch-glass and heat it.

(c) Add a piece of metallic zinc to some dilute tetraoxosulphate(VI) acid in a boiling-tube. When the reaction is complete, evaporate the solution to dryness. In each case, record your observations.

Result

(a) The magnesium burns with a dazzling white flame and a white ash (magnesium oxide) is obtained.

(b) The sugar burns to give a black residue (carbon) and drops of wtaer which condense under the watch-glass. The sugar cannot be recovered when the water droplets are added to the black residue.

(c) Gas bubbles (hydrogen) are released (i.e. effervescence occurs) as the zinc gradually dissolves. On complete evaporation of the solution, a white residue, zinc tetraoxosulphate(VI), is left behind.

Conclusion The burning of magnesium, the charring of sugar, and the dissolution of zinc in acid are chemical changes because new products are formed and the original materials cannot be recovered by physical means.

Elements

An element is a substance which cannot be split into simpler units by an ordinary chemical process.

Scientists have discovered over a hundred elements which include familiar substances like iron, tin, gold, oxygen and iodine, as well as unfamiliar ones like rubidium, actinium and xenon. These can be found in the Earth's crust, in the air and in the sea.

Elements constitute the building units of all other substances. Those substances which are built up of elements are known as compounds.

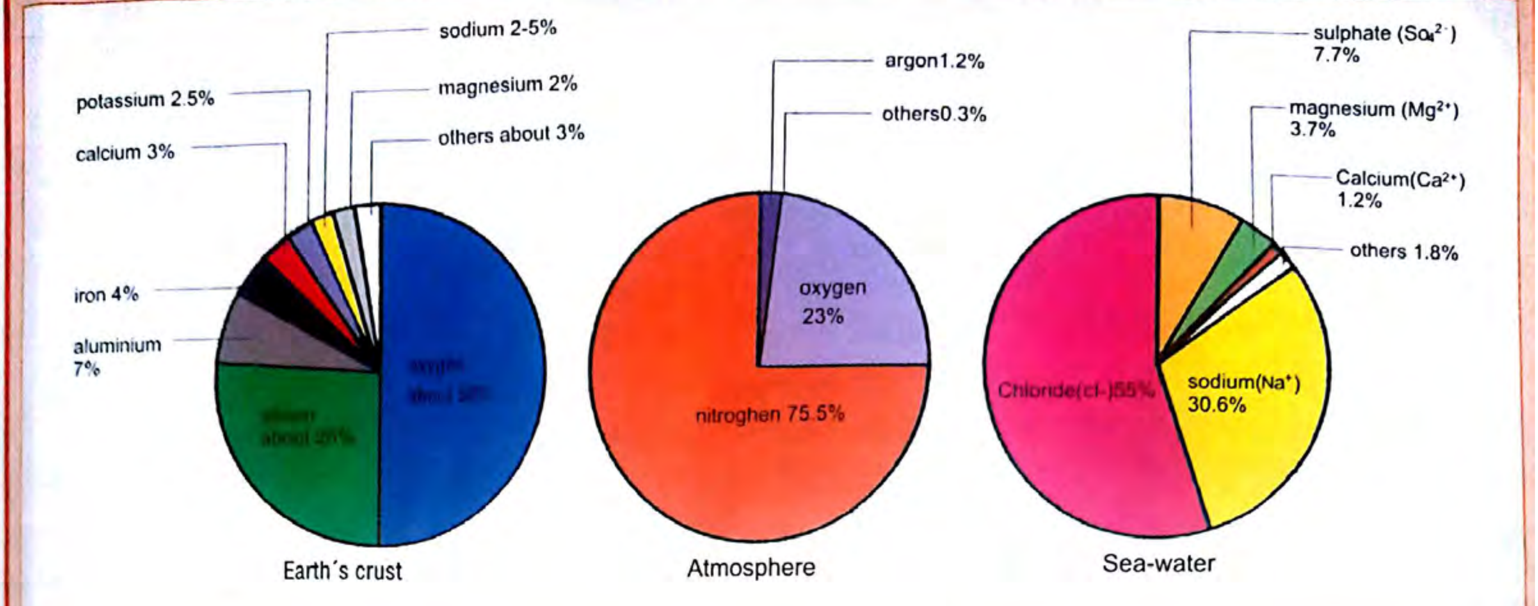
There are 109 known elements. Ninety of them occur naturally; the rest are made artificially in the laboratory. We use abbreviations or symbols to represent elements, e.g. "O" for oxygen and "H" for hydrogen.

Elements can be grouped in the form of a Periodic Table. There are six types of elements: the *reactive metals*, *transition metals*, *lanthanides* and *actinides*, *pure metals*, *non-metals* and *noble gases*. More commonly, elements are grouped as *metals*, *semi-metals* or *metalloids*, and *non-metals*.

Table 2.2 Classification of elements.

Element	Property	Examples
Metals	Conductors of electricity	Iron, tin, lead
Metalloids	Poor conductors (semiconductors) of electricity	Silicon, germanium
Non-metals	Non-conductors of electricity	Oxygen, chlorine, argon

Fig. 2.1 Main constituents in the earth´s crust,atmosphere and sea-water.



Compounds

A compound is a substance which contains two or more elements chemically combined together.

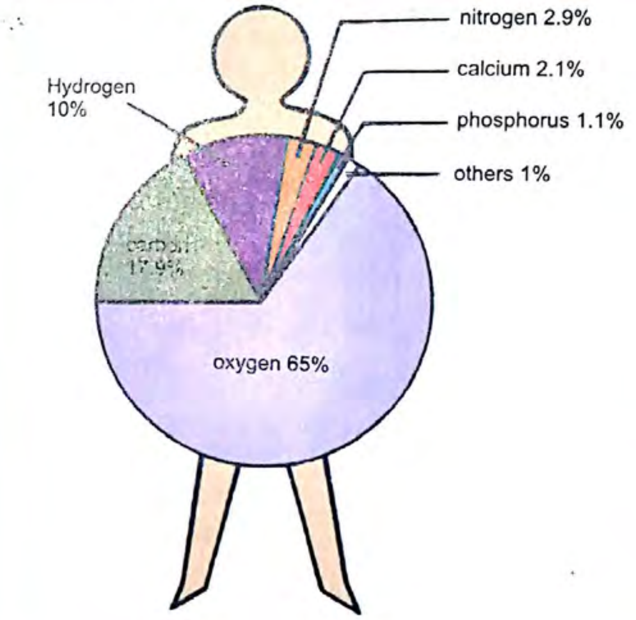
A compound is formed as a result of a chemical change. It is a new substance with entirely different properties from those of

- the substance(s) from which it was formed, or
- its component elements.

The component elements of a given compound are always present in a fixed ratio by mass. For example,

- water is a compound formed as a result of a chemical reaction between the component elements, hydrogen and oxygen, in the ratio of 1:8 respectively;
- carbon dioxide is a compound in which the component elements, carbon and oxygen, are in the ratio of 3 : 8.

Fig. 2.2 What are you made of?



Experiment 2.3 To find out if red mercury(II) oxide is a compound.

Method Heat some red mercury(II) oxide strongly. Introduce a glowing splinter into the tube. What happens? Examine the residue, if any.

Result The red mercury(II) oxide decomposes on heating to liberate a gas (oxygen) which rekindles the glowing splinter. A metallic residue (mercury) remains in the tube.

$$\text{Red mercury(II) oxide} \xrightarrow{\text{heat}} \text{metallic mercury} + \text{oxygen}$$

Conclusion Red mercury(II) oxide is composed of two components, mercury and oxygen, which differ in nature and properties from mercury(II) oxide. Red mercury(II) oxide is, therefore, a compound.

Table 2.3 *Compounds and their component elements.*

Compound	Component elements	Formula
Water	Hydrogen, oxygen	H_2O
Sand	Silicon, oxygen	SiO_2
Limestone	Calcium, carbon, oxygen	$CaCO_3$
Common salt	Sodium, chlorine	$NaCl$
Sugar (sucrose)	Carbon, hydrogen, oxygen	$C_{12}H_{22}O_{11}$
Ethanol	Carbon, hydrogen, oxygen	C_2H_5OH
Washing soda	Sodium, carbon, oxygen, hydrogen	$Na_2CO_3.10H_2O$
Hard Soap	Sodium, hydrogen, carbon, oxygen	$C_{17}H_{35}COONa$
Caustic soda	Sodium, oxygen, hydrogen	$NaOH$

Mixtures

A mixture contains two or more constituents which can easily be separated by physical methods.

The constituents of mixtures can be elements or compounds, or both. In samples of a given mixture, the constituents may be present in different proportions, e.g. different samples of cement contain variable proportions of calcium and aluminium trioxosilicates (IV). The constituents of a mixture retain their individual identities because their physical and chemical properties are not changed by simple mixing. Hence, air, which is a mixture of gases, retains the properties of each of the component gases. In fact, many familiar things around us are mixtures.

Experiment 2.4 To study some characteristics of a mixture, and the differences between a mixture and a compound.

Requirements Iron filings, yellow sulphur powder, iron(II) sulphide, dilute hydrochloric acid, carbon(IV) sulphide, a bar magnet, watch-glasses.

Method Carry out the following activities on (i) iron filings (ii) powdered yellow sulphur, (iii) mixture of iron filings and powdered sulphur (iv) iron(II) sulphide, and record your observations.

(a) Hold a magnet just above the substance.

(b) Add dilute hydrochloric acid to the substance.

(c) Add carbon(IV) sulphide to the substance.

NOTE Make a sample of iron(II) sulphide by grinding 7 parts by mass of iron filings together with 4 parts by mass of sulphur and heating the mixture.

Result

Substance	**(i) Iron filings**	**(ii) Sulphur**	**(iii) Mixture**	**(iv) Iron(II) sulphide**
Activity (a)	Attracted	Not attracted not attracted	Iron attracted, sulphur	Not attracted
Activity (b) gas given off	Dissolves, hydrogen	No reaction iron dissolves, sulphur remains	Hydrogen gas given off, sulphide gas given off	Dissolves, hydrogen
Activity (c)	Does not dissolve	Dissolves remains	Sulphur dissolves, iron	Does not dissolve

Conclusion Constituents of a mixture retain their individual properties. They are not bound together chemically, and are easily separable by physical methods. A compound (iron(II) sulphide in this experiment) has properties which are entirely different from its component elements.

Mixture	Constituents
Air	Oxygen, carbon(IV) oxide, nitrogen, rare gases, dust, moisture
Soil	Sand, clay, humus, water, air, mineral salts
Urine	Urea, water, mineral salts
Palm wine	Water, sugar, alkanol, mineral salts, vitamins, yeast, proteins, fat
Coca-cola	Water, sugar, carbon(IV) oxide, coca cola concentrate
Milk	Water, sugar, fat, proteins, mineral salts, vitamins
Sea-water	Water, mineral salts, bacteria, remains of organic matter
Blood	Water, proteins, fat, oil, sugar, mineral salts, vitamins, hormones, enzymes, blood cells, haemoglobin
Crude oil	Petrol, heavy oil, gas oil, kerosene, naptha, bitumen, gas, etc
Brass	Copper, zinc

Some examples of mixtures

Sea Water

Molten Steel

Smoke

able 2.5 Comparison of mixtures and compounds.

Mixture	Compound
• It may be homogeneous or heterogeneous.	• It is always homogeneous.
• The constituents are not chemically bound together and can, therefore, be easily separated and recovered by physical means.	• The component elements are chemically bound together and cannot be separated by physical means.
• The constituents can be added together in any ratio by mass. Hence, a mixture cannot be represented by a chemical formula.	• The components are present in a fixed ratio by mass. Hence, a compound can always be represented by a chemical formula.
• The properties of a mixture are the sum of those of its individual constituents.	• The properties of a compound differ entirely from those of its component elements.

SEPARATION TECHNIQUES

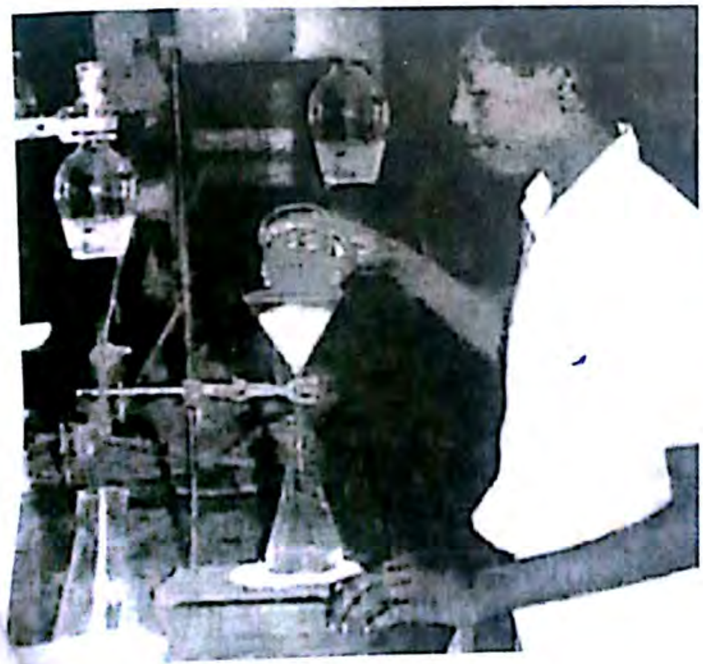
A mixture contains two or more different substances. Each constituent of a mixture still retains its individual properties. We can take advantage of this characteristic to separate mixtures. Thus, the techniques employed in separating mixtures make use of the physical properties of their constituents.

Types of Separation Techniques

Table 2.6 Techniques for separating mixtures.

Techniques	To separate . . .
Sieving	solids of different sizes.
Magnetic separation	magnetic solids from non-magnetic ones.
Sublimation	solids which sublime, from other solids.
Decantation; Filtration; Centrifugation	insoluble solid from a liquid.
Evaporation; Crystallization; Fractional Precipitation	soluble solid from a solution.
Distillation	solvent from its solution.
Fractional distillation	miscible liquids.
Using separating funnel	immiscible liquids.
Chromatography	solutes from a solution.

A student at work in the laboratory.



Sieving

Sieving is used to separate solid particles of different sizes. The mixture is placed on a sieve with a mesh of a particular size. Particles smaller than the mesh size of the sieve will pass through the sieve while the bigger particles remain on the sieve.

Mining industries, such as those involving diamond and gold, use this method extensively. *Gari* industries in West Africa also use this method to separate the *gari* particles before they are fried.

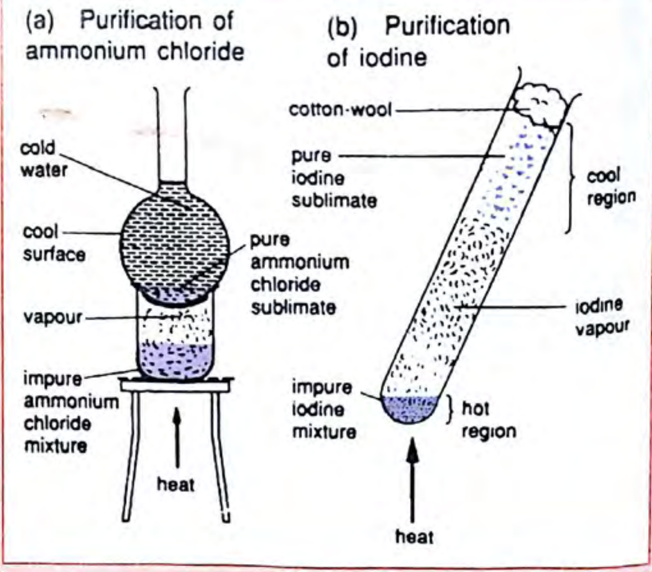
Magnetic separation

A magnet is used to separate magnetic substances from non-magnetic particles. This method is used in the steel industry and to remove magnetic impurities from tin ore.

Sublimation

When some solids are heated, they sublime, i.e. they change directly to the gaseous state without passing through the liquid state. Examples of such solids are iodine and ammonium chloride. These substances can be separated from other solids by sublimation. They are also purified industrially by the same method.

Fig. 2.3 Purification by sublimation



(a) Purification of ammonium chloride

(b) Purification of iodine

Decantation

A mixture containing a liquid and solid particles, separate into two distinct layers on standing: a lower solid layer and an upper clear layer. Using a glass rod, the upper layer of clear liquid can be carefully poured or decanted into a second container. This is a quick but inaccurate method of separating the components of a mixture.

Filtration

A porous material like filter paper can be used to separate insoluble particles from liquids. For example, if a suspension of chalk dust in water is poured onto a filter paper, the water passes through, leaving the chalk particles on the filter paper.

Industries such as water purification plants and breweries use filtration to remove solid particles from liquids.

In the purification of pipe-borne water, the water strains through the various layers of the filter bed, leaving all forms of suspended material behind. This filtered water is then treated with chemicals to kill any bacteria in it before being piped to the consumers.

Centrifugation

A centrifuge is a machine which can spin test-tubes containing suspensions at high speed. The spinning causes heavier solid particles in the suspension to be thrown to the bottom of the test-tube. They settle there while the clear liquid separates out as an upper layer which can easily be decanted.

Centrifugation is often used when there is only a small amount of material. In hospitals, blood samples are centrifuged to separate the blood cells from the plasma.

NOTE When a test-tube of material is placed in a centrifuge, it must be counterbalanced by a similar tube containing about the same amount of water.

Evaporation to dryness

Evaporation can be used to recover a solid solute from a solution. In this process, the solvent is usually sacrificed.

solution → solute + solvent

A water-bath or a sand-bath is used to bring about a steady rate of evaporation. The solute required is left behind in the dish while the solvent escapes into the air as vapour. This method is not suitable for salts easily destroyed by heating.

Evaporation is used in salt-making industries. Along the western coast of Africa, sea-water is pumped into trenches and allowed to evaporate under the heat of the sun. The salt is left behind when all the water dries up.

Fig. 2.4 Decantation. 2

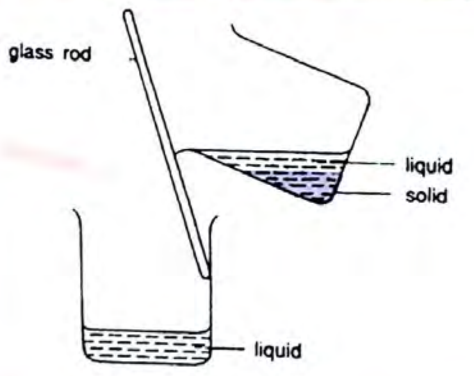


Fig. 2.5 Filtration of a chalk suspension.

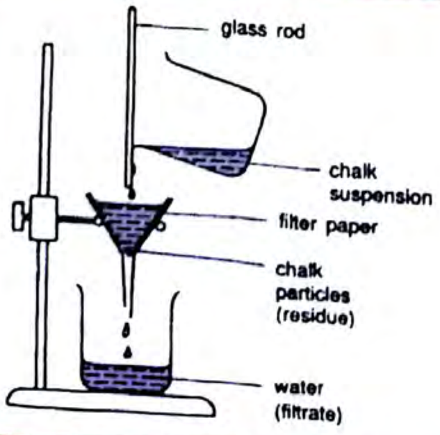


Fig. 2.6 Action of a simple centrifuge. 3

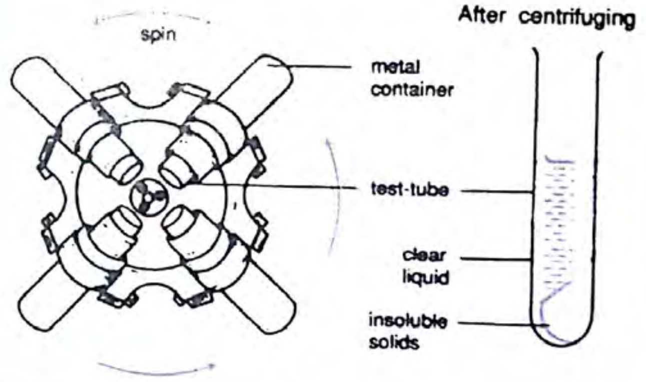
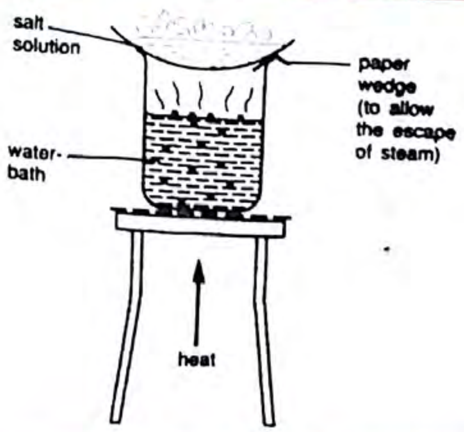


Fig. 2.7 Evaporation of a salt solution.



Making salt from sea–water by evaporation

Crystallization

Crystallization is used to separate salts, which decompose easily on heating, from their solutions. The salt crystals obtained in this way are pure, and usually contain water of crystallization, for example,

- copper(II) tetraoxosulphate(VI)-pentahydrate,
- copper(II) trioxonitrate(V)-trihydrate,
- iron(II) tetraoxosulphate(VI)-heptahydrate.

The salt solution is first heated to evaporate some of the solvent. The solution becomes saturated. When the saturated solution is cooled, crystals of the solute begin to form. To induce crystal formation,

- crystals of the same salt are added into the solution to serve as seeds; or
- inside of the vessel containing the solution is scratched.

Crystallization is used in industries where purity of the product is important as in the manufacture of drugs and in sugar production.

Fractional crystallization

Fractional crystallization is used to separate two or more solid solutes which are present in the same solution in roughly equal amounts. The solubilities of different solutes in the given solvent must differ at different temperatures. During the cooling process, at a particular temperature, crystals of the relevant solute *will come out of solution, leaving behind the others which are still within their limits of solubility.*

Precipitation

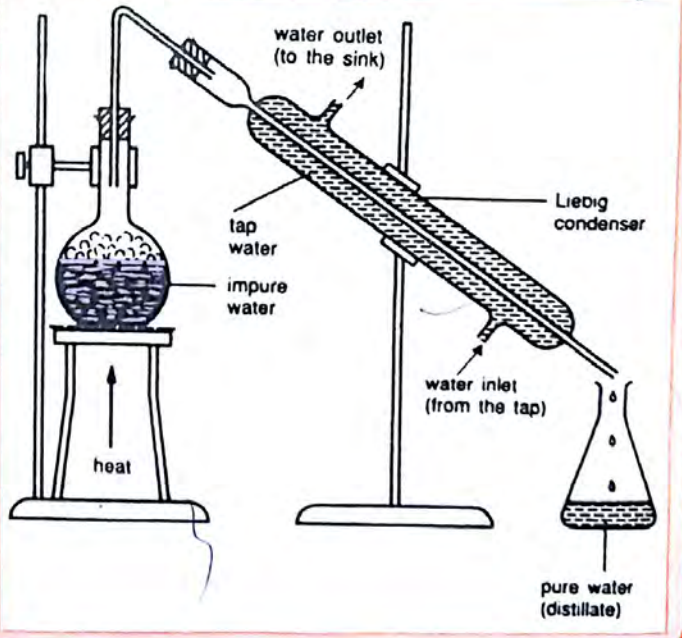
A difference in the solubility of a solid in two different miscible liquids is used to precipitate the solid when it is dissolved in one of them. Iron(II) tetraoxosulphate (VI), for example, is soluble in water but not in ethanol. If ethanol (which is miscible with water) is added to a solution of iron(II) tetraoxosulphate(VI) in water, the iron(II) tetraoxosulphate(VI) will be precipitated out of the solution and can then be separated by filtration.

Distillation

Distillation is used to recover a solvent from a solution. The solution is heated in a flask to vaporize the solvent. The vapour passes along a *condenser* which is cooled by circulating water in its outer jacket. This recondenses the vapour into a liquid, called the *distillate*, which is then collected in a receiver. The solute and other impurities are left behind in the distillation flask.

Distillation is used in gin distilleries and water distilleries for the manufacture of gin and distilled water respectively.

Fig. 2.8 Distillation of water.



Fractional distillation

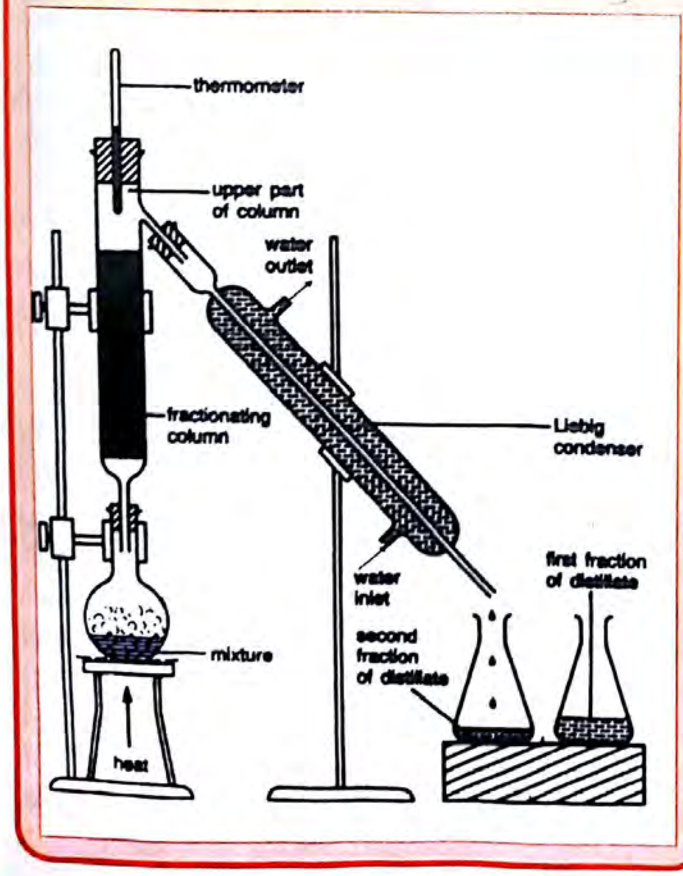
Simple distillation cannot be used to separate a mixture of two or more miscible liquids. Fractional distillation is used to separate such a mixture into its component parts or fractions. The fractions distil over in ascending order of their boiling points, starting with the fraction with the lowest boiling point. For efficient fractional distillation, the difference in the boiling points between successive fractions must be more than 10 °C.

In the laboratory, the apparatus for fractional distillation is same as the apparatus for simple distillation, except that a fractionating column is introduced between the distillation flask and the condenser. The fractionating column is packed with glass beads, and does the actual separation. The upper part of the column is at a lower temperature than the lower part. Only the vapour with the same temperature as the upper part of the fractionating column passes on to the condenser. (This is the fraction with the lowest boiling point.) Vapours with higher boiling points condense as they enter the upper part of the fractionating column and flow back into the distillation flask. This process is repeated until the fraction with the lowest boiling point is distilled over completely. Then, the temperature in the upper part of the column rises until the boiling point of the next fraction is reached. This fraction then starts distilling over.

The fractional distillation process continues until all the component fractions in the mixture distil over.

Crude oil or petroleum contains many important natural products such as petrol, kerosene, diesel, heavy oil, natural gases and bitumen. Each of these products can be recovered in its pure form by fractional distillation. The fractional distillation plant is made up of two main parts — the boiler, where the crude oil is kept boiling, and the fractionating tower, where the actual separation takes place.

Fig. 2.9 Fractional distillation of a mixture.

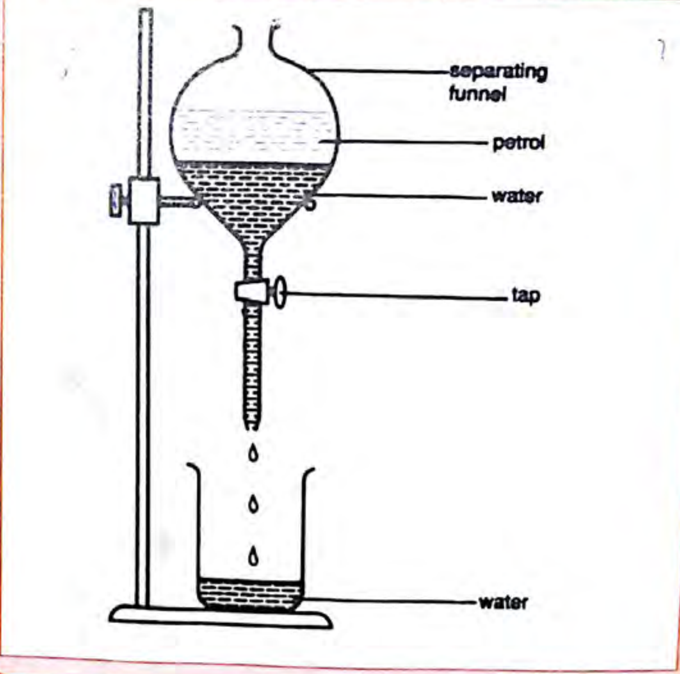


The fractions with the lower boiling points will emerge near the top part of the tower while those with higher boiling points will come out near the lower part of the tower.

Separating funnel method

Petrol and water do not mix together to form a single liquid. Instead, they separate out into two distinct layers when they are added together. To separate the two layers, a separating funnel is used. The lower denser liquid layer is tapped off, leaving the upper less dense liquid layer in the funnel.

Fig. 2.10 Separation of petrol and water using a separating funnel.



Chromatography

Chromatography uses a solvent moving over a porous, *adsorbent* medium (e.g. paper or gel) to separate a mixture of solutes. There are many types of chromatographic procedures. They are widely used to separate coloured as well as colourless substances, e.g. amino-acids.

The commonest method, which is *ascending paper chromatography*, makes use of a strip of chromatographic or filter paper. The solution, containing the mixture of solutes to be separated, is spotted onto the strips near one end. The paper is then suspended in a closed air-tight jar with the spotted end (but not the spot) dipping into an appropriate solvent. The solvent moves up the paper strip. The different solutes in the mixture also move along the paper strip together with the solvent at different speeds and, hence, become separated. The paper strip is removed from the jar when the solvent has moved about three-quarters way up the strip. It is dried and, if necessary, sprayed with the appropriate chemical reagents to locate the positions of the various solutes along the strip. Each solute can then be identified by the distance it has travelled. This is done by comparing its distance with those of known standard substances.

The rate at which the different solutes move up the paper strip is determined by two processes:

- the adsorption of the solutes by the paper; and
- the dissolution of the solutes in the solvent.

As the solvent ascends the paper, it dissolves the mixture of solutes. Some solutes are strongly adsorbed by the paper, and so the ascending solvent finds it difficult to dissolve them. When the solvent eventually dissolves them and carries them up, they become adsorbed by the next portion of the paper. This process of adsorption and dissolution is repeated continuously, and the solutes travel up the paper slowly. Solutes which are weakly adsorbed by the paper are easily redissolved by the ascending solvent. Such solutes travel quickly up the paper strip. In addition, solutes which are very soluble in the solvent move up at a faster rate than those which are not so soluble. Thus, we see that the rate at which each solute moves up the paper depends on how strongly it is adsorbed by the paper, and how soluble it is in the solvent.

Fig. 2.11 Ascending paper chromatography.

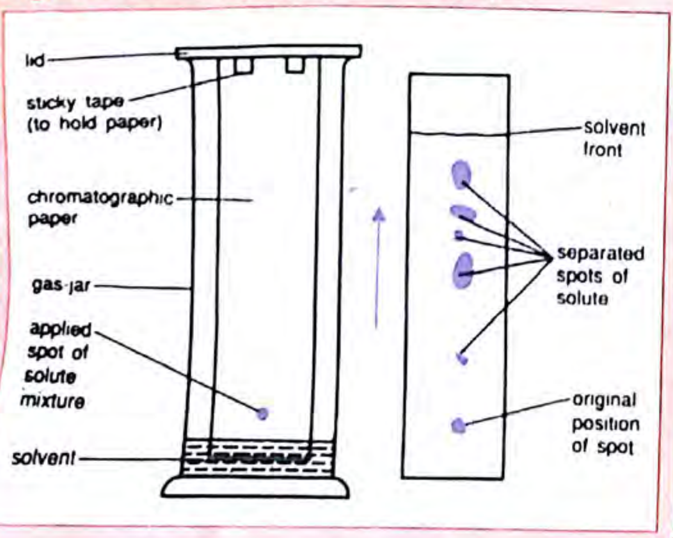
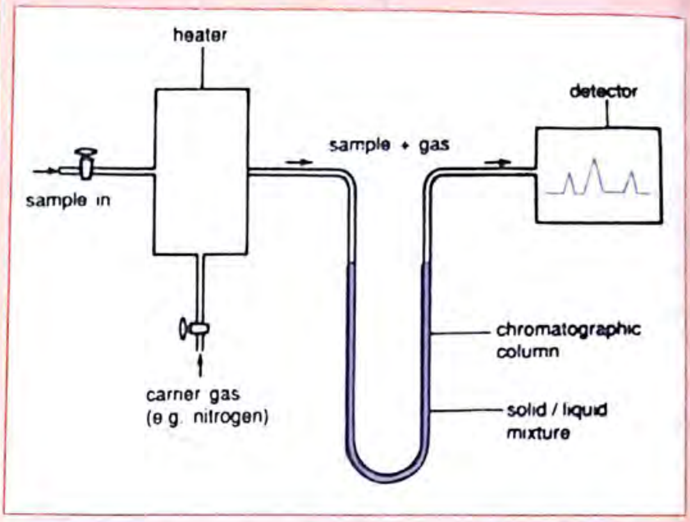


Fig. 2.12 Gas chromatography.



In chromatography, there are two phases:

- a *stationary phase* on which the solutes are adsorbed, and
- a *moving phase* which dissolves the solutes and carries them.

In the above example, the paper is the stationary phase and the solvent is the moving phase.

Although paper chromatography is a commonly used technique, *gas chromatography* is important in industry, biomedical analysis and research because it is an extremely sensitive technique. In gas chromatography, the stationary phase is a liquid mixed with a solid packed into a long glass column with a small diameter. The moving phase is a fairly inert gas like nitrogen or helium, and referred to as the carrier gas. The mixture to be separated may be solid, liquid or gaseous. It is mixed with the carrier gas and heated to vaporize it where necessary, and passed through the column where separation occurs.

Chromatography is used extensively in scientific research to analyze and identify substances. In the petroleum industry, chromatography is used for identifying the various constituents of the fractions obtained from the distillation of crude oil. In hospitals, this method is used to determine the presence of certain substances in the blood and urine of patients in order to help doctors in their diagnosis. Health departments use chromatography to check that food products do not contain more than the maximum legal amount of preservatives. In addition, they also use this method to check the constituents of chemical products.

Purification of Substances

An impure substance is a mixture, so the impurities may be removed by using the appropriate separation technique(s) outlined earlier.

Tests for purity

Once we have obtained a pure sample of a substance, we can use the following criteria to determine its purity.

1 The melting point or the boiling point of a given pure substance is fixed at a certain temperature. This temperature is affected if impurities are present. To assess the purity of a substance, we determine its melting point if it is a solid, or its boiling point if it is a liquid. If the value obtained agrees with that given in a *book of data*, the substance is probably pure. Impure substances melt or boil over a temperature range. Impurities

Experiment 2.5 To obtain pure samples of the constituents of a mixture of common salt and sand.

Method Add distilled water to the mixture and stir. Filter the mixture and dry the solids found on the filter paper. Evaporate the filtrate by heating it gently.

Result The salt dissolves in water to form a solution. The sand is insoluble and collects on the filter paper, while the salt solution filters through. The salt is then recovered from the filtrate by evaporation.

Conclusion A mixture of common salt and sand can be separated by physical methods.

Experiment 2.6 To obtain pure samples of the constituents of a mixture of ammonium chloride and common salt.

Method Place the mixture in a long test-tube and heat it gently. What do you notice?

Result Ammonium chloride sublimes and condenses on the cooler side of the upper part of the test-tube, while common salt is unaffected by the heat and remains at the bottom of the tube.

Conclusion A mixture of ammonium chloride and common salt can be separated by sublimation; a physical method.

Experiment 2.7 To obtain pure samples of the constituents of a mixture of water, kerosene, chalk dust and potassium trioxonitrate(V).

Method and Result (a) Stir the mixture to dissolve the potassium trioxonitrate(V) and filter it to separate the chalk suspension.

(b) Pour the filtrate into a separating funnel and allow it to stand. Two liquid layers will separate out. The top layer is kerosene while the bottom layer is an aqueous solution containing the dissolved potassium trioxonitrate(V). Tap off the lower layer into a round-bottomed flask, leaving the pure kerosene in the funnel.

(c) Connect the flask containing the aqueous solution of potassium trioxonitrate(V) to a distillation apparatus. Distil the water into a receiving beaker. When most of the water has been distilled over, remove the distillation flask and cool the residual solution in it. Crystals of potassium trioxonitrate(V) come out of the solution.

Conclusion A mixture may be separated into its constituents by a series of physical methods according to the properties of the constituents.

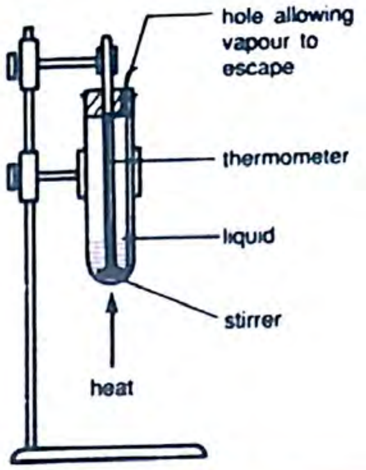
elevate boiling points while it depresses melting points.

2 A pure substance gives one spot on a paper chromatogram. This is used to check the purity of coloured substances like dyes and pigments.

The apparatus shown in fig. 2.13 is used to determine the boiling point of a liquid. A pure sample of a liquid will boil at a fixed temperature. If it is not pure, it will boil over a range of temperatures above the boiling point of the pure liquid.

Note A flammable liquid is heated over a water-bath.

Fig. 2.13 Determining the boiling point of a liquid.



Impurities generally tend to lower the melting point of a substance and raise its boiling point. This property is made use of in countries where the temperature falls below 0 °C. During such weather conditions, people add antifreeze to their car radiators to prevent the water in them from freezing. They also sprinkle salt on the icy roads to lower the melting point of ice so that it melts. This prevents the roads from becoming too slippery and makes them safe for cars to travel on.

Experiment 2.8 To investigate the purity of two substances, *A* and *B*.

Method Grind a sample of each substance to be tested into a fine powder so that it can be packed into a thin capillary tube (called the melting-point tube). Set up the apparatus as shown. Heat the beaker slowly. Stir the oil vigorously at the same time.

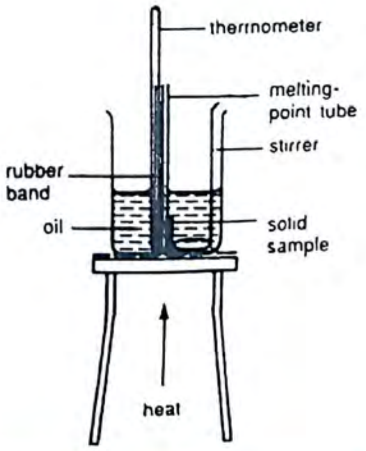
Result (a) The sample of substance *A* melts at a fixed temperature — one which the thermometer shows for some time until all the solid has melted.

(b) The sample of substance *B* melts over a range of temperatures below the melting point of the pure solid.

Conclusion (a) Sample of substance *A* is pure.

(b) Sample of substance *B* has impurities.

Fig. 2.14 Determining the melting point of a solid.



SUMMARY

- Matter is anything that has mass and occupies space.
- The mass of an object is the quantity of matter that the object contains.
- Matter is built up of one or more of the three elementary particles — atoms, molecules and ions.
- Matter exists in three states — solid, liquid and gas.
- Matter undergoes change. A physical change is one which is easily reversed and in which no new substances are formed. A chemical change is one which is not easily reversed and in which a new substance is formed.
- Matter can be classified into elements, compounds and mixtures.
- An element is a substance which cannot be split into simpler units by ordinary chemical processes.
- A compound is a substance which contains two or more elements chemically combined together.
- A mixture contains two or more constituents which can easily be separated by physical methods.
- Methods of separating mixtures include sieving, magnetic separation, sublimation, decantation, filtration, centrifugation, evaporation to dryness, crystallization, fractional crystallization, precipitation, distillation, fractional distillation, separation of immiscible liquids by using the separating funnel and chromatography.
- Applications of the methods of separating mixtures include the following — sieving in mining industries, filtration in water purification plants, evaporation in salt-making industries, distillation in making gin and distilled water, fractional distillation in the petroleum industry, crystallization in sugar and drug manufacture, and chromatography as a tool in the identification and analysis of substances.
- Separation techniques can be used to obtain samples of pure substances. Their purity can be easily checked by determining their melting points (for solids) or their boiling points (for liquids).

EXERCISES

1. In the discovery of proton, the instrument used is
A cathode ray tube.
B glass tube and discharge tube.
C discharge tube with terminal cathode.
D discharge tube with central cathode.

2. Electron was discovered by
A John Dalton
B R. Millikan
C J. J. Thomson
D None of the above

3. One of the following scientists bombarded thin gold foil with alpha particles in his attempt to produce the shape of the atom.
A Millikan
B Rutherford
C J. Thomson
D Newton

4. What phenomenon is represented by; $^{32}_{16}X$, $^{32}_{16}X$.
A Isomerism
B Isotopy
C Atomic number
D Mass number

5. All these are electromagnetic waves except
A white light.
B photon.
C x-ray.
D infra-red.

6. Bombardment of beryllium sheet using alpha particles led to the discovery of an atomic particle called
A neutron.
B positron.
C proton.
D electron.

7. The greatest weakness of Rutherford's model of the atom lies in the fact that his atom
A is like a solar system.
B did not explain why atom does not die even when charged electron emits energy while revolving round the nucleus.
C did not make use of quantum theory in the interpretation of his model.
D did not make use of emission spectra in the interpretation of his model.

8. In using atomic emission spectra to confirm the electronic structure of the atom, every element used showed characteristic discrete lines of different colours. This characteristic is due to
A nature of the atom.
B the shape of the atom.
C the wavelength of the lines produced.
D the type of medium in which the experiment was carried out.

9. Bohr's model of the atom explained why atoms do not die because
A atoms are immortal.
B atoms consists of energy levels.
C atoms occupying energy levels equal to its own energy neither radiates nor absorb energy.
D energy levels are characteristic of their frequencies.

10. Bohr's model was inadequate in using spectral lines in the explanation of
A hydrogen atoms.
B gaseous atoms.
C solid atoms.
D complicated atoms.

11. Energy of an electron in any atom is characterized by quantum numbers numbering

A 1
B 2
C 3
D 4

12. Electronic configuration of an element 13X in the subsidiary energy level is

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
B $1s^2\ 2s^2\ 2p^4\ 3s^2\ 3p^1$
C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
D $1s^1\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

13. If an element Z has an orbital configuration of $1s^1\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$ and $3d^0$ what is the relative atomic number of Z

A 18
B 19
C 20
D 21

14. From ${}^{12}_{6}Q$, ${}^{13}_{6}Q$, what phenomenon does Q show.

A isomerism
B allotropy
C spectroscopy
D isotopy

15. The major reason why relative atomic masses of elements are not whole numbers is due to the phenomenon called

A isomerism.
B allotropy.
C isotopy.
D stearic factor.

16. Which of the following statements is incorrect?

A The addition of water to quicklime is an example of a physical change.
B A chemical change is irreversible and a new substance is formed.
C A physical change can easily be reversed and no new substances are formed.
D Separating a mixture by distillation is an example of a physical change.

17. Fractional distillation is used to separate

A an insoluble substance from a soluble volatile substance.
B substances which are adsorbed differently, and which differ in their solubilities in a solvent.
C liquids with differing boiling points.
D gas, liquid or solid impurities from a mixture.

18. A mixture of oil and water can be easily separated by

A sublimation.
B evaporation to dryness.
C using a separating funnel.
D fractional crystallization.

19. Classify each of the following changes as either a physical or a chemical change.

(a) The addition of water to quicklime (i.e. the slaking of lime).
(b) The melting of candle wax.
(c) The change in colour of zinc oxide from white to yellow and vice versa during heating and after cooling respectively.
(d) The dissolution of copper in concentrated trioxonitrate(V) acid.
(e) The dissolution of common salt in water.
(f) The hardening of cement by the absorption of carbon(IV) oxide.

20. (a) Define the terms *mixture* and *compound*. Give three differences between them. Classify the following substances as an element, a mixture or a compound.

(i) Limestone
(ii) Diamond
(iii) Sand
(iv) Soil
(v) Urine
(vi) Bronze
(vii) Sugar
(viii) Gold
(ix) Clay
(x) Urea
(xi) Antimony
(xii) Soap
(xiii) Milk
(xiv) Air
(xv) Neon
(xvi) Iron

(b) Why is sodium chloride solution regarded as a mixture?

21. How would you separate out any one of the components in the pure form from each of the following mixtures?

(a) A mixture of sodium chloride and ammonium chloride.

* (b) A mixture of anhydrous sodium trioxocarbonate(IV) and sodium hydrogentrioxocarbonate(IV).

(c) A mixture of iron dust and zinc dust.

(d) A mixture of water and sugar.

(e) A mixture of sodium chloride and potassium trioxonitrate(V).

(f) A mixture of chlorine and hydrogen chloride gas.

22. What method would you use to separate the following?

(a) A mixture of two solids which have widely different solubilities in water.

(b) A mixture of two liquids which have widely different boiling points.

(c) A pure solid from a concentrated solution of its salt.

(d) The component colours of a leaf.

(e) An aqueous solution of lead(II) and copper(II) ions.

23. Describe the industrial applications of these processes, explaining clearly the procedures.

(a) Filtration

(b) Crystallization

(c) Fractional distillation

(d) Sieving

(e) Evaporation

3

ATOMS • MOLES • FORMULAE • EQUATIONS

PARTICULATE NATURE OF MATTER

Matter is made up of discrete particles, the main ones being *atoms*, *molecules* and *ions*.

Atoms

The ancient Greeks were the first to use the word *atom*, which means *indivisible*, to describe the smallest particle of any substance. Its actual existence was not established until the nineteenth century when John Dalton, an English chemist, put forward a theory to describe the nature of the atom. The atom is now considered to be the basic unit of simple substances or elements.

> *An atom is the smallest particle of an element which can take part in a chemical reaction.*
>
> *or*
>
> *An atom is the smallest part of an element that can ever exist and still possess the chemical properties of that element.*

Molecules

Most atoms cannot exist alone. They generally bond with other atoms to form molecules. Molecules may be made-up of atoms of the same element or of different elements.

The number of atoms in each molecule of an element is called the *atomicity* of the element. This number is usually small. Most gaseous elements, like oxygen and chlorine are diatomic, i.e. the molecule consists of two atoms. Others, like phosphorus and sulphur exist as polyatomic molecules. The molecules of helium are monatomic, i.e. they can exist independently as single atoms.

Table 3.1 *Atomicity of some molecular elements.*

Element	Formula of molecule	Atomicity
Neon	Ne	1
Argon	Ar	1
Hydrogen	H_2	2
Nitrogen	N_2	2
Oxygen	O_2	2
Ozone	O_3	3
Phosphorus	P_4	4
Sulphur	S_8	8

Most compounds exist as molecules. The smallest particle possessing the chemical properties of a given compound is its molecule. The number of atoms in the molecule of a compound may be small or large, e.g. a hydrogen chloride molecule contains only two atoms, while a starch molecule contains thousands of atoms.

> *A molecule is the smallest particle of a substance that can normally exist alone and still retain the chemical properties of that substance, be it an element or a compound.*

Ions

Some substances are not built up of atoms or molecules, but are made up of charged particles called ions. There are two types of ions: the positively charged ions or cations and the negatively charged ions or anions. An ionic substance has the same number of positive and negative ions, so that it is electrically neutral.

> *An ion is any atom or group of atoms which possesses an electric charge.*

Symbols of Elements

In 1814, Berzelius suggested a simple system of representing elements with *symbols*. The first letter of the name of an element was taken as the symbol for that element: H for hydrogen, S for sulphur, O for oxygen and C for carbon. Such symbols are written in capital. Where the first letter had already been adopted, the initial letter, in capital, together with a small letter from its name was used: Ca for calcium, Cl for chlorine, Al for aluminium, He for helium and Sr for strontium. The symbols for some metals were derived from their Latin names in a similar way.

Table 3.2 Symbols of elements from Latin names.

Element	Latin name	Symbol
Sodium	Natrium	Na
Iron	Ferrum	Fe
Copper	Cuprum	Cu
Silver	Argentum	Ag
Tin	Stannum	Sn
Gold	Aurum	Au

Formulae of Elements and Compounds

A molecule of a substance is represented by the symbols of its component elements. Such a representation is known as a *chemical formula*.

Where an element exists as a molecule, a number representing its atomicity is written as a subscript after the symbol of that element. For example,

- diatomic hydrogen is written as H_2 to show that it contains two atoms of hydrogen;
- triatomic molecule of ozone is written as O_3 to show that it contains three atoms of oxygen

A molecule of a compound contains whole numbers of atoms of the component elements. Its *molecular formula* is written as follows:

- the symbols of all the component elements are written close together as a group;
- the number of atoms of each component element is written as a subscript after the symbol of that element.

Thus, the molecular formula of calcium trioxocarbonate(IV) is $CaCO_3$ since it contains one atom of calcium, one atom of carbon and three atoms of oxygen.

Table 3.3 Symbols of the first twenty elements in the Periodic Table.

Atomic number	Element	Symbol
1	Hydrogen	H
2	Helium	He
3	Lithium	Li
4	Beryllium	Be
5	Boron	B
6	Carbon	C
7	Nitrogen	N
8	Oxygen	O
9	Fluorine	F
10	Neon	Ne
11	Sodium	Na
12	Magnesium	Mg
13	Aluminium	Al
14	Silicon	Si
15	Phosphorus	P
16	Sulphur	S
17	Chlorine	Cl
18	Argon	Ar
19	Potassium	K
20	Calcium	Ca

Groups of atoms, like trioxonitrate(V), $-NO_3$, hydroxide, $-OH$, trioxocarbonate(IV), $-CO_3$, and ammonium $-NH_4$, are known as *radicals*. Each radical is treated as a single unit in a molecular formula. When more than one unit of a radical is present in a molecule, we write the formula by enclosing the radical within parentheses, with the relevant numerical subscript after the parentheses. Thus, calcium hydroxide is written as $Ca(OH)_2$ rather than CaO_2H_2. The subscript outside the parentheses applies to every symbol within it so that the subscript 2 in $Ca(OH)_2$ indicates two atoms, of both oxygen and hydrogen.

Table 3.4 Formulae of some compounds.

Compound	Molecular formula
Hydrochloric acid	HCl
Water	H_2O
Ammonia	NH_3
Carbon(IV) oxide	CO_2
Lead(II) chloride	$PbCl_2$
Calcium trioxonitrate(V)	$Ca(NO_3)_2$
Zinc tetraoxosulphate(VI)	$ZnSO_4$

Particles: Size, Mass and Quantity

Size of a molecule

Scientists can prove that molecules exist. Yet they have not been able to see them even with an electron microscope which magnifies an object up to about 200 000 times its normal size. How small, then, is a molecule? Is there a way by which we can measure it?

When a drop of oil is placed on a water surface, it will spread out into a very thin film or layer about one molecule thick. Using this fact, we can find the size of a molecule which is usually about $n \times 10^{-7}$ cm, where $0 < n < 10$.

Relative atomic mass

Early scientists expressed the mass of atoms as a ratio by comparing the mass of one atom of any element with the mass of the hydrogen atom, the lightest known atom. The mass of an atom or the *relative atomic*

Experiment 3.1 To estimate the size of a molecule.

Method Fill a large basin of water and sprinkle some talcum powder to cover the whole water surface. Make a dilute solution of oil by dissolving 0.1 cm^3 of oil in 1 dm^3 of a solvent such as petroleum ether. Measure the volume of 50 drops of the diluted oil, delivered by a dropper. Place a drop of the dilute oil solution onto the centre of the water surface in the basin. The oil drop will spread and push aside the powder to form a clear circular oil layer. The ether will evaporate eventually, leaving a one-molecule thick oil layer floating on the water surface. measure the diameter of the oil film and hence its area.

Result *Specimen readings*

Volume of oil in 1 dm^3 of dilute oil solution = 0.1 cm^3
Volume of 50 drops of oil from a dropper = 2.50 cm^3
Approximate area of oil layer = 2.50 cm^2

Conclusion

$$\text{Volume of 1 drop of dilute solution} = \frac{2.50\ \text{cm}^2}{50} = 0.05\ \text{cm}^3$$

$$\text{Volume of oil in 1 drop of dilute solution} = \frac{0.05 \times 0.1}{1000}\ \text{cm}^3$$

$$\text{Thickness of oil patch} = \frac{\text{Volume}}{\text{Area}} = \frac{0.05 \times 0.1}{1000 \times 25}\ \text{cm}$$

$$= 2.0 \times 10^{-7}\ \text{cm}$$

NOTE The thickness of the oil patch gives the approximate length of an oil molecule.

Conclusion The approximate length of an oil molecule is 2.0×10^{-7} cm.

Fig. 3.1a The oil film experiment

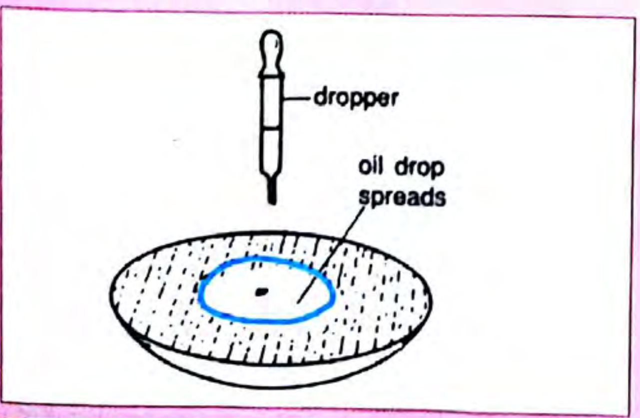
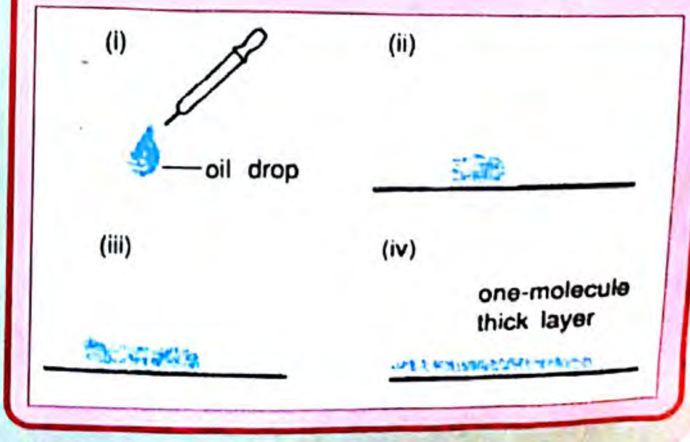


Fig. 3.1b How an oil drop spreads.



mass carries no units; it is only a ratio.

The relative atomic mass of oxygen was found to be 16 times that of hydrogen, while that of sodium was 23 times that of hydrogen. The hydrogen atom was then assigned a basic mass value of 1. When using the hydrogen atom as the standard, the relative atomic mass of oxygen was 16 while that of sodium was 23.

Today, the mass of atoms can be measured very accurately with the mass spectrometer. The mass of the hydrogen atom is 1.67×10^{-24} g, while that of the oxygen atom is 2.66×10^{-23} g. These mass values are too small to be of practical use. So the masses of atoms of elements are still expressed as relative atomic masses.

Mass spectrometric studies show that the atoms of most elements exist in more than one form known as *isotopes*. For instance, chlorine exists as two isotopes: one isotope, ^{35}Cl, has a relative atomic mass of 35 and the other, ^{37}Cl, a relative atomic mass of 37. Isotopes of a given element exist in a constant ratio in nature.

Each isotope of an element has its own mass, known as the *isotopic mass*. The atomic mass of an element is actually the weighted average isotopic mass of the isotopes of the element. This also applies to the relative atomic mass of an element. The standard used for comparing relative atomic masses also had to be defined correctly in view of the presence of isotopes.

Carbon has two stable isotopes, ^{12}C and ^{13}C, which are present in nature in relative quantities of 98.9% and 1.1% respectively. The atom of carbon–12 has now been adopted by modern chemists as the standard for defining the relative atomic mass of the other elements and has been given a basic mass value of 12 units. The earlier relative atomic masses of elements were readjusted. Now the relative atomic mass of hydrogen is 1.008, oxygen, 15.999, and sodium, 22.989.

The relative atomic mass, A of an element is the number of times the average mass of one atom of that element is heavier than one-twelfth the mass of one atom of carbon–12.

From the definition, the relative atomic mass, A_r, of oxygen is given by

$$\frac{\text{average mass of 1 atom of oxygen}}{\frac{1}{12}\text{mass of 1 atom of carbon} - 12}$$

Table 3.5 A_r *values of the first twenty elements in the Periodic Table.*

Atomic number	Element	A_r
1	Hydrogen	1.008
2	Helium	4.0026
3	Lithium	6.939
4	Beryllium	9.0122
5	Boron	10.81
6	Carbon	12.011
7	Nitrogen	14.0067
8	Oxygen	15.9994
9	Fluorine	18.9984
10	Neon	20.183
11	Sodium	22.9898
12	Magnesium	24.312
13	Aluminium	26.9812
14	Silicon	28.086
15	Phosphorus	30.9738
16	Sulphur	32.06
17	Chlorine	35.453
18	Argon	39.948
19	Potassium	39.102
20	Calcium	40.08

The relative atomic mass of each element has been verified accurately with the aid of the mass spectrometer.

The term *atomic mass unit (amu)* is sometimes used, where *1 amu is an amount of matter that has a mass one-twelfth that of carbon–12*. From this definition, one carbon atom has a mass of 12 amu, one oxygen atom, a mass of 16 amu and one hydrogen atom, a mass of 1 amu.

Relative molecular mass

Every molecule must have a mass, or *molecular mass*, since it is composed of atoms. The mass of a molecule is very small; it is also expressed as a ratio of the carbon–12 atom.

The relative molecular mass, M_r of an element or a compound is the number of times the average mass of one molecule of it is heavier than one-twelfth the mass of one atom of carbon–12

The relative molecular mass, M_r, of an element or a compound is the sum of the relative atomic masses of all the atoms in one molecule of that substance. It is also referred to as the *formula mass*, which is a more general term.

NOTE The relative molecular mass refers only to the relative mass of a molecule. The formula mass refers not only to the relative mass of a molecule, but also that of an ion, radical, electron or any other specified groups or nuclear particles.

EXAMPLE

Calculate the relative molecular mass of limestone, $CaCO_3$. *(Ca = 40, C = 12, O = 16)*

One molecule of $CaCO_3$ has 1 Ca, 1 C and 3 O atoms.

$\therefore$ relative molecular mass of $CaCO_3$

$= 1 \times A_r$ of Ca $+ 1 \times A_r$ of C $+ 3 \times A_r$ of O

$= (1 \times 40 + 1 \times 12 + 3 \times 16)$

$= 100$

Mole

Chemical reactions take place between individual particles, such as atoms, molecules and ions, of the reacting substances. For example, in a certain chemical reaction, one particle of a reactant *A* may need to react with one particle of another reactant *B* to give one particle of the product *C*, i.e.

$$A + B \rightarrow C$$

An equal number of particles of *A* and *B* are always needed to yield a definite number of particles of *C*.

Since particles, like atoms and molecules, are extremely small, it is diffficult to work with individual particles when we carry out chemical reactions. We weigh out the reacting substances that are needed and carry out the chemical reaction, i.e. we work with very large quantities of reacting particles. We need a unit for measuring the amount of particles in a given mass of a substance. This unit should contain a specified number of particles. Such a quantitative unit is called the *mole*. It is the number of atoms in exactly 12 grams of the isotope carbon–12

One mole of a substance is the amount containing as many elementary entities as the number of atoms in exactly 12 grams of carbon–12. (The short form for mole is mol.)

NOTE Elementary entities of matter may be atoms, molecules, ions, electrons or any other particles.

Through experimental work, it was found that 1 mole or 12 grams of carbon-12 contains 6.02×10^{23} atoms. This number is known as the *Avogadro Number*.

Avogadro number $= 6.02 \times 10^{23}$

Therefore,

- 1 mole of oxygen atoms contains 6.02×10^{23} oxygen atoms,

just as

- 1 dozen eggs means 12 eggs.

The definition of a mole also gives the following relationship:

$$\text{Number of moles of a substance} = \frac{\text{Number of particles}}{6.02 \times 10^{23}}$$

The relative atomic and molecular masses of substances give the relationship between the mass of a substance and the mole. The relative atomic mass of any element in grams contains one mole of atoms (i.e. 6.02×10^{23} atoms) of the element. The relative molecular mass of an element or compound in grams contains one mole of molecules (i.e. 6.02×10^{23} molecules) of that element or compound. In the case of substances containing other particles, the formula mass in grams contains one mole of the particles of that substance.

Table 3.6 *Relationship between the mass of a substance and the mole.*

Substance and its formula	Type of particle	A_r,M_r of formula mass	Mass of 1 mole	Mass of 2 moles
Oxygen atom, O	Atom	16	16 g	32 g
Oxygen gas, O_2	Molecule	32	32 g	64 g
Ozone, O_3	Molecule	48	48 g	96 g
Hydrogen chloride, HCl	Molecule	36.5	36.5 g	73 g
Sodium ion, Na^+	Ion	23	23 g	46 g
Hydroxide ion, OH^-	Ion	17	17 g	34 g

When we say one mole of substance, we must specify the type of particle. One mole of a given substance is written in its formula form as one particle of the substance, regardless of whether it is a whole molecule, an atom or even an ion. Thus, C stands for 1 mole of carbon atoms. Similarly,

- Cl^- stands for 1 mole of chloride ions;
- HCl stands for 1 mole of hydrogen chloride molecules.

If there are 2 moles of carbon atoms, place a 2 in front of C, i.e. 2C. Similarly,

- 6K means 6 moles of potassium atoms;
- $3O_2$ means 3 moles of oxygen molecules or 6 moles of oxygen atoms;
- $3CaCO_3$ means 3 moles of calcium trioxocarbonate(IV) molecules composed of 3 moles of calcium atoms, 3 moles of carbon atoms and 9 moles of oxygen atoms.

In the case of the earlier chemical reaction, i.e.

$$A + B \rightarrow C$$

we can now say that one mole of A will react with exactly one mole of B in the above reaction, to give one mole of C. Similarly,

$$X + 2Y \rightarrow Z$$

we say that one mole of X will need two moles of Y to give one mole of Z.

Molar mass

The *molar mass* of any substance is the mass of one mole of that substance expressed in grams. Its unit is grams per mole (g mol^{-1}). Since a mole of any substance can be represented by its formula, the molar mass of a substance will be its formula mass expressed in grams. For example, the molar mass of an element will be its relative atomic mass expressed in grams, and the molar mass of a compound will be its relative molecular mass expressed in grams.

Table 3.7 Formula mass and molar mass.

Substance	Formula	Formula mass	Molar mass
Oxygen gas	O_2	32	32 g mol^{-1}
Sodium	Na	23	23 g mol^{-1}
Hydrogen ions	H^+	1	1 g mol^{-1}
Calcium oxide	CaO	56	56 g mol^{-1}
Chloride	Cl^-	35.5	35.5 g mol^{-1}

EXAMPLES

1 *What is the mass of 3 moles of oxygen, gas O*
(O = 16)
Mass of 1 mole of O_2 = (2 × 16) g = 32 g
Mass of 3 moles of O_2 = (3 × 32) g = 96 g

2 *How many atoms are there in 6 g of carbon,* C
(1 mole = 6×10^{23}; C = 12)
12 g of C = 1 mole

$$6 \text{ g of C} = \frac{6}{12} \text{ mole} = \frac{1}{2} \text{ mole}$$

$$\text{Number of atoms in } \frac{1}{2} \text{ mole of } C = \frac{6\times10^{23}}{2}$$
$$= 3\times10^{23}$$

3 *How many moles are there in 20 g of* $CaCO_3$
($CaCO_3$ = 100)

Molar mass of $CaCO_3$ = 100 g
100 g of $CaCO_3$ = 1 mole

$$20 \text{ g of } CaCO_3 = \frac{20}{100}\times1 \text{ mole}$$
$$= 0.2 \text{ mole}$$

Calculations using masses and formulae

Percentage mass of an element in a compound

The mass of 1 mole of a compound is the sum of the masses of the moles of its component elements.

Mass of 1 mole of $MgCl_2$		Mass of 1 mole of Mg atoms		Mass of 2 moles of Cl atoms
	=	24 g	+	71 g
	=	95 g		

We can calculate the percentage by mass of a component element of a compound from its formula.

EXAMPLES

1 *Calculate the percentage by mass of nitrogen in trioxonitrate(V) acid.* (H = *1*, N = *14*, O = *16*)
Molecular formula of trioxonitrate(V) acid is HNO_3.
In 1 mole of HNO_3, there are 1 mole of H, 1 mole of N and 3 moles of O atoms.
∴ molar mass = M_r in grams
= (1 × A_r of H + 1 × A_r of N + 3 × A_r of O) g
= (1 × 1 + 1 × 14 + 3 × 16) g = 63 g
63 g of HNO_3 contains 14 g of nitrogen.

$$\therefore \% \text{ by mass of nitrogen} = \frac{14}{63} \times 100\% = 22.2\%$$

2 *Calculate the percentage by mass of all the component elements in sodium trioxonitrate(V), $NaNO_3$.* (Na = *23*, N = *14*, O = *16*)

$$\% \text{ by mass of sodium} = \frac{(\text{Na})}{(\text{NaNO}_3)} \times 100\%$$
$$= \frac{23}{(23 + 14 + 3 \times 16)} \times 100\%$$
$$= \frac{23}{85} \times 100\%$$
$$= 27.0\%$$

$$\% \text{ by mass of nitrogen} = \frac{(\text{N})}{(\text{NaNO}_3)} \times 100\%$$
$$= \frac{14}{85} \times 100\%$$
$$= 16.5\%$$

$$\% \text{ by mass of oxygen} = \frac{3(\text{O})}{(\text{NaNO}_3)} \times 100\%$$
$$= \frac{3 \times 16}{85} \times 100\%$$
$$= 56.5\%$$

NOTE *The results above can be interpreted as follows. 100.0 g of sodium trioxonitrate(V) contains 27.0 g of sodium, 16.5 g of nitrogen and 56.5 g of oxygen. Thus, the percentage by mass of any element also represents its reacting mass in forming that compound.*

Empirical formula and molecular formula

The empirical formula of a compound is its simplest formula. It tells us

- the component elements in a molecule of the compound,
- the ratio in which these elements are combined together, i.e. the mole ratio.

Mole ratio of each component element in a compound

$$\text{or} \quad = \frac{\% \text{ by mass of the element in the compound}}{\text{Relative atomic mass of the element}}$$

$$= \frac{\text{Reacting mass of the element in the compound}}{\text{Molar mass of the element}}$$

The empirical formula of a compound only gives the whole number ratio of the component elements.

The *molecular formula* of a compound gives the exact number of moles of atoms of the component elements in one mole of the compound.

In most cases, the empirical formula and the molecular formula are the same. In some cases, the molecular formula is a simple multiple, *n*, of the empirical formula. For example, both ethyne and benzene have the same empirical formula, but different molecular formulae (see table 3.8).

Where the empirical formula and molecular formula of a compound are not the same, the molecular formula can be calculated if

- the empirical formula, and
- the formula mass/the relative molecular mass are known.

Table 3.8 Empirical and molecular formulae.

Compound	Empirical formula	Molecular formula
Water	H_2O	$(H_2O)_n = H_2O$ ($n = 1$)
Hydrogen peroxide	HO	$(HO)_n = H_2O_2$ ($n = 2$)
Ethyne	CH	$(CH)_n = C_2H_2$ ($n = 2$)
Benzene	CH	$(CH)_n = C_6H_6$ ($n = 6$)

LAWS OF CHEMICAL COMBINATION

There are four laws of chemical combination which describe the general features of a chemical change. Although research has shown that these laws are only approximately correct, they still form the basis of chemistry.

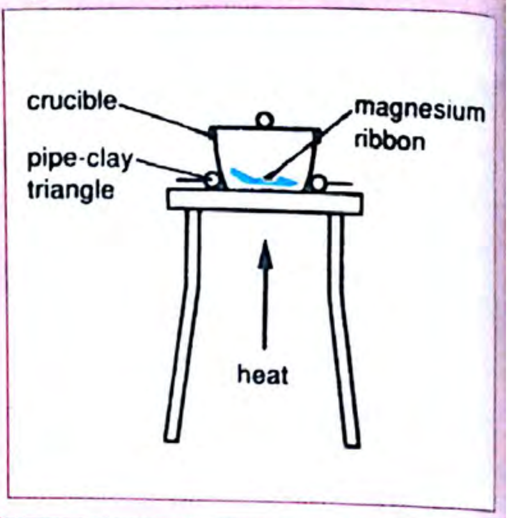
The Law of Conservation of Mass

The Atomic Theory proposed by John Dalton states that atoms can neither be created nor destroyed but change from one form to another. Since matter is made up of atoms, matter too can neither be created nor destroyed. This is stated in the *Law of Conservation of Mass or Matter* which is now accepted as the basis of all chemical reactions. Experiment 3.3 verifies its validity.

Experiment 3.2 To find the mole ratio in which magnesium and oxygen combine to form magnesium oxide, and hence determine its empirical formula.

Method Weigh an empty crucible and its lid. Put a piece of magnesium in it and weigh again. Find the mass of the magnesium. Heat the crucible and its contents strongly. Open the lid occasionally to let the air in to bring about complete combustion. When the reaction is complete, cool the crucible and its contents in a desiccator and weigh it again.

Fig. 3.2 How an oil drop spreads.



Result *Specimen readings*

Mass of magnesium alone = 0.48 g

Mass of magnesium oxide = 0.80 g

[mass of the combined oxygen = (0.80 – 0.48) g

= 0.32 g

Calculation

Element	Magnesium, Mg	Oxygen, O
Reacting mass	0.48 g	0.32 g
Molar mass	24 g	16 g
Mole ratio of element		
$= \frac{\text{Reacting mass}}{\text{Molar mass}}$	$\frac{0.48}{24} = 0.02$	$\frac{0.32}{16} = 0.02$
$\frac{\text{Mole ratio of element}}{\text{Smallest mole ratio (i.e. 0.02)}}$	$\frac{0.02}{0.02} = 1$	$\frac{0.02}{0.02} = 1$
Empirical formula	MgO	

Conclusion Since 1 mole of magnesium atoms combine with 1 mole of oxygen atoms to form 1 mole of magnesium oxide, therefore, the empirical formula is MgO.

NOTE When the crucible lid is lifted for oxygen to enter, particles of magnesium oxides may escape. Then, the gain in mass of the system will be smaller than what it should be. This inaccuracy is known as experimental error.

EXAMPLE

A certain compound on analysis yielded 2.00 g carbon, 0.34 g hydrogen and 2.67 g oxygen. If the relative molecular mass of the compound is 60, calculate its molecular formula. (C = 12, H = 1, O = 16)

Element	Carbon, C	Hydrogen, H	Oxygen, O
Relative mass	2.00 g	0.34 g	2.67 g
Mole ratio of element $= \frac{\text{Reacting mass}}{\text{Molar mass}}$	$\frac{2.00}{12} = 0.17$	$\frac{0.34}{1} = 0.34$	$\frac{2.67}{16} = 0.17$
$\frac{\text{Mole ratio of element}}{\text{Smallest mole ratio (i.e. 0.17)}}$	1	2	1

The empirical formula of the compound is CH_2O. Let the molecular formula of the compound be $(CH_2O)_n$.

Relative molecular mass = $(A_r \text{ of } C + A_r \text{ of } H \times 2 + A_r \text{ of } O) \times n = (12 + 2 + 16) \times n$

$$= 30n$$

$$30n = 60$$

$$n = 2$$

The molecular formula is $C_2H_4O_2$ or CH_3COOH.

NOTE To convert the mole ratios of the elements in a compound to whole numbers, divide all of them by the smallest mole ratio among them. Round each up to the nearest whole number.

The Law of Conservation of Mass states that matter is neither created nor destroyed during chemical reaction but changes from one form to another.

In some cases, such as the burning of coal, it may appear that the law does not hold and that the piece of coal has actually been destroyed. If we weigh the mass of the two reactants, i.e. the piece of coal and all the oxygen which reacted with it, and that of all the products, which include water vapour, carbon(IV) oxide, ash, soot and others, we will find the law does hold and that there is no overall loss or gain of mass.

Experiment 3.3 To verify the Law of Conservation of Mass (or Matter)

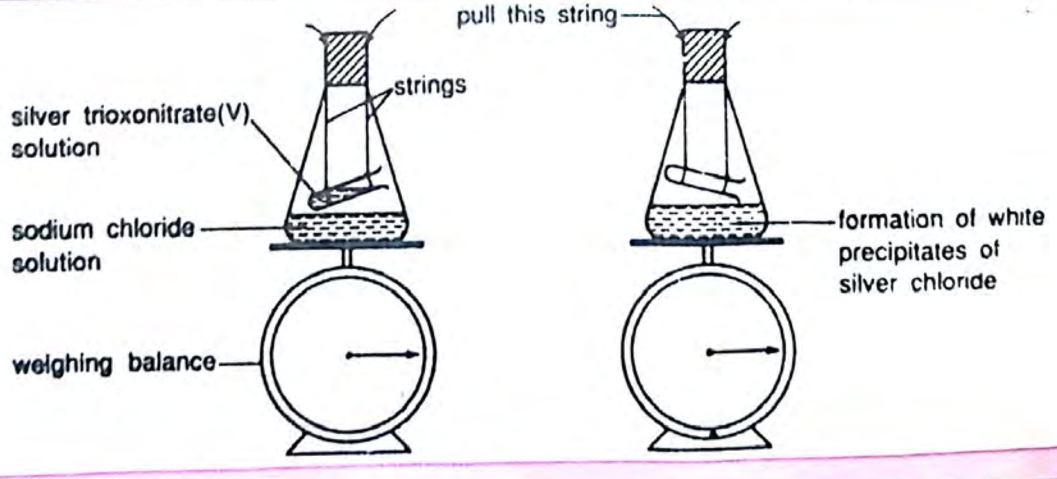
Theory The equation of the chemical reaction chosen for study is as follows:

silver trioxonitrate(V) + sodium chloride → silver chloride + sodium trioxonitrate(V)
white precipitate

Method Put some sodium chloride solution in a conical flask. Fill a small test-tube with silver trioxonitrate(V) solution and by means of two pieces of string, suspend it in a conical flask as shown. Insert the stopper and weigh the whole apparatus on a balance. Note the mass of the whole system.

Mix the two liquids by pulling the string attached to the bottom end of the small test tube. Weigh the whole apparatus again.

Fig. 3.3 Verification of the Law of Conservation of Mass.



Result When the two reactants are mixed together, a white precipitate is formed indicating that a chemical reaction has taken place. The new substances formed are known as the products of the chemical reaction. The masses of the system taken before and after the reaction are found to be the same, indicating that the mass of the reactants equals that of the products.

Conclusion Since there is no overall change in mass when the products are formed, we can infer that matter is neither created nor destroyed during the chemical reaction. The law is, hence, verified.

The Law of Definite Proportions

> *The Law of Definite Proportions states that all pure samples of a particular chemical compound contain similar elements combined in the same proportion by mass.*

The second law of chemical combination which is supported by the Atomic Theory was proposed by Proust (1755–1826). Known as the *Law of Definite Proportions or Constant Composition*, it is based on the fact that when elements combine to form a given compound, they do so in fixed proportions by mass so that all pure samples of that compound are identical in composition by mass.

Consider water for example. Chemical analyses showed that as long as it is pure, its composition is always in the ratio of one mole of oxygen molecules (i.e. 32 g) to two moles of hydrogen molecules (i.e. 4 g), irrespective of whether the water comes from the river, sea, rain, wine, saliva or any other source.

Experiment 3.4 verifies this law.

The Law of Multiple Proportions

> *The Law of Multiple Proportions states that if two elements, A and B, combine to form more than one chemical compound, then the various masses of one element, A, which combine separately with a fixed mass of the other element, B, are in simple multiple ratio.*

Some examples of paired elements that form more than one compound are as follows:

1. Copper and oxygen combine to give black copper(II) oxide, CuO, and red copper(I) oxide, Cu_2O.
2. Iron and oxygen form brown iron(III) oxide, Fe_2O_3, and black iron(II) oxide, FeO.
3. Iron and chlorine combine to give brownish-yellow iron(III) chloride, $FeCl_3$, and green iron(II) chloride, $FeCl_2$.
4. Lead and sulphur combine to give black lead(II) sulphide, PbS, and lead(IV) sulphide, PbS_2.

We can use any of the above pairs of compounds to verify the law in the laboratory. We can also verify the law easily by comparing the formulae of these compounds. This is illustrated for the chlorides of iron(II) and iron(III) in table 3.9.

The Law of Reciprocal Proportions

The fourth law of chemical combination is known as the *Law of Reciprocal Proportions* and is defined as follows:

> *The Law of Reciprocal Proportions states that the masses of several elements, A, B, C, which combine separately with a fixed mass of another element, D, are the same as, or simple multiples of, the masses in which A, B, C, themselves combine with one another.*

VALENCY

We have seen that substances react together in definite proportions by mass. The early chemists carried out many experiments to work out the ratios of these combining masses and work out the combining powers of the various elements. From experimental evidence, they thought that hydrogen had the lowest combining power, so they gave its combining power a value of one. They called the combining power of elements *valency* and defined it as *the number of hydrogen atoms that can combine with or replace (either directly or indirectly) one atom of that element.*

The valency of an element is a property of its atomic structure. It can be regarded as the oxidation number of an element. For the present, we will think of valency as *a number, which may be positive or negative, that is given to an element or a group of elements to indicate its combining power.* The valency allows us to construct the formulae of compounds from component elements.

Table 3.9 Comparing the formulae of the chlorides of iron to verify the Law of Multiple Proportions.

Compounds	Iron(II) chloride	Iron(III) chloride
Formulae	$FeCl_2$	$FeCl_3$
Iron atoms(fixed mass in moles)	1	1
Chlorine atoms (variable masses in moles)	2	3
Ratio of the various masses of chlorine in the chlorides of iron	2 :	3

Experiment 3.4 To verify the Law of Definite Proportions (or Constant Composition).

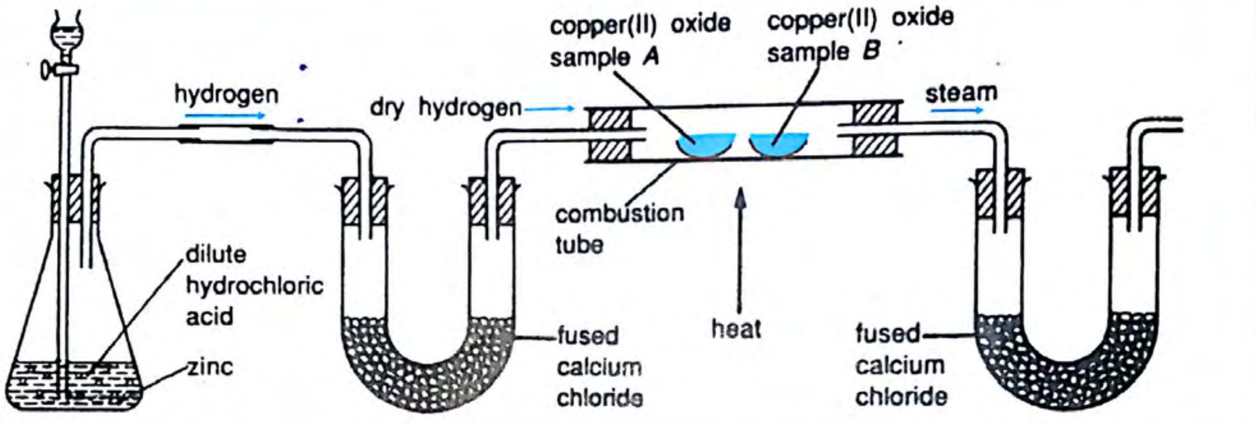
Method Prepare two samples of black copper(II) oxide, each by a different method as given below.

Sample A Place some copper turnings in a crucible and add some concentrated trioxonitrate(V) acid, a little at a time, until the copper dissolves completely. Evaporate the resulting green solution of copper(II) trioxonitrate(V) to dryness. Continue to heat the residue until it decomposes to give a black solid which is copper(II) oxide. Keep this black residue dry in a desiccator.

Sample B Place some copper(II) trioxocarbonate(IV) in a crucible and heat it strongly to decompose it into black copper(II) oxide and carbon(IV) oxide. Store the residue in a desiccator.

Analysis Determine the amount of copper present in the two samples of copper(II) oxide by reducing the oxides in a stream of hydrogen or carbon(II) oxide as follows. Weigh two clean metal boats. Add a reasonable amount of sample *A* to one and sample *B* to the other. Reweigh and determine the mass of each sample. Place the boats inside a hard glass tube as shown.

Fig. 3.4 Verification of the Law of Definite Proportions.



Heat the samples strongly while passing a stream of dry hydrogen gas through the tube. After some time, a reddish-brown copper residue is left in each boat. Remove the flame, but continue passing the hydrogen as the copper residues cool down. This prevents the re-oxidation of the hot copper residues by atmospheric oxygen. Any water formed during the reaction is absorbed by the fused calcium chloride in the adjacent U-tube.

When the copper residues have cooled, weigh them and calculate the percentage of copper in each sample.

Result

Sample	*A*	*B*
Mass of copper(II) oxide	3.55 g	3.02 g
Mass of copper residue	2.81 g	2.42 g
[percentage of copper present in copper(II) oxide	= 79.2	= 80.1

The percentage of copper residue in the two samples is approximately 80.0, irrespective of the method of preparation of the copper(II) oxide samples.

Conclusion In pure copper(II) oxide, copper and oxygen are always present in a definite proportion by mass of approximately 4 to 1, i.e.

copper(II) oxide	=	copper	+	oxygen
100%		80%		20%
Ratio	=	4	:	1

Experiment 3.5 To verify the Law of Multiple Proportions.

Method Weigh two metal boats and place some copper(I) oxide in one and copper(II) oxide in the other. Weigh each boat again and find the mass of the oxide. Next, place the two boats containing the samples of oxides in a hard-glass combustion tube and carry out their reduction as described in experiment 3.4. Weigh the copper residues obtained after reduction and find the masses of the two samples of copper.

Result

	Copper(I) oxide	Copper(II) oxide
Mass of sample (oxide)	3.04 g	1.91 g
Mass of copper residue	2.55 g	1.38 g
Mass of oxygen removed from oxide	0.49 g	0.53 g

Calculation Calculate the various masses of copper which would combine separately with a fixed mass (say 1 g) of oxygen.

Copper(I) oxide

0.49 g O_2 combines with 2.55 g Cu to form copper(I) oxide.

$$\therefore \ 1.0 \text{ g of } O_2 \text{ will combine with } \frac{1.0 \times 2.55}{0.49} = 5.2 \text{ g Cu.}$$

Copper(II) oxide

0.53 g O_2 combines with 1.38 g Cu to form copper(II) oxide.

$$\therefore \ 1.0 \text{ g of } O_2 \text{ will combine with } \frac{1.0 \times 1.38}{0.53} = 2.6 \text{ g Cu.}$$

Oxide of copper	Copper(II) oxide		Copper(I) oxide
Mass of copper	2.6 g		5.2 g
Ratio of copper	1	:	2

Conclusion The masses of copper which combined separately with a fixed mass of oxygen in copper(II) oxide and copper(I) oxide are in a simple multiple ratio of 1:2.

Valencies of elements and radicals

Valencies are usually small whole numbers. Generally, metals exhibit positive valencies while non-metals tend to have negative valencies. Some elements exhibit more than one valency.

Sometimes, a few atoms of different elements may also come together and react as a single unit. Such a group is referred to as a *radical*. The radicals may be charged and have valencies which are usually represented by the net number of positive or negative charges that they carry.

NOTE The valency or oxidation number of hydrogen in compounds is usually +1 except in metallic hydrides where it is −1. Oxygen usually has a valency or oxidation number of −2 except in peroxides where it is −1.

Writing formulae from valencies

Formulae of compounds can be deduced from the valencies of the component elements or radicals. The following rules apply in writing these chemical formulae.

1 The sum of positive valencies of a compound must be equal to the sum of its negative valencies.

2 The number of atoms of the component elements in a formula must be written as a numerical subscript after the element concerned. If a radical occurs more than once, it must be enclosed within parentheses, and the subscript written after the parentheses.

From the examples in table 3.12, the formula of a compound may generally be deduced as shown below.

Component element or radical	Valency	Formula
A	x	A_yB_x
B	y	

Table 3.10 Valencies of some elements.

Element	Symbol	Valency
Aluminium	Al	+3
Argon	Ar	nil
Barium	Ba	+2
Bromine	Br	−1
Calcium	Ca	+2
Carbon	C	+(2 or 4)
Chlorine	Cl	−1
Copper	Cu	+(1 or 2)
Gold	Au	+1
Helium	He	nil
Hydrogen	H	+1
Iodine	I	−1
Iron	Fe	+(2 or 3)
Krypton	Kr	nil
Lead	Pb	+(2 or 4)
Magnesium	Mg	+2
Mercury	Hg	+(1 or 2)
Neon	Ne	nil
Nitrogen	N	−(3 or 5)
Oxygen	O	−2
Phosphorus	P	−(3 or 5)
Potassium	K	+1
Silver	Ag	+1
Sodium	Na	+1
Sulphur	S	−(2, 4 or 6)
Zinc	Zn	+2

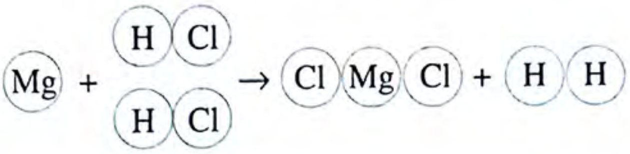
Table 3.11 *Valencies of some radicals*

Radical	Formula	Valency
Ammonium	NH^-_4	+1
Hydroxide	OH^-	−1
Trioxonitrate(V)	NO^-_3	−1
Dioxonitrate(III)	NO^-_2	−1
Trioxocarbonate(IV)	CO_3^{2-}	−2
Hydrogentrioxobonate(IV)	HCO_3^-	−1
Tetraoxosulphate(VI)	SO_4^{2-}	−2

CHEMICAL EQUATIONS

Chemical reactions can be represented simply on paper by chemical equations involving only formulae and symbols. The reactants are written in their formulae form on the left-hand side (LHS) of the equation while the products are written, also in their formulae form, on the right-hand side (RHS). An arrow symbol (→) leads from the reactants to the products. A simple equation like:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$



means that one mole of magnesium atoms reacts with two moles of hydrogen chloride molecules to produce one mole of magnesium chloride molecules and one mole of hydrogen molecules. An 'atom count' for each element in the equation shows that the total number of moles of atoms for each element is the same before and after the reaction, i.e. on the left-hand side and the right-hand side of the equation.

Atom count in moles		
Atoms	LHS	RHS
Mg	1	1
H	2	2
Cl	2	2

Where a chemical reaction is impossible, it is wrong to write an equation to represent it. For example, the following equation is wrong because copper does not react with hydrochloric acid.

$$Cu + 2HCl \rightarrow CuCl_2 + H_2$$

Table 3.12 *The use of valencies in writing formulae.*

Compound	Element/Radical	Valency	Formula
(a) Sodium hydroxide	Sodium, Hydroxide	+1, −1	$NaOH$
(b) Calcium oxide	Calcium, Oxygen	+2, −2	CaO
(c) Water	Hydrogen, Hydrogen, Oxygen	+1, +1 } +2, −2	H_2O
(d) Ammonia	Nitrogen, Hydrogen, Hydrogen, Hydrogen	−3, +1, +1, +1 } +3	NH_3
(e) Calcium hydroxide	Calcium, Hydroxide, Hydroxide	+2, −1, −1 } −2	$Ca(OH)_2$

Table 3.13 *More examples of writing formulae.*

Valency		-1	-2	-3
	Element	Cl	O	N
+1	Na	NaCl	Na_2O	Na_3N
+2	Ca	$CaCl_2$	CaO	Ca_3N_2
+3	Al	$AlCl_3$	Al_2O_3	AlN
	Radical/ metal	OH	SO_4	PO_4
+1	NH_4	NH_4OH	$(NH_4)_2SO_4$	$(NH_4)_3PO_4$
+2	Cu	$Cu(OH)_2$	$CuSO_4$	$Cu_3(PO_4)_2$
+3	Fe	$Fe(OH)_3$	$Fe_2(SO_4)_3$	$FePO_4$

Balancing equations

All equations must be balanced in order to comply with the Law of Conservation of Matter, which states that matter is neither created nor destroyed in the course of a chemical reaction. An unbalanced equation would imply that atoms have been created or destroyed.

When balancing equations, we must remember that

- the formulae of the reactants and products in an equation are fixed and cannot be altered, so the only way of balancing an equation is
- by taking appropriate numbers of moles of the reactants and the products concerned.

Do an 'atom count' to check that an equation is balanced.

EXAMPLE

To balance the equation for the combustion of ammonia gas in air.

Step 1 The reactants (LHS) are NH_3 and O_2, while the products (RHS) are NO and H_2O.

$$NH_3(g) + O_2(g) \rightarrow NO(g) + 6H_2O(g)$$

Step 2 Place a 4 in front of NH_3 and a 6 in front of H_2O. There are now 12 hydrogen atoms on both sides of the equation.

$$4NH_3(g) + O_2(g) \rightarrow NO(g) + 6H_2O(g)$$

Step 3 Place a 4 in front of NO to balance with the 4 nitrogen atoms on the left-hand side of the equation.

$$4NH_3(g) + O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Step 4 Place a 5 in front of O_2. An 'atom count' show that the equation is balanced.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Importance of chemical equations

A balanced chemical equation provides certai information about the reaction. Let us consider the equation of a reaction between hydrochloric acid and calcium trioxocarbonate(IV).

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g$$

Information provided by the equation

1 It tells us the reactants and products involved in the reaction. In this case, the reactants are HCl and $CaCO_3$, and the products are $CaCl_2$, H_2O and CO_2.

2 It tells us the individual elements and radicals involved. In this case, the elements involved are H, Cl, Ca, C and O. The radical is CO_3^{2-}.

3 It gives a mental picture of the movement of the elements and radicals during the reactions.

4 It tells us the *stoichiometry of the reaction* (i.e. the relationship between the amounts of the reactants and the products) in terms of the mole ratio, and the mass ratio of the reactants and products involved. These ratios are easily calculated since the numerical coefficients of a balanced equation represent the numbers of moles of reactants and products.

5 It tells us the direction of the reaction and whether the reaction is reversible.

6 It tells us the states of matter in which the substances are present, as indicated by the state symbols – (s) for solid, (l) for liquid, (g) for gas, (aq) for aqueous solution – which are placed after the formulae of the substances in the equation.

The followings are some of the stoichiometric relationships that we can obtain from the balanced chemical equation given in table 3.14.

- 1 mole of $CaCO_3$ produces 1 mole of CO_2.
- 2 moles of HCl are needed to react with 1 mole of $CaCO_3$.

Table 3.14 The numerical coefficients of the reactants and products give the stoichiometric relationships for the equation.

	$2HCl(aq)$	+	$CaCO_3(s)$	→	$CaCl_2(aq)$	+	$H_2O(l)$	+	$CO_2(g)$
Number of moles	2		1		1		1		1
Mole ratio	2	:	1	:	1	:	1	:	1
Molar mass	36.5 g		100 g		111 g		18 g		44 g
Formula mass	36.5		100		111		18		44
Mass ratio	2(36.5)	:	100	:	111	:	18	:	44
i.e.	73	:	100	:	111	:	18	:	44

NOTE The mass ratio of the reactants and products is obtained by multiplying the formula masses by the relevant numerical coefficients.

- 100 g of $CaCO_3$ produce 44 g of CO_2.
- 100 g of $CaCO_3$ react with 73 g of HCl to produce 111 g of $CaCl_2$.

Information not provided by the equation

1 The speed of the reaction.
2 The heat changes during the reaction. This, however, may be indicated where required.
3 The colours of the reactants and products.

Calculations from equations

From an equation, we can calculate the amounts of reactants reacted and products formed. These are important in chemical industries that are engaged in the manufacture of basic chemicals.

EXAMPLES

1 The equation for the formation of water is:

$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$

Calculate the number of moles of O_2 required to yield 6 moles of water.

2 moles of H_2O is produced by 1 mole of O_2.

$$6 \text{ moles of } H_2O \text{ is produced by } \frac{6}{2}\times 1 \text{ moles}$$

$$= 3 \text{ moles of } O_2$$

2 Sodium combines with oxygen as follows:

$4Na\,(s) + O_2\,(g) \rightarrow 2Na_2O\,(s)$

What is the mass of O_2 needed to burn 4.6 g of sodium?

From the equation,

4 moles of Na reacts with 1 mole of O_2.

Mass of 4 moles of Na = 4 × 23 = 92 g

Mass of 1 mole of O_2 = 32 g

92 g of Na reacts with 32 g of O_2.

$$4.6 \text{ g of Na reacts with } \frac{4.6}{92} \times 32 = 1.6 \text{ g of } O_2$$

SUMMARY

- An atom is the smallest particle of an element which can take part in a chemical reaction.
- A molecule is the smallest particle of a substance that can normally exist alone and still retain the chemical properties of that substance.
- An ion is any atom or group of atoms which possesses an electric charge.
- All atoms of elements are represented by symbols. Ions, molecules and radicals are represented by formulae.
- The number of atoms in a single molecule of an element is known as its atomicity.
- A radical is a group of atoms that functions as a single unit in chemical reactions.
- The relative atomic mass, A_r, of an element or a compound is the number of times the average mass of one atom of that element is heavier than one-twelfth the mass of one atom of carbon–12.
- The relative molecular mass, M_r, of an element or a compound is the number of times the average mass of one molecule of it is heavier than one-twelfth the mass of one atom of carbon–12.
- The formula mass of a substance is the sum of the relative atomic masses of the atoms present in the formula of a substance.
- One mole of a substance is the amount containing as many elementary entities as the number of atoms in exactly 12 g of carbon–12. (This number is 6.02×10^{23}.)
- The molar mass of a substance is its relative molecular mass expressed in grams.
- The empirical formula of a compound gives only the simplest whole number ratio of the component elements in the compound. In most cases, the empirical and molecular formulae of a compound are the same. In some cases, the molecular formula is a simple multiple of the empirical formula.
- The Law of Conservation of Mass states that matter is neither created nor destroyed during a chemical reaction but changes from one form to another.
- The Law of Definite Proportions states that all pure samples of a particular chemical compound contain similar elements combined in the same proportion by mass.
- The Law of Multiple Proportions states that if two elements combine to form more than one chemical compound, then the various masses of one element which combine separately with a fixed mass of the other element are in a simple multiple ratio.
- The Law of Reciprocal Proportions states that the masses of several elements, *A*, *B*, *C*, which combine separately with a fixed mass of another element, *D*, are the same as, or simple multiples of, the masses in which *A*, *B*, *C*, themselves combine with one another.
- Valency is the combining power of an element or radical. (It is actually the oxidation number assigned to the element or group of elements.)
- Chemical equations are brief representations of chemical reactions using only formulae and symbols.
- A balanced chemical equation gives the stoichiometry of the reaction, i.e. the relationship between the amounts of the reactants and products in terms of mole ratio and mass ratio. The numerical coefficients in a balanced equation give the number of moles of reactants and products, enabling easy calculations of mole and mass ratios.

EXERCISES

1. There are basic particles from which matter could be made except

A salt.

B atom.

C ion.

D molecules.

2. Atom is

A the smallest part of a substance that can take part in a chemical change.

B the smallest part of a compound that can take part in a chemical change.

C the smallest part of an element which can take part in a chemical change.

D the smallest part of a lattice which can take part in a chemical change.

3. Atomicity of Ozone is

A 1

B 2

C 3

D 4

4. A molecule is the smallest particle of

A a matter that can exist in free state.

B an element that can exist in free state.

C a radical that can exist in free state.

D a lattice that can exist in free state.

5. $3NH_3$ is

A three moles of ammonium.

B three moles of ammonia.

C six moles of ammonia.

D six moles of ammonium.

6. The major difference between (i) SO_3 and (ii) SO_3^{2-} is that

A (i) is a molecule while (ii) is an atom.

B (i) is a radical while (ii) is a molecule.

C (i) is a molecule while (ii) is a radical.

D (i) is a radical while (ii) is an atom.

7. The relative atomic mass of calcium atom is 40. This means that

A the mass of calcium is 40 g.

B the calcium is 40 times heavier than that of 1 atom of hydrogen.

C calcium is 40 times that of 1 g of hydrogen.

D calcium is related to hydrogen through 40 digits.

8. Modern standard element with which chemists define relative atomic mass is

A ^{12}C.

B ^{13}C.

C ^{3}H.

D ^{14}C.

9. The relative molecular mass of Lead II trioxonitrate V is (Pb = 108, N = 14, O = 16).

A 170

B 222

C 232

D 132

10. Which one is heavier? 1 mole of Pbd_4, 1 mole of H_2 and 1 mole of $Pb(NO_3)_2$

A Pbd_4

B H_2

C None of them

D $Pb(NO_3)_2$

11. How many atoms are contained in 1 mole of hydrogen molecule.

A 18.09×10^{23} atoms
B 12.06×10^{23} atoms
C 6.02×10^{23} atoms
D 6.02×10^{23} molecules

12. The percentage of oxygen in Sulphur IV oxide (S = 32, O = 16) is

A 5%
B 50%
C 500%
D 25%

13. The empirical formula of C_6H_6 is

A CH
B C_3H_3
C C_6H_6
D 3CH

14. If the relative molecular mass of CH_2O is 60, calculate its empirical formula. (C = 12, H = 1, O = 16)

A 4
B 1
C 2
D 3

15. From $XNH_3(g) + YO_2\ g \rightarrow ZNO(g)$, the value of Z is

A 4
B 7
C 6
D 5

16. A molecule of neon is

A diatomic.
B ionic.
C positively charged.
D triatomic.
E monatomic.

17. One mole of oxygen atoms

A has a molar mass of 32 g.
B has 6.02×10^{23} molecules.
C can be represented as O_2.
D has a formula mass of 16.
E contains Avogadro's number of atoms.

18. The numerical coefficients in a balanced equation give

A the number of moles of reactants and products.
B the molar mass of the reactants and products.
C the number of moles of reactants only.
D the number of molecules and atoms of products only.
E the mass ratio of the reactants.

19. (a) Define the relative atomic mass of an element.

(b) Calculate the relative molecular mass of:
(i) slaked lime, $Ca(OH)_2$,
(ii) sodium trioxonitrate(V), $NaNO_3$,
(iii) hydrated copper(II) tetraoxo sulphate (VI), $CuSO_4.5H_2O$.

(c) What do you understand by *the atomicity of an element*?

20. Calculate the percentage by mass of each of the following component elements in the respective compounds.

(a) Sulphur in tetraoxosulphate(VI) acid, H_2SO_4.
(b) Phosphorus in tetraoxophosphate(V) acid, H_3PO_4.
(c) Oxygen in calcium trioxonitrate(V), $Ca(NO_3)_2$.

21. Find the empirical formulae of the following compounds from their percentage composition by mass.

(a) N = 26.17%; H = 7.48%; Cl = 66.35%.
(b) Ca = 71.43%; O = 28.57%.
(c) Ag = 63.53%; N = 8.23%; O = 28.24%.
(d) Na = 32.40%; O = 45.07%; S = 22.53%.
(N = 14, H = 1, Cl = 35.5, Ca = 40, O = 16, Ag = 108, Na = 23, S = 32)

22. 6 g of metal M react completely with 23.66 g of chlorine to form 29.66 g of the metallic chloride. Find the empirical formula of the metallic chloride. ($M = 27$, $Cl = 35.5$)

23. (a) State the Law of Multiple Proportions.

(b) A metal X forms two different chlorides. If 12.7 g of chloride A and 16.3 g of chloride B contain 7.1 g and 10.7 g of chlorine respectively, show that the figures agree with the Law of Multiple Proportions. Write their formulae.

24. (a) State the Law of Constant Composition (or Definite Proportions).

(b) How would you prove the Law of Constant Composition experimentally?

(c) Two different samples, A and B, of zinc oxide were obtained from different sources. When heated in a stream of hydrogen, they were reduced to yield the following results:

ZnO	Mass of sample	Mass of zinc residue
Sample A	10.0g	8.11g
Sample B	13.2g	10.70g

Show that the figures above illustrate the Law of Constant Composition.

25. (a) If 6.0 g of carbon is heated in air, the mass of the product obtained could be either 22.0 g or 14.0 g depending on the amount of air present. With what law would this be in accordance? ($C = 12$, $O = 16$)

(b) Balance the following equations.

$$KClO_3(s) \rightarrow KCl(s) + O_2(g)$$
$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
$$NH_3(g) + O_2(g) \rightarrow H_2O(g) + N_2(g)$$
$$Cu_2S(s) + O_2(g) \rightarrow Cu_2O(s) + SO_2(g)$$

4 ATOMIC STRUCTURE • CHEMICAL COMBINATION

DALTON'S ATOMIC THEORY

In 1808, John Dalton proposed the *Atomic Theory* which can be summarized as follows:

1 All elements are made up of small, indivisible particles called *atoms*.
2 Atoms can neither be created nor destroyed.
3 Atoms of the same element are alike in every aspect, and differ from atoms of all other elements.
4 When atoms combine with other atoms, they do so in simple ratios.
5 All chemical changes result from the combination or the separation of atoms.

The Atomic Theory was partially supported by experimental evidences deduced from the Law of Conservation of Mass, the Law of Definite Proportions, the Law of Multiple Proportions and so on. It could not explain electrolysis and certain other phenomena. As a result of new discoveries Dalton's original Atomic Theory has undergone several modifications but the principal aspects as outlined above are still useful in the study of chemistry.

ATOMIC STRUCTURE

According to Dalton's Atomic Theory, atoms were indestructible solid particles. However, experiments involving electrolysis indicate that certain compounds contain charged particles called *ions*. The formation of ions could not be explained by Dalton's Atomic Theory. As a result of this and other observations, scientists had to modify their views.

Table 4.1 Characteristics of the sub–particles.

Sub-particle	Location	Relative charge	Relative mass
Proton	Nucleus	+	1
Electron	Outside nucleus	–	≈0.000 5
Neutron	Nucleus	Zero	1

A series of experiments carried out towards the end of the nineteenth century and the beginning of the twentieth century led to the discovery of the fundamental sub-particles of the atom — the *electrons*, the *protons* and the *neutrons*.

The proton has a positive (+) charge and a relative mass of 1 (using carbon-12 as standard). The electron has a negative (–) charge of the same magnitude as the positive charge on the proton, and negligible mass. The neutron has no charge but has a relative mass of 1. In fact, each characteristic of the neutron is the sum of that of the proton and the electron.

Atomic Sub-particles

Discovery of electrons

Scientists noted that although gases do not conduct electricity at ordinary air pressures, some changes were observed when the pressure was reduced and a very high potential difference was applied.

In 1897, J J Thomson showed that when a potential difference of 5 000 V was applied across a glass tube containing a gas at a very low pressure of about

Fig. 4.1 Structure of an atom.

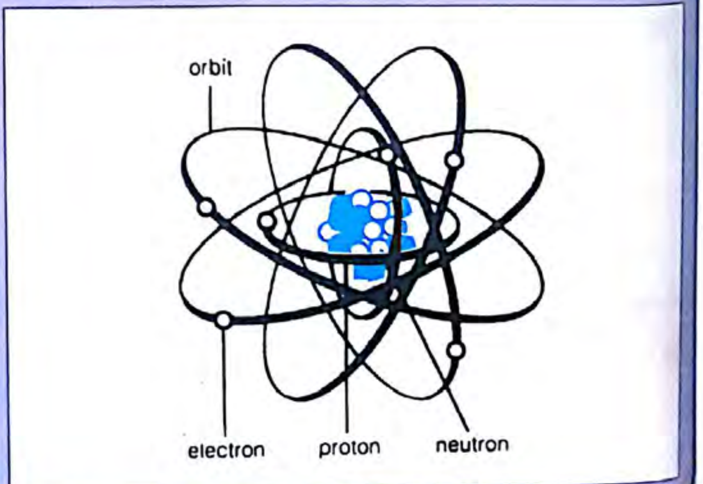
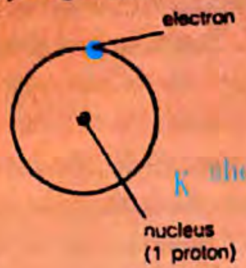
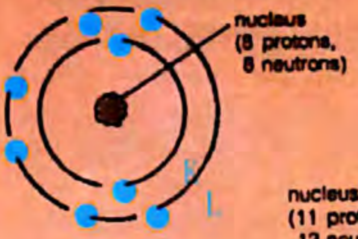
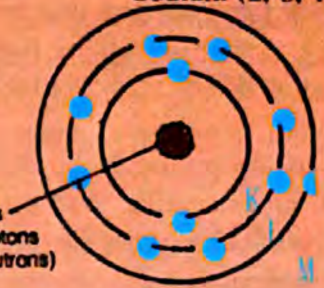


Table 4.2 Structures of the atoms of hydrogen, oxygen and sodium.

Atom	Hydrogen (1)	Oxygen (2, 6)	Sodium (2, 8, 1)
Diagrammatic representation			
Number of protons	1	8	11
Number of electrons	1	8	11
Number of neutrons	–	8	12
Electronic distribution	K^1	K^2L^6	$K^2L^8M^1$

0·0001 atm, the tube began to glow. When the potential difference was increased to 15 000 V, a bright green glow appeared on the glass. Thomson was able to prove that the glow was due to some kind of rays which travelled in straight lines from the cathode. He called these rays *cathode rays.*

Further experiments showed that cathode rays

- travel in straight lines and cast shadows of opaque objects placed in their paths;
- are composed of only negatively charged particles;
- are capable of producing mechanical motion;
- are identical in nature and in the ratio of charge to mass, irrespective of the nature of the residual gas in the discharge tube or of the metals used in the electrodes.

Thomson argued that these particles were fundamental particles, i.e. they were present in all matter. He concluded that these particles must be the electrons proposed earlier by other scientists to explain the conduction of an electric current in wires and in solutions of electrolytes. Thomson measured the ratio,

$$\frac{\text{charge}}{\text{mass}},$$

which is the *specific charge* of the electron. The accurate value the specific charge obtained for the electron is $1{\cdot}76 \times 10^{11}$ C kg^{-1}.

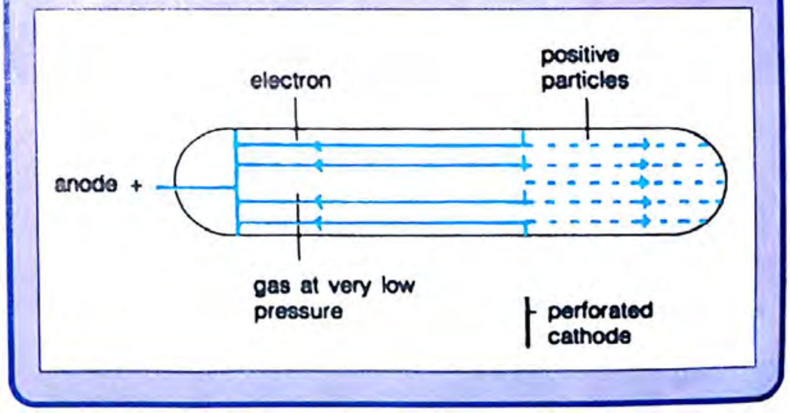
In 1910, R A Millikan successfully measured the charge of the electron in his oil drop experiment. This charge is $-1{\cdot}6 \times 10^{-19}$C. Using the above values, the mass of an electron is found to be only $9{\cdot}1 \times 10^{-31}$ kg. This mass is so small that it hardly makes any difference to the mass of the atom.

These experiments are important because they proved the existence of the electron which carries the fundamental unit of electric charge, the negative charge, and provided a vital clue to the structure of the atom.

Discovery of protons

Since the atom as a whole is electrically neutral, there must exist inside the atom enough positively charged components to balance the negative charge of the electrons. Thomson repeated his earlier experiments, but used a discharge tube with a central cathode which had a hole in it. He noticed a reddish glow in the opposite direction to the green glow and proved that this reddish glow was due to positively charged rays.

Fig. 4.2 An apparatus for producing cathode rays and positive rays.



Further experiments showed that

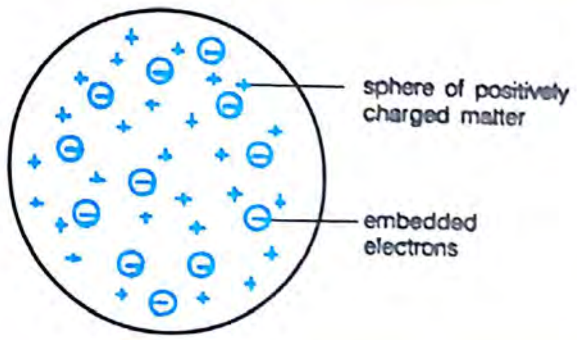
- unlike the cathode rays, the positive rays required much larger magnetic fields to cause their deflections (indicating that they are much heavier than the electrons);
- the mass of the positively charged particles depended on the nature of the gas in the tube.

Positive ions with the lightest mass were produced when the gas in the tube was hydrogen. These positive ions (or the hydrogen ion) were called *protons*. Each proton carries a unit of positive charge. Thomson determined the $\frac{\text{charge}}{\text{mass}}$ ratio of the proton to be $9{\cdot}58 \times 10^{7}$ C kg^{-1} which is 1 840 times smaller than that of the electron. If we assume the charge on the proton to be +1, and that on the electron as −1, then the proton is 1 840 times heavier than the electron.

Thomson's model of the atom

In 1898, J J Thomson proposed that the atom is a sphere of positively charged matter in which negatively charged electrons are embedded. Thomson's model of the atom resembles a pudding studded with currants. This model was later abandoned as it could not account for the results of later experiments conducted by Geiger and Marsden.

Fig. 4.3 Thomson's atom.



Rutherford's atom

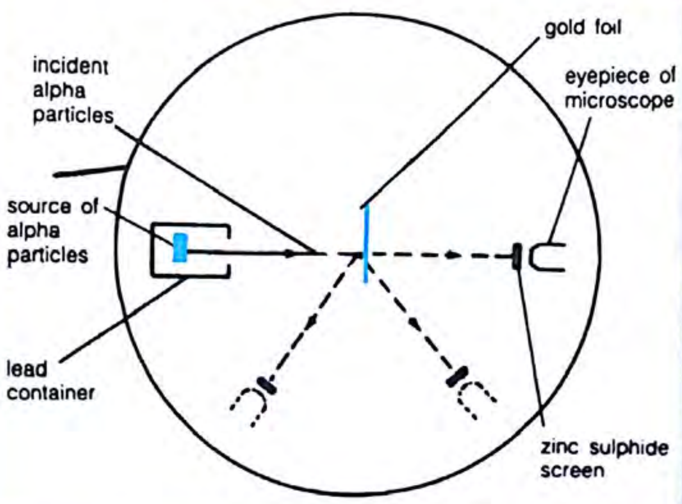
To find out what is inside an atom, Geiger and Marsden, at the suggestion of Rutherford, used positively charged particles called alpha particles to bombard the atom. In their classical experiment, they used a narrow beam of alpha particles emitted from a radioactive source to bombard a thin gold foil. The scattering of the particles from the gold foil was detected by a movable zinc sulphide screen which could be rotated to various positions around the foil. Each time an alpha particle hit the screen, a visible flash of light or scintillation was produced. This was observed by a microscope attached to the screen.

Geiger and Marsden found that most of the alpha particles followed a straight path through the gold foil. But some of them were scattered through large angles and a few were even scattered in the backward direction. As alpha particles are relatively heavy (compared to the electrons), and those used in the experiment travelled at great speeds, very strong forces must have acted on the deflected alpha particles to cause such marked deviations from their straight paths.

Rutherford commenting on the observation noted: "I remember Geiger coming to me in great excitement and saying, 'We have been able to get some of the alpha particles coming backwards ...' It was the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration, I realized that the backward scattering must be the result of a single collision and when I made calculations, I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greatest part of the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive centre carrying a positive charge."

Studying the experimental results, Rutherford (in 1911) deduced that the atom consists largely of empty space, since the majority of the alpha particles passed through the gold foil without being deflected. He explained that the alpha particles which were deflected through large angles or rebounded must have collided

Fig. 4.4 Geiger and Marsden's experiment.



with that part of the atom in which the positive charge and mass of the atom were concentrated.

To account for the observations in the gold-foil experiment, Rutherford proposed a nuclear theory of the atom. According to this theory, the atom consists of a positive core called the nucleus, where most of the mass of the atom is contained, and electrons which move around the nucleus.

From the angles through which the alpha particles were deflected, Rutherford calculated that the nucleus of an atom would have a radius of about 10^{-14} m whereas the radius of the atom would be about 10^{-10} m.

The model of the atomic structure as put forward by Rutherford has been compared to the solar system. Each atom is a miniature solar system with electrons orbiting the nucleus, like the planets orbiting the sun. Rutherford was later awarded the Nobel Prize for his work on the structure of the atom. Although Rutherford's idea of a central nucleus stood the test of time, his views on the planetary electrons had to be modified as a result of subsequent discoveries.

Atomic number

In 1885, Roentgen discovered that when high energy electrons in a discharge tube collide with the anode, a penetrating radiation, which he called *X-rays,* is produced.

In 1914, Moseley found that he could assign a number, called the *atomic number,* to an element based on the frequency of the X-rays the element emits, when it is used as the anode of an X-ray tube. Further experiments enabled Moseley to conclude that the atomic number represented the number of protons in the nucleus.

Calculations based on the work of Geiger and Marsden indicated that the number of positive charges (protons) in the nucleus of the atom was approximately half its relative atomic mass. Rutherford, therefore, suggested that particles of zero charge and of mass exactly the same as the proton were also present in the nucleus. The existence of these particles was confirmed by Chadwick, an English scientist.

Discovery of neutrons

In 1932, Chadwick bombarded a thin sheet of beryllium with alpha particles and discovered a new sub-particle called the neutron. The neutron had a mass equal to that of a proton but carried no charge. The discovery of the neutron indicated that the atomic nucleus was made up of protons and neutrons. It also explained the existence of isotopes of an element. Further experiments were carried out to find out how the nuclear particles were held together, but these are beyond our scope.

Electronic Structure of the Atom

In Rutherford's model of atomic structure, the electrons moved in orbits around the nucleus and were held in their orbits by electrostatic attraction to the positively charged nucleus. This attraction varied inversely as the square of the distance between the nucleus and the electron. There was, however, one contradiction to this theory. According to classical electromagnetic theory, an accelerating electrical charge must radiate energy. Thus, an electron moving in an orbit around a nucleus must radiate energy and move in a decreasing spiral path until it finally disappears into the nucleus. But this does not happen.

Further developments in atomic structure had to depend on advances in physics — on the nature of light, the Quantum Theory and the interpretation of atomic emission spectra. Research on all these fronts were proceeding simultaneously. We shall consider each of these developments that played an important role in understanding atomic structure — particularly on the arrangement of the electrons round the nucleus.

Bohr's model of the atom

In 1913, Niels Bohr used the Quantum Theory ideas developed by Planck and Einstein to account for the spectrum of hydrogen. He made the following assumptions.

1 Rutherford's model of the atom is basically correct.
2 Each spectral line is caused by an electron.
3 Electrons can exist only in circular orbits of definite quantum energy.
4 An electron emits energy in the form of radiation when it moves from a higher to a lower permitted orbit — this produces a line in the atomic emission spectrum. Since the energies of the higher and lower orbits are fixed, the line will be of a particular energy and frequency.

5 The difference in energy, ΔE, of the two orbits is related to the frequency of radiation given by Planck's equation:

$$\Delta E = E_{n_2} - E_{n_1}$$

where E_{n_1} is a state with a lower energy level compared to E_{n_2}.

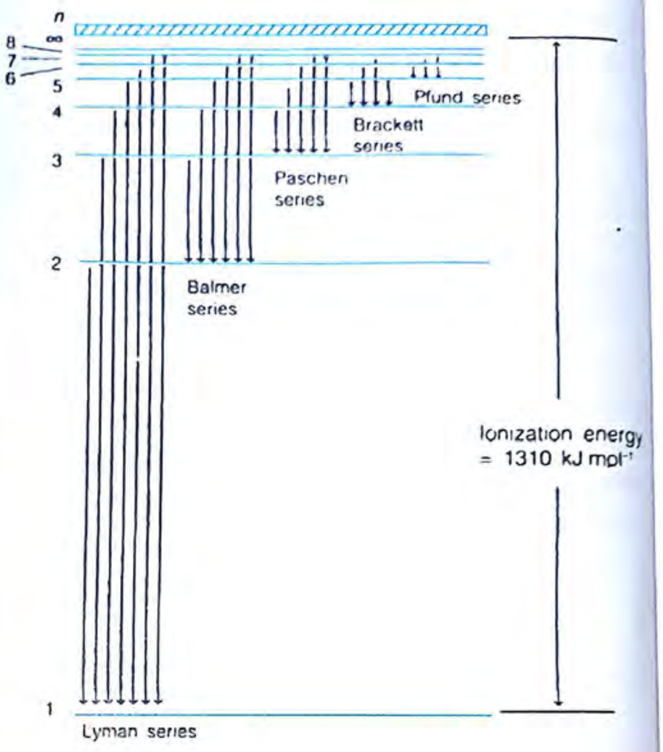
Investigation of the hydrogen atom led Niels Bohr to postulate that the circular orbits of the electrons were quantized, i.e. the electrons were orbiting at certain specific energy levels within the atom. This was a major breakthrough in describing the way electrons are arranged in an atom.

While the Bohr's model of the atom was able to predict the observed spectral lines of hydrogen with great accuracy, it had to be modified to account for the spectrum of more complicated atoms. Bohr's model has now been replaced by the Wave Mechanics Model.

The Wave Mechanics Model assumes that electrons show wave-like properties. (This has been demonstrated experimentally.) The wave like properties of the electron make it very elusive. This led Heisenberg (in 1927) to postulate the famous *Uncertainty Principle*. According to this principle, if we measure the momentum of an electron accurately, then we cannot know its position with certainty and vice versa.

According to Bohr, the electron was restricted to certain energy levels and was thought to move along certain circular orbits around the nucleus. These energy levels were identified by means of the principal quantum number, *n*. The Wave Mechanics Model of the atom does not restrict the electrons to certain energy levels only. Instead, it describes a region around the nucleus called an *orbital* where there is a possibility of finding an electron with a certain amount of energy (that is given by a wave function). The orbital is identified by a set of three quantum numbers. According to the postulates of wave mechanics, the energy levels are composed of one or more orbitals and the distribution of electrons around the nucleus is determined by the number and kind of energy levels that are occupied. Therefore, to predict how electrons are arranged in space, we have to examine the energy levels in the atom. This can be done by discussing the quantum numbers.

Fig. 4.5 Energy levels in the hydrogen atom.



The four quantum numbers

A hydrogen atom has a nucleus consisting of one proton and an electron orbiting round the nucleus. This electron has a number of orbits to choose from, but it will invariably choose the orbit of minimum energy. When this electron absorbs sufficient amount of energy, it could jump to the next higher orbit and to even higher orbits, depending on the amount of energy it absorbs. The atom is now in an *excited state*. If the electron falls to its lowest orbit, the atom is said to return to the *ground state*. This process results in the emission of energy in the form of light, which produces a line in the emission spectrum of hydrogen. Thus, depending on the orbits from which the electron has fallen, a number of different lines are produced as shown in fig. 4.6.

Each orbit in the Bohr's atom is denoted by the *principal quantum number, n*, which is a positive integer. The orbit closest to the nucleus, which is also the orbit of minimum energy (or the ground state of the atom) has a principal quantum number, $n = 1$. The other orbits have values of $n = 2, 3, \ldots$, and so on up to infinity. Letters are also associated with these orbits or shells as shown.

Principal quantum number	1	2	3	4	5	6
Letter associated	*K*	*L*	*M*	*N*	*O*	*P*

For example, the orbit with $n = 1$ is known as the *K* shell, the orbit with $n = 2$ is known as the *L* shell, and so on. More detailed spectroscopic study shows that the main energy levels of an atom designated by the principal quantum number, *n*, are capable of subdivision. Studies show that the energy of an electron may be characterized by four quantum numbers.

1 The principal quantum number, *n*, has integral values 1, 2, 3, 4, etc. The energy levels or shells are determined by the principal quantum numbers. **NOTE** The maximum possible number of electrons in a shell is given by $2n^2$.

2 The *subsidiary or azimuthal quantum number, l*, has integral values ranging from 0 to $(n-1)$. The electrons with subsidiary quantum numbers 0,1, 2 and 3 are usually referred to as the *s*, *p*, *d* and *f* electrons respectively. Thus, this quantum number shows how many energy sublevels there are in each electron shell.

3 The *magnetic quantum number, m*, which has integral values ranging from −1 through 0 to 1, shows the number of orbitals in each energy sublevel, e.g. the *p* subshell has three *p* orbitals.

4 The *spin quantum number, s*, has values

$$-\frac{1}{2} \text{ and } +\frac{1}{2}.$$

NOTE An orbital can only hold two electrons which spin on their axes in opposite directions. Their spins are denoted by the spin quantum numbers.

Before we can apply the quantum numbers to express the electronic configuration of atoms, it is essential to understand a very important principal. known as the *Pauli Exclusion Principle*. According to this principle, two electrons in the same atom cannot have the same values for all four quantum numbers. In other words, two electrons in an atom cannot behave in the same manner.

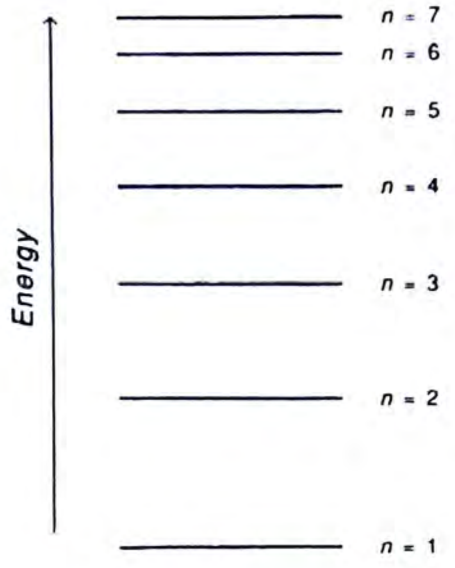


Fig. 4.6 The energy levels in an atom as indicated by the principal quantum number, *n*.

Using these quantum numbers, scientists could work out the electronic configuration of the atoms of all the known elements. They could also explain the properties of the transition elements, the lanthanides and the actinides series.

Probability distribution of electron in its shell

When the probability of finding an electron in a given spherical shell around the nucleus is plotted against *r* (the distance of the electron from the nucleus) for the hydrogen atom, the graph indicates that the probability of finding the electron increases as the

Table 4.4 The energy sublevels.

Name of electrom shell	Value of *n*	Values of *l*	Number of values of *l*	Number of sublevels	Names of the sublevels
K	1	0	One	One	*s*
L	2	0 and 1	Two	Two	*s* and *p*
M	3	0, 1 and 2	Three	Three	*s*, *p* and *d*
N	4	0, 1, 2 and 3	Four	Four	*s*, *p*, *d* and *f*

Table 4.5 The number of orbitals in each sublevel.

Value of *l*	Name of sublevel	Values of *m*	Number of values of m	Number of orbitals	Names orbitals
0	*s*	0	One	One	*s*
1	*p*	1, 0, −1	Three	Three	*p*
2	*d*	2, 1, 0, −1, −2,	Five	Five	*d*
3	*f*	3, 2, 1, 0, −1, −2, −3	Seven	Seven	*f*

distance between the electron and the nucleus decreases.

Note In Bohr's theory, the electron was restricted to being found in a definite region, i.e. it had to be found in that orbit and nowhere else. In the Wave Mechanics Model, however, there is a slight chance that the electron may be located at distances other than that indicated.

Shapes of the s and p orbitals The electrons found in a given shell do not have the same amount of energy. This is because electrons move about the nucleus in different ways.

The *s* electrons move about to produce the effect of a spherical cloud around the nucleus. Thus, s orbitals are spherically symmetrical.

Fig. 4.7 Probability distribution tor the 1s orbitals of the hydrogen atom.

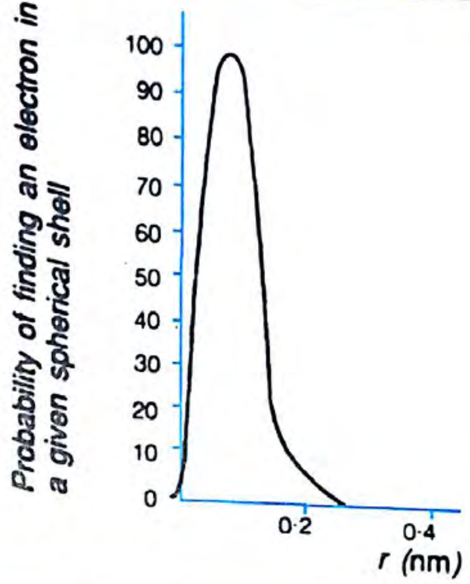


Table 4.6 Electronic configurations of the atoms of elements using the 4 quantum numbers.

Element	Atomic number	The four quantum numbers				Maximum electrons in sublevels	Maximum electrons in principsl sublevels	Configuratio of atoms in ground state
		Principal	Subsidiary	Magnetic	Spin			
Hydrogen	1	$n = 1$	$l = 0$	$m = 0$	$\pm\frac{1}{2}$	2 *s* electrons	2	$1s^1$
Helium	2							$1s^2$
Lithium	3		$l = 0$	$m = 0$	$\pm\frac{1}{2}$	2 *s* electrons		$1s^22s^1$
Beryllium	4							$1s^22s^2$
Boron	5							$1s^22s^22p^1$
Carbon	6	$n = 2$						$1s^22s^22p^2$
Nitrogen	7			$m = 1$	$\pm\frac{1}{2}$		8	$1s^22s^22p^3$
Oxygen	8		$l = 1$	$m = 0$	$\pm\frac{1}{2}$	6 *p* electrons		$1s^22s^22p^4$
Fluorine	9			$m = -1$	$\pm\frac{1}{2}$			$1s^22s^22p^5$
Neon	10							$1s^22s^22p^6$

Fig. 4.8 The shape of an s orbital.

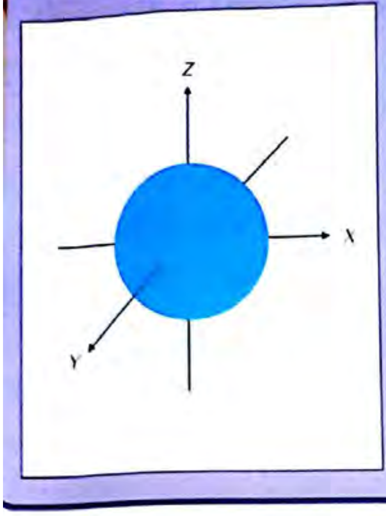
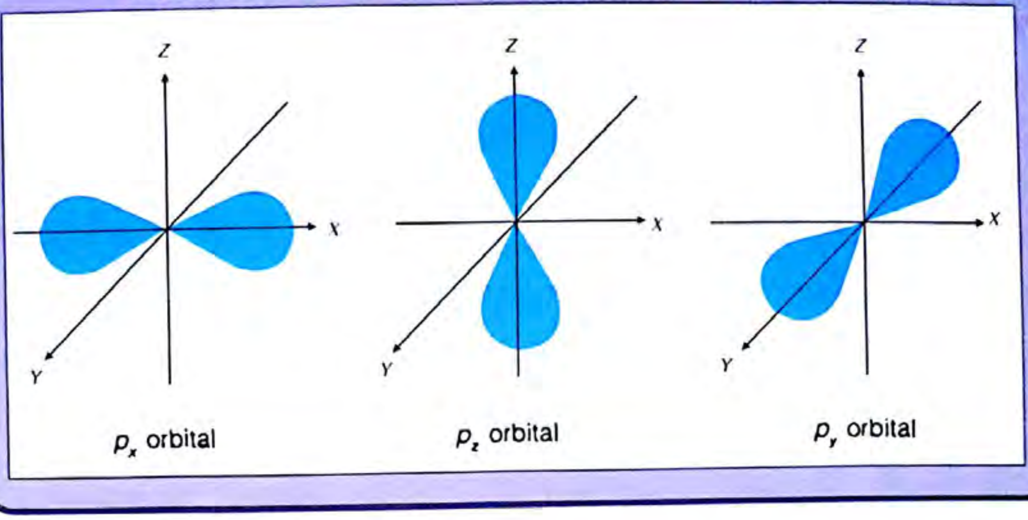


Fig. 4.9 The shapes and relative positions of the three p orbitals in a p subshell.



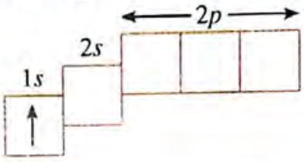
p_x orbital p_z orbital p_y orbital

We can infer the shape of the electron cloud from the subsidiary quantum number, *l*, of an electron. The *p* electrons move about three axes *x*, *y* and *z* that are at right angles to one other. Thus, the *p* orbitals have a marked directional character. The three *p* orbitals are represented as p_x, p_y and p_z.

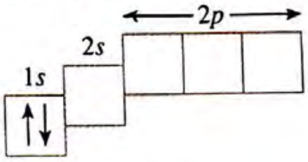
Arrangement of electrons in an atom

The way electrons are arranged in an atom is determined by the order in which the subshells occur on a scale of increasing energy levels. This is so because in the ground state the electrons will be found in the lowest energy levels available.

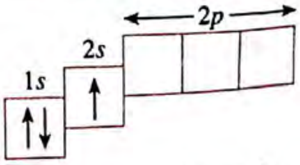
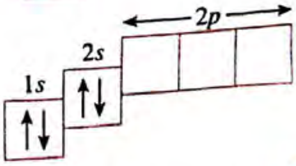
In hydrogen, which has an atomic number of 1, the electron must occupy the 1s sublevel. The number indicates the principal quantum number and the letter the subsidiary quantum number. In the case of hydrogen there is only one electron in the subshell so we denote it as $1s^1$. To keep a check on the spin of the electron, we use an arrow pointing up, i.e. ↑, to show an electron with its spin in one direction, and an arrow pointing down, i.e. ↓, to show an electron with an opposite spin. Thus, the distribution of the electron in a hydrogen atom is as shown below. This is an orbital diagram.

Element	Orbital electrons	Electron sublevels
Hydrogen	$1s^1$	

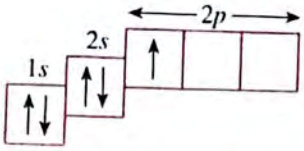
The next atom is the helium atom with an atomic number of 2. It has two electrons which can be accommodated in the 1s orbital. The electronic configuration is $1s^2$. The orbital diagram of helium is as shown.

Element	Orbital electrons	Electron sublevels
Helium	$1s^2$	

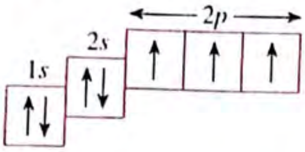
The atoms of the next two elements, lithium and beryllium, have three and four electrons respectively. Since the 1s orbital is already filled, the third and fourth electrons are accommodated in the 2s orbital. The orbital diagrams for some elements are as follows.

Element	Orbital electrons	Electron sublevels
Lithium	$1s^22s^1$	
Beryllium	$1s^22s^2$	

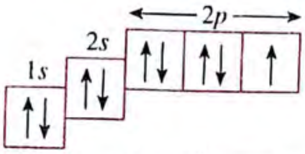
Boron $1s^22s^22p^1$



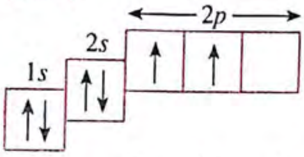
Nitrogen $1s^22s^22p^3$



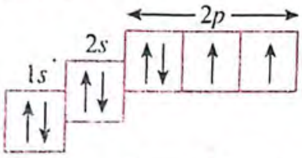
Fluorine $1s^22s^22p^5$



Carbon $1s^22s^22p^2$



Oxygen $1s^22s^22p^4$



Neon $1s^22s^22p^6$

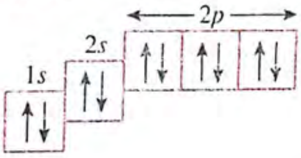


Table 4.7 *The electronic configurations of the first twenty elements of the Periodic Table.*

Element	Atomic number	Electronic configuration									
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
H	1	1									
He	2	2									
Li	3	2	1								
Be	4	2	2								
B	5	2	2	1							
C	6	2	2	2							
N	7	2	2	3							
O	8	2	2	4							
F	9	2	2	5							
Ne	10	2	2	6							
Na	11	2	2	6	1						
Mg	12				2						
Al	13				2	1					
Si	14		10 electrons		2	2					
P	15				2	3					
S	16				2	4					
Cl	17				2	5					
Ar	18	2	2	6	2	6					
K	19	2	2	6	2	6		1			
Ca	20	2	2	6	2	6		2			

We notice that there are three p orbitals in the p sublevel. How would the electrons occupy these orbitals? According to Hund, electrons occupy each orbital singly first before electron-pairing takes place (because mutual repulsion exists between any paired electrons). We can now represent the electronic structures of the next six elements i.e. boron, carbon, nitrogen, oxygen, fluorine and neon, as shown above.

In a similar manner, from the electronic configurations given in table 4.7, we can use orbital diagrams to represent the first twenty elements of the Periodic Table.

Atomic number and mass number

The atomic number, Z, of an element is the number of protons in one atom of that element.

All the atoms of a particular element have the same number of protons in their nuclei. The number of protons or atomic number, Z, is a basic property of an element, since no two elements have the same number of protons in their atoms. Hydrogen, carbon and oxygen contain 1, 6 and 8 protons in their respective atoms. Their atomic numbers are 1, 6 and 8 respectively. Elements can be arranged in a series on the basis of their atomic numbers.

The proton has the same mass as the neutron. This mass is taken to be 1 unit of atomic mass. If an atom has 2 protons and 2 neutrons, then it has 4 units of atomic mass or a *mass number* of 4.

The mass number, A, of an atom of an element is the sum of the protons and neutrons in it.

We can describe an atom of an element by writing its symbol together with its atomic number and mass number.

mass number (superscript) → A
X ← symbol of an atom of the element
atomic number (subscript) → Z

Table 4.8 The first twenty elements arranged in order of increasing atomic numbers.

Element	Symbol	Number of protons (or atomic number)	Number of electrons and their distribution in the shells K	L	M	N
Hydrogen	H	1	1			
Helium	He	2	2			
Lithium	Li	3	2	1		
Beryllium	Be	4	2	2		
Boron	B	5	2	3		
Carbon	C	6	2	4		
Nitrogen	N	7	2	5		
Oxygen	O	8	2	6		
Fluorine	F	9	2	7		
Neon	Ne	10	2	8		
Sodium	Na	11	2	8	1	
Magnesium	Mg	12	2	8	2	
Aluminium	Al	13	2	8	3	
Silicon	Si	14	2	8	4	
Phosphorus	P	15	2	8	5	
Sulphur	S	16	2	8	6	
Chlorine	Cl	17	2	8	7	
Argon	Ar	18	2	8	8	
Potassium	K	19	2	8	8	1
Calcium	Ca	20	2	8	8	2

Thus, the atoms of hydrogen, oxygen and sodium can be written as $^{1}_{1}$H, $^{16}_{8}$O and $^{23}_{11}$Na.

Isotopy

Isotopy is a phenomenon whereby atoms of an element exhibit different mass numbers but have the same atomic number. This is due to differences in the number of neutrons present in these atoms. Such atoms are known as *isotopes*. Isotopes of an element have slightly different physical properties but exhibit the same chemical properties. This is because neutrons contribute only to the mass of an atom, not its chemical behaviour.

Isotopes of an element are represented by the symbol of the element with the mass and atomic numbers. For example, $^{35}_{17}$Cl and $^{37}_{17}$Cl represent atoms of the two common isotopes of chlorine. For each atom, the number of neutrons can be obtained by finding the difference between the mass and atomic numbers, i.e. $A-Z$.

Table 4.9 An analysis of the chlorine isotopes.

	Isotope $^{35}_{17}$Cl	Isotope $^{37}_{17}$Cl
Mass number, A	35	37
Atomic number, Z	17	17
Number of protons	17	17
Number of electrons	17	17
Number of neutrons ($A-Z$)	$35 - 17 = 18$	$37 - 17 = 20$
Abundance in nature (%)	75	25

The relative atomic mass of an element which exhibits isotopy is the average mass of its various isotopes as they occur naturally in any quantity of the element. The relative atomic mass of chlorine is 35.5 because a given quantity of chlorine always contains 75% of $^{35}_{17}$Cl and 25% of $^{37}_{17}$Cl, i.e.

$$\left(\frac{75}{100}\times 35\right)+\left(\frac{25}{100}\times 37\right)=35.5$$

Table 4.10 *Isotopes of some elements.*

Element	Carbon		Oxygen		
Isotopes	$^{12}_{6}C$	$^{13}_{6}C$	$^{16}_{8}O$	$^{17}_{8}O$	$^{18}_{8}O$
Abundance in nature (%)	98.9	1.1	99.76	0.04	0.20

Practically every element exhibits isotopy. The presence of two or more isotopes of an element explains why the relative atomic masses of elements are not whole numbers.

Rare gases (stable electronic configuration)

The rare gases exhibit great chemical stability. All of them except helium have 8 electrons in their outermost shells. This electronic arrangement is known as the *octet*. Helium, with 2 electrons in its outermost shell, has a *duplet* arrangement.

The duplet and the octet arrangements seem to represent stability, as the rare gases are chemically inactive. Other elements undergo chemical reactions to achieve the duplet and octet arrangements in their outermost shells.

Electronic configuration and the Periodic Table

Let us arrange the first twenty elements in increasing atomic numbers and in a horizontal manner such that each row ends with a rare gas. What we get is an arrangement of these elements like that in the modern *Periodic Table.*

In this arrangement, a certain pattern is revealed. Elements with similar chemical properties appear at regular intervals or *periods*. As a result, elements in each vertical column have similar chemical properties and similar electronic configurations. Their atoms have the same number of electrons in their outermost shells. For example,

- lithium, sodium and potassium are similar reactive metals, with each of their atoms having a single electron in the outermost shell;
- fluorine and chlorine are similar reactive non-metals, with each of their atoms having 7 electrons in the outermost shell;
- neon and argon are rare gases with the same number of electrons in their outermost shells.

In contrast, elements in the same horizontal row have chemical properties which change from metallic (on the left) to non-metallic (on the right). The number of electrons in the outermost shells of their atoms also increases progressively from left to right.

These trends indicate that electrons in the outermost shells of atoms are probably the ones responsible for the chemical properties of elements.

CHEMICAL COMBINATION

Owing to their electronic configuration, the rare gases are very stable. The tendency of the other elements is to try to attain this stable duplet or octet structure possessed by the rare gases. This is achieved during chemical combination. There are two main types of chemical combination.

1 *Electrovalent* (or *ionic*) combination.
2 *Covalent* combination, which is classed into:
  (a) *Ordinary covalent* combination,
  (b) *Coordinate covalent* combination.

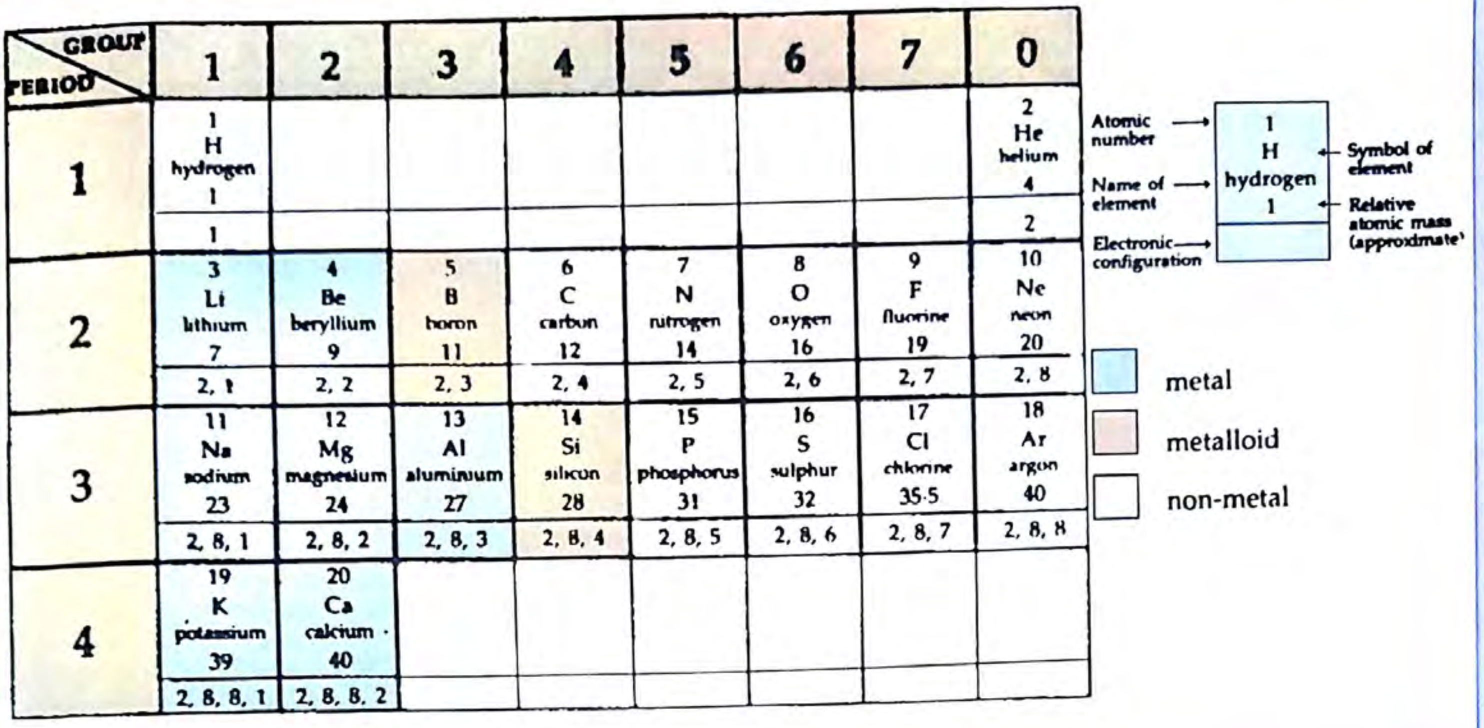
Electrovalent Combination

In electrovalent combination, there is a transfer of electrons from one atom (usually metallic) to another (usually non-metallic). Thus, we have atoms which act as donors of electrons and those which act as acceptors of electrons. The electrons involved reside in the outermost shells of the atoms and are known as *valence electrons*.

Table 4.11 *Electronic configuration of the rare gases.*

Rare gas	Symbol	Number of protons (for atomic number)	Number of electrons and their distribution in the shells					
			K	*L*	*M*	*N*	*O*	*P*
Helium	He	2	2					
Neon	Ne	10	2	8				
Argon	Ar	18	2	8	8			
Krypton	Kr	36	2	8	18	8		
Xenon	Xe	54	2	8	18	18	8	
Radon	Rn	86	2	8	18	32	18	8

Fig. 4.10 Arrangement of the first twenty elements in the Periodic Table.



GROUP / PERIOD	1	2	3	4	5	6	7	0
1	1 H hydrogen 1 1							2 He helium 4 2
2	3 Li lithium 7 2, 1	4 Be beryllium 9 2, 2	5 B boron 11 2, 3	6 C carbon 12 2, 4	7 N nitrogen 14 2, 5	8 O oxygen 16 2, 6	9 F fluorine 19 2, 7	10 Ne neon 20 2, 8
3	11 Na sodium 23 2, 8, 1	12 Mg magnesium 24 2, 8, 2	13 Al aluminium 27 2, 8, 3	14 Si silicon 28 2, 8, 4	15 P phosphorus 31 2, 8, 5	16 S sulphur 32 2, 8, 6	17 Cl chlorine 35·5 2, 8, 7	18 Ar argon 40 2, 8, 8
4	19 K potassium 39 2, 8, 8, 1	20 Ca calcium 40 2, 8, 8, 2						

Elements whose atoms have only one or two valence electrons require less energy to give away these electrons. Their ease in releasing these electrons in order to attain the stable duplet or octet structure makes them very reactive. Such elements readily combine with many other elements and compounds in their environment to form compounds. Examples are the alkali metals such as sodium and potassium. Each of their atoms has only one valence electron to donate in order to obtain a stable electronic octet. Calcium is comparatively less reactive since each of its atoms has two valence electrons. A greater amount of energy is required to dispose of the two electrons and attain the stable octet. Aluminium, with three valence electrons, is even less reactive while carbon, with four valence electrons, does not transfer its electrons at all.

On the other hand, non-metals like fluorine and chlorine are extremely reactive like the alkaline metals. This is because each of their atoms has seven valence electrons and needs to accept only one more electron to attain a stable octet configuration. Large amounts of energy are released during this process.

In electrovalent combinations, after donating their valence electrons, metallic particles become positively charged; non-metallic particles become negatively charged after acquiring extra electrons. These charged particles are known as *ions*.

The number of protons, i.e. the atomic number is unaffected by the transfer of electrons that occur in an electrovalent combination. Therefore, the character of an element is unchanged by the chemical combination since it is determined by the atomic

Table 4.12 Number of electrons in the outermost shell and the chemical reactivity of an element.

Element	**Sodium, Na**	**Calcium, Ca**	**Aluminium, Al**	**Chlorine, Cl**	**Oxygen, O**
Number of electrons in outermost shell	1	2	3	7	6
To achieve stable electronic configuration	Donates 1 electron	Donates 2 electrons	Donates 3 electrons	Accepts 1 electron	Accepts 2 electrons
Chemical reactivity	Very reactive	Reactive	Fairly reactive	Very reactive	Reactive

EXAMPLES OF ELECTROVALENT COMBINATIONS

1 *Formation of sodium chloride* (Na^+Cl^-).

	Before combination		**After combination**	
	Sodium atom	Chlorine atom	Sodium ion (+)	Chloride ion (-)
Proton	11	17	11	17
Electron	2, 8, 1	2, 8, 7	2,8 (stable octet; loss of an electron results in a net positive charge)	2, 8, 8 (stable octet; one excess electron results in a net negative charge)

Equations of reaction

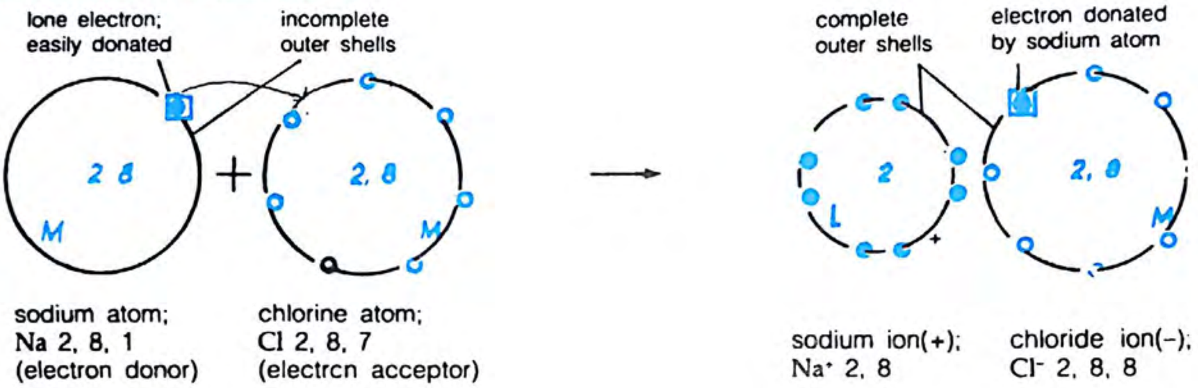
$Na - e^- \rightarrow Na^+$

$Cl + e^- \rightarrow Cl^-$

$(Na - e^-) + (Cl + e^-) \rightarrow Na^+ + Cl^-$

$\therefore Na + Cl \rightarrow Na^+Cl^-$

Diagrammatic representation



2 *Formation of magnesium oxide* ($Mg^{2+}O^{2-}$).

	Before combination		**After combination**	
	Magnesium atom	Oxygen atom	Magnesium ion (2+)	Oxide ion (2-)
Proton	12	8	12	8
Electron	2, 8, 2	2, 6	2, 8 (stable octet; loss of two electrons results in two net positive charges)	2, 8 (stable octet; two excess electrons result in two net negative charges)

Equations of reaction

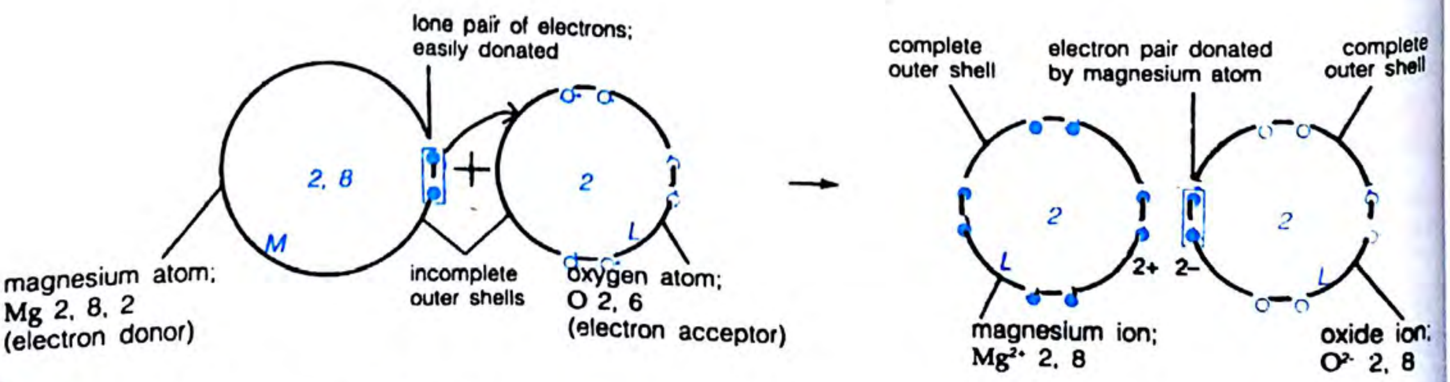
$Mg - 2e^- \rightarrow Mg^{2+}$

$O + 2e^- \rightarrow O^{2-}$

$(Mg - 2e^-) + (O + 2e^-) \rightarrow Mg^{2+} + O^{2-}$

$\therefore Mg + O \rightarrow Mg^{2+}O^{2-}$

Diagrammatic representation



3 *Formation of magnesium chloride* ($Mg^{2+}2Cl^-$).

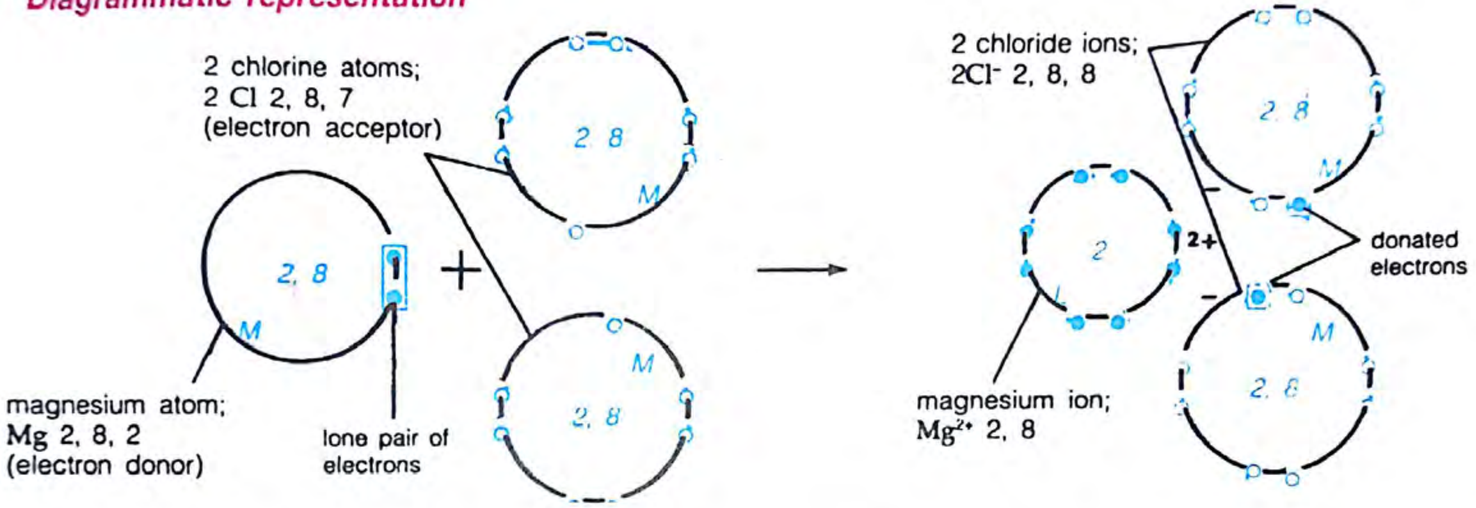
	Before combination		After combination	
	Magnesium atom	Two chlorine atoms	Magnesium ion (2+)	Two chloride ions (2-)
Proton	12	17 17	12	17 17
Electron	2, 8, 2	2, 8, 7 2, 8, 7	2, 8 (stable octet; loss of two electrons results in two net positive charges)	2, 8, 8 2, 8, 8 (stable octet; two excess electrons result in two net negative charges)

Equations of reaction

$Mg - 2e^- \rightarrow Mg^{2+}$ $\quad (Mg - 2e^-) + (2Cl + 2e^-) \rightarrow Mg^{2+} + 2Cl^-$

$2Cl + 2e^- \rightarrow 2Cl^-$ $\quad \therefore Mg + 2Cl \rightarrow Mg^{2+}2Cl^-$

Diagrammatic representation



NOTE In the diagrammatic representations of the combinations, only the electronic distributions in the outermost shells of the atoms have been shown. The electronic distributions in the inner shells are indicated by the figures inside. A vacant shell is not represented.

number and not by the number of electrons. For example, the sodium atom which donates an electron to chlorine in order to attain the octet configuration of neon still contains 11 protons, whereas a neon atom has 10 protons in its nucleus.

Electrovalent or Ionic Compounds

Electrovalent combinations result in the formation of positive and negative ions, which are held together by strong electrostatic forces of attraction. This attractive force between oppositely charged ions constitute the *electrovalent or ionic bond*. The oppositely charged ions do not pair up to form molecules, because they exert their force of attraction equally in all directions.

The formula of an electrovalent compound, for example NaCl, does not represent a mole of sodium chloride molecules, but a mole of sodium and chloride ions (where the number of sodium ions is equal to the number of chloride ions).

We can analyze the structures of the crystals of electrovalent compounds by X-ray diffraction studies. These crystals are strong structures because of the great electrostatic forces of attraction between the positive and negative ions.

We shall now discuss the important characteristics of electrovalent compounds.

Structure

Electrovalent compounds exist mainly as solids at room temperature. They consist of positive and negative ions

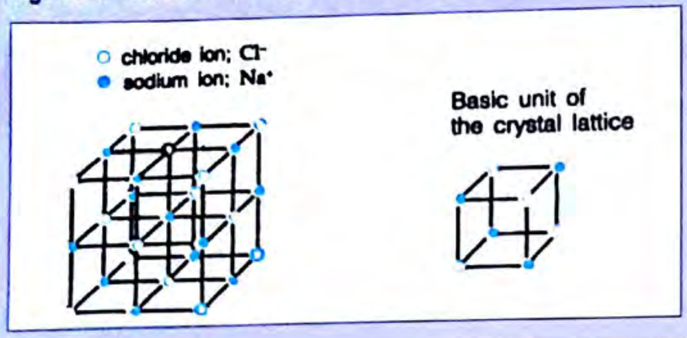


Fig. 4.11 Model of a sodium chloride crystal.

arranged in an orderly pattern to form three-dimensional crystal lattices. A positive ion will be surrounded by negative ions, while a negative ion will be surrounded by positive ions.

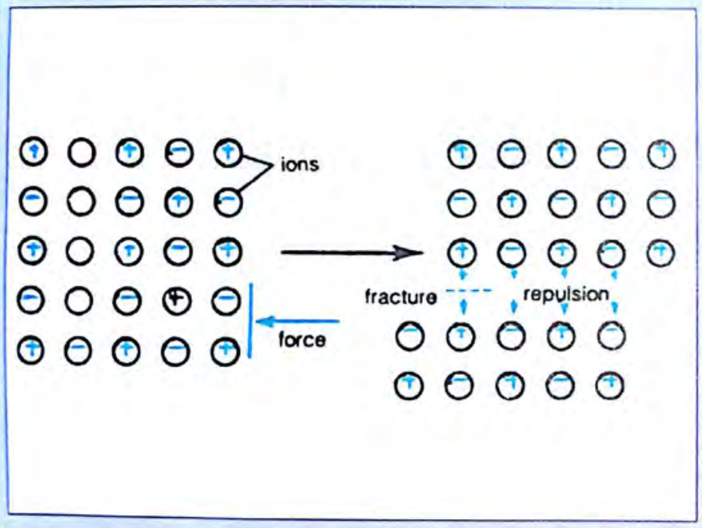


Fig. 4.12 Crystal of an Ionic compound undergoing fracture (two-dimensional representation).

Fig. 4.11 shows a crystal of sodium chloride composed of sodium and chloride ions. These ions are definitely orientated in relation to one another. Each sodium ion in the crystal is surrounded by six chloride ions, each equidistant from the central sodium ion. Each chloride ion is also surrounded by six sodium ions, which are equidistant from the central chloride ion. Crystals of an electrovalent compound are hard and brittle. If a force is applied to such a crystal, it does not change the shape of the crystal, but it can shatter or fracture the crystal.

High melting and boiling points

Electrovalent compounds have high melting and boiling points because of the strong electrovalent bonds between the ions. Sodium chloride melts at 801 °C because a great deal of energy is needed to break down its crystal lattice. This is why most ionic compounds are solids at room temperature. The boiling point of sodium chloride is 1 467 °C.

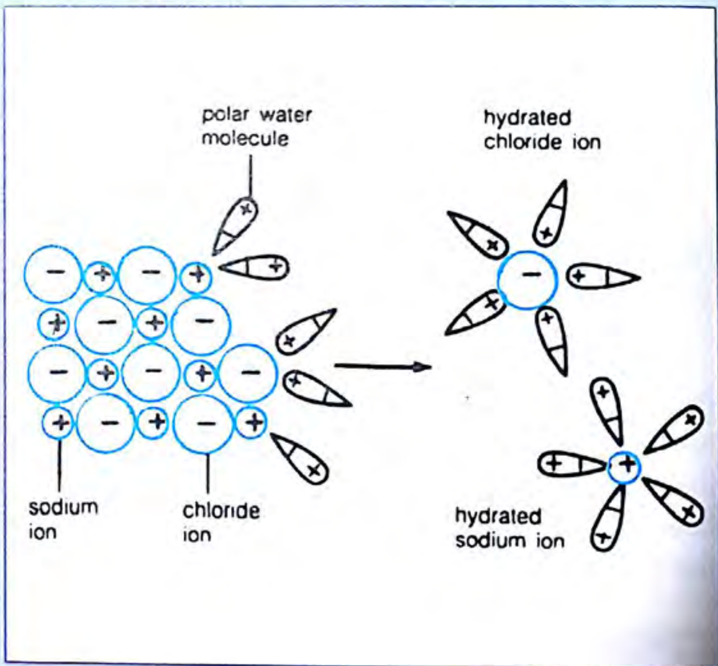
Solubility

Most ionic compounds readily dissolve in water. When an ionic compound is placed in water, the force between the ions in the crystal weakens. As a result, the ions separate and become surrounded by water molecules, i.e. *hydrated.*

Energy is needed to break up the electrovalent bonds in the crystal. It is also liberated when water molecules become attached to the ions. Sodium chloride readily dissolves in water because:

energy needed to break up bonds < energy liberated on hydration of ions

Fig. 4.13 How water dissolves a sodium chloride crystal.



Some ionic compounds, like magnesium oxide, do not dissolve readily in water because:

energy needed to break up bonds > energy liberated on hydration of ions

So there is not enough energy to bring about the dissolution of these compounds.

Experiment 4.1 To test if an aqueous solution of a substance is an electrolyte and hence determine if the substance is ionic.

Method Prepare aqueous solutions of sodium chloride, trioxonitrate(V) acid, ethanoic acid, sodium hydroxide, aqueous ammonia, sugar and ethanol.

Set up the apparatus. Partially immerse the carbon electrodes in a beaker containing about 100 cm^3 sodium chloride solution. Then complete the circuit by pressing down the switch. Note if the bulb lights up. Repeat the procedure with the other solutions.

Result The bulb lights up only if an electric current flows in the circuit when the switch is closed. For an electric current to flow, the solution must conduct electricity

Name of aqueous solution	Does bulb light up?	Electrolyte or non-electrolyte?	Is it ionic?

Conclusion Aqueous solutions of ionic compounds like inorganic salts, acids and alkalis conduct electricity.

Fig. 4.14 Testing for an electrolyte

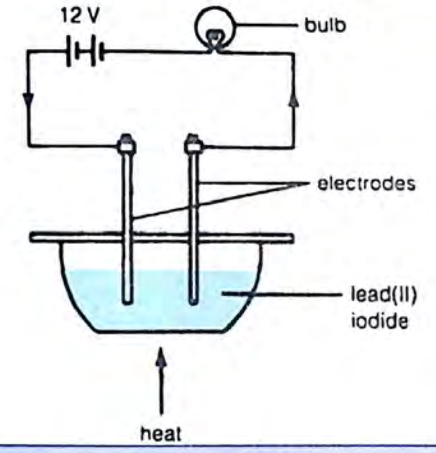
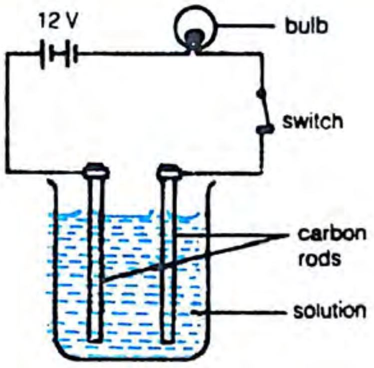


Fig. 4.15 To test it an aqueous solution is an electrolyte.



Ionic compounds generally dissolve in water and other polar solvents like ethanol. They do not dissolve in non-polar solvents like benzene and tetrachloromethane.

Fig. 4.13 shows how water molecules which are polar dissolve a crystal of sodium chloride. They do so by surrounding the individual ions on the surface of the sodium chloride crystal and removing them. This exposes the inner layers of sodium chloride ions to the action of the water molecules. The process continues until the whole crystal dissolves.

Electrolytes

Liquids which conduct electricity are known as *electrolytes*. Ionic compounds can conduct electricity when molten or when dissolved in water. This is because the ions are free to move about when the compound is in a liquid or an aqueous state. In the solid state, the ions are in fixed positions in the crystal lattice, and so cannot conduct electricity.

To test if a molten compound conducts electricity, set up an apparatus as shown in fig. 4.14. Place some lead(II) iodide crystals in the crucible. The bulb does not light up at the beginning when the lead(II) iodide is solid. On heating, the lead(II) iodide melts. Violet iodine vapour forms at one electrode, while globules of metallic lead form at the other. At the same time, the bulb lights up, showing that an electric current is flowing. This experiment proves that ions are present in lead(II) iodide.

Ordinary Covalent Combination

In covalent combination, there is no transfer of electrons between the atoms. Instead, there is a sharing of a pair of electrons between the two reacting atoms

Table 4.13 *Electron pairs in covalent molecules.*

Molecule	Lone pair of of electrons	Shared pair of electrons
Water	2	2
Ammonia	1	3

so that both can attain the stable octet structure. This pair of electrons is known as the *shared pair*. Each reacting atom contributes one member of a shared pair. Sometimes, more than one pair of electrons may be shared between two reacting atoms. *The shared electrons may be regarded as revolving in orbits controlled by both nuclei, thereby forming the covalent bond*. Thus, molecules and not ions are formed in covalent combination.

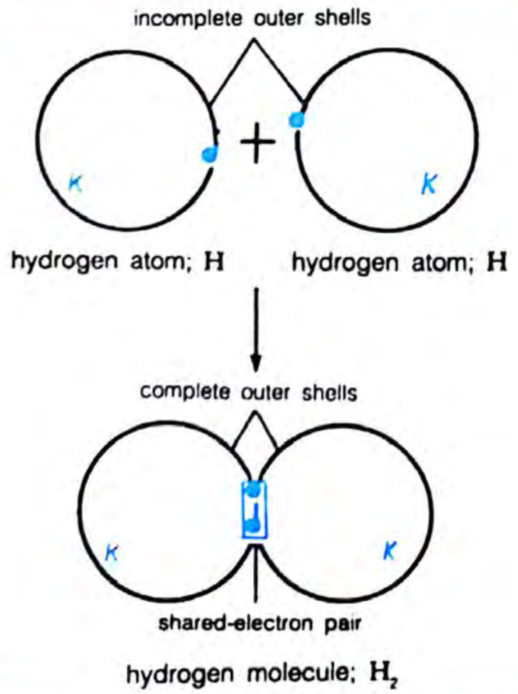
Diatomic molecules of elements are formed by covalent combination. Examples are the chlorine and the hydrogen molecules. Organic compounds are also formed by this method, e.g. the formation of methane.

Conventionally, the shared pair is represented by a stroke between the two atoms in the association, e.g. H–H and Cl–Cl.

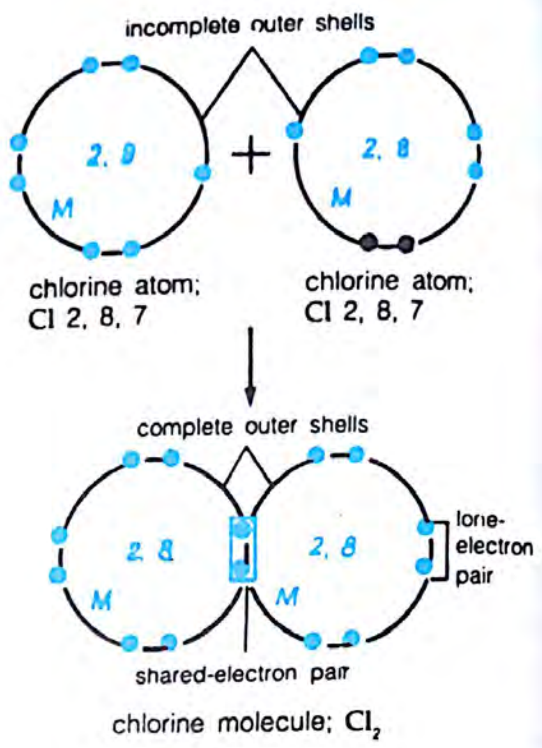
Study the examples of covalent combinations carefully. Are all the electrons in the outermost shells involved in the formation of covalent bonds? In the hydrogen molecule, both electrons (i.e. one from each atom) are used to form a shared electron pair. In the chlorine molecule, only one electron per atom is used in forming a covalent bond – the other six electrons in each atom form three *lone-electron pairs*.

EXAMPLES OF COVALENT COMBINATIONS

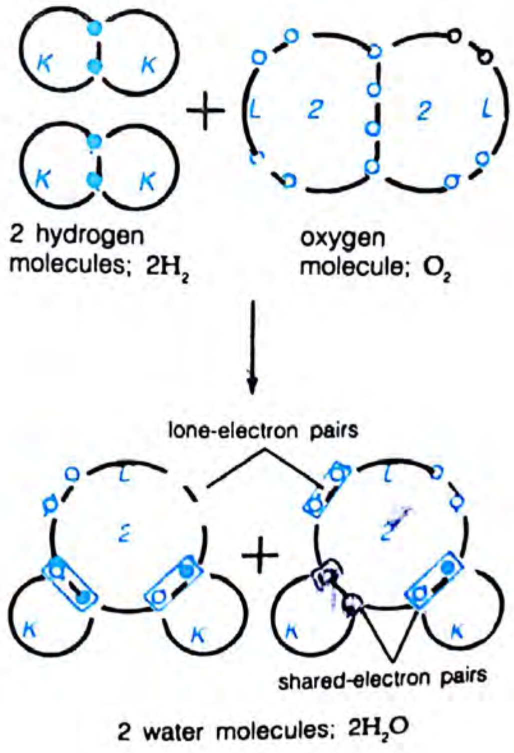
1 Formation of a hydrogen molecule, H_2.



2 Formation of a chlorine molecule, Cl_2.

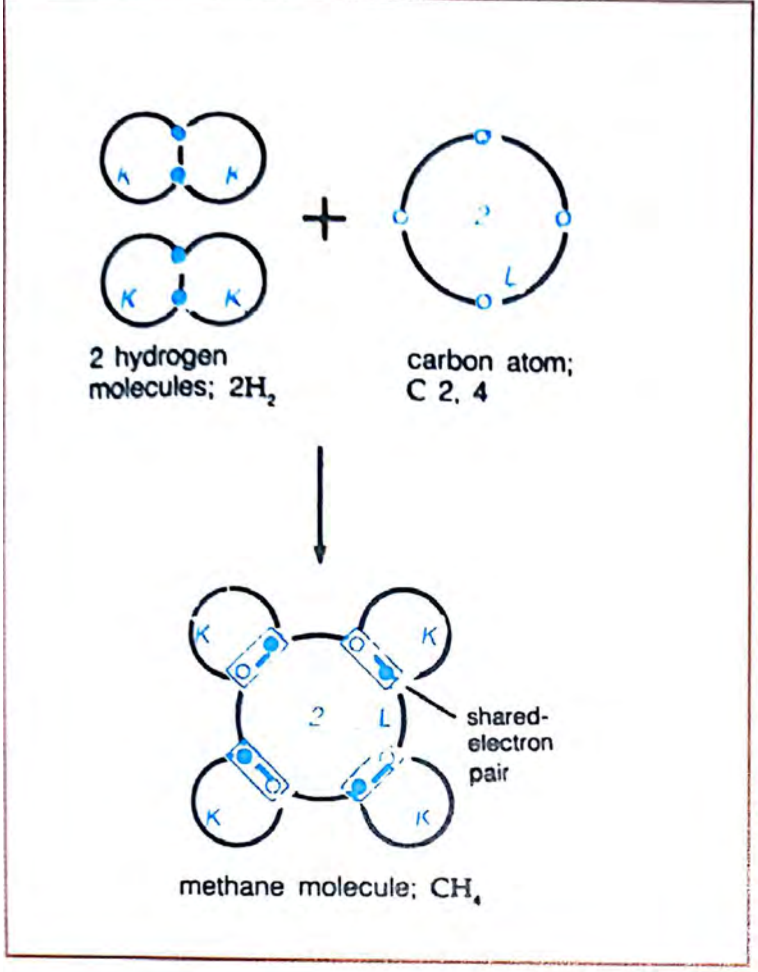


3 Formation of a water molecule, H_2O.



H

4 *Formation of a methane molecule*, CH_4.



5 *Formation of ammonia molecules*, NH_3.

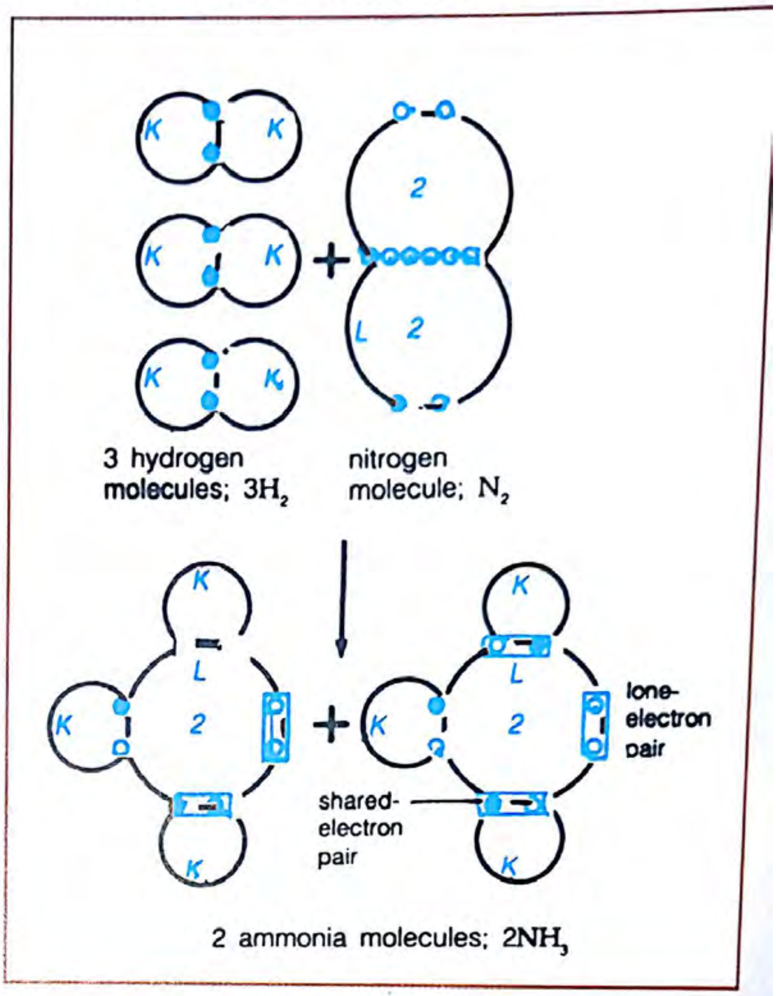
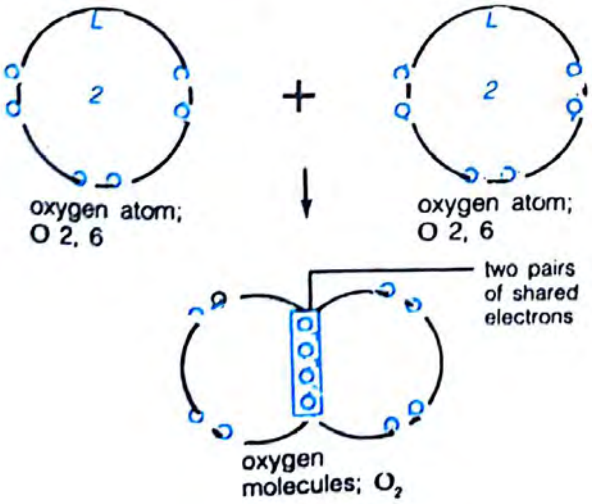


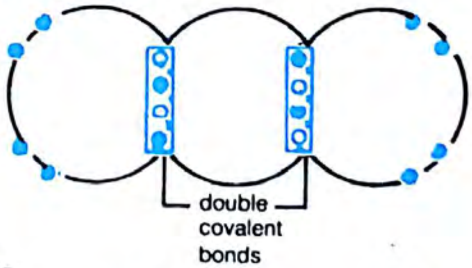
Fig. 4.16 Molecules with double bonds.

Formation of an oxygen molecule



Carbon(IV) oxide molecule

O=C=O



Ethene molecule

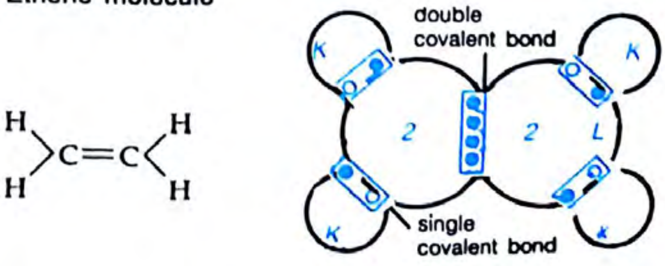


Fig. 4.17 Molecules with triple covalent bonds.

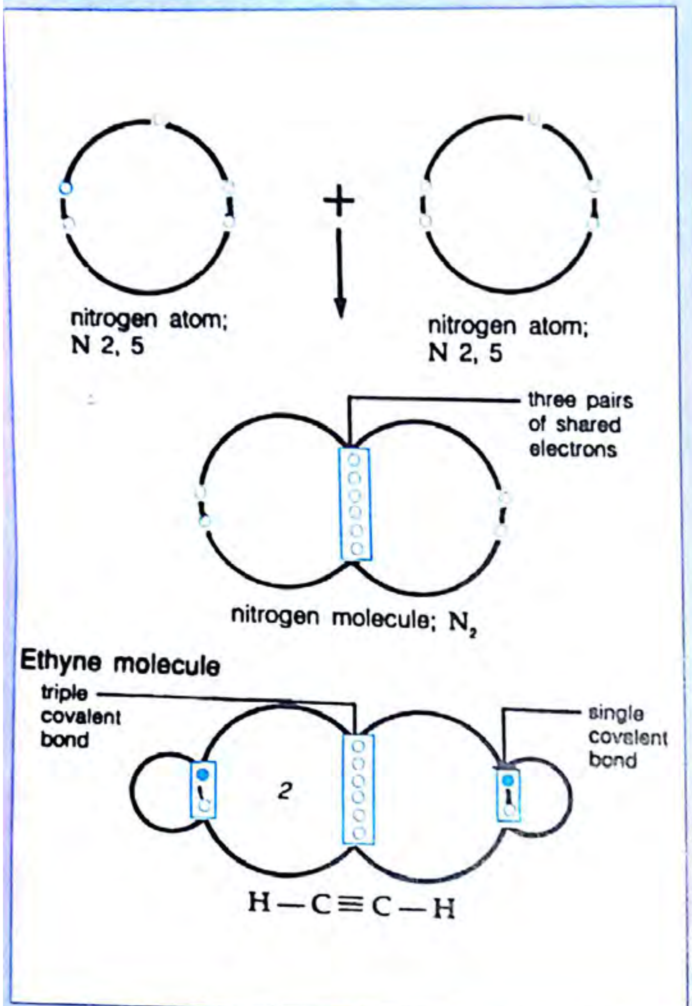
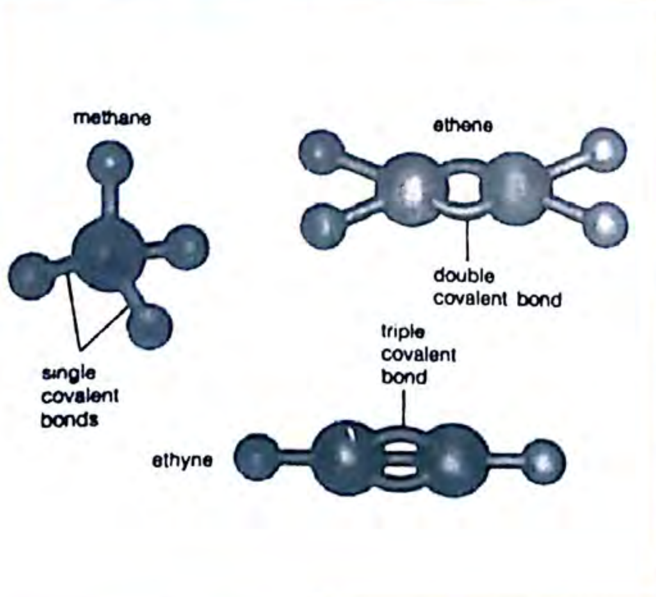


Fig. 4.18 Three-dimensional representations of the methane, ethena and ethyne molecules.



The bonds formed in hydrogen and chlorine molecules are called *single covalent bonds* or simply *single bonds*. They are formed when each of the two atoms involved in the bond contributes one electron to the bond.

In some covalent combinations, each atom involved in the bond contributes two or even three electrons to the bond formation. For example, in an oxygen molecule, the oxygen atoms are bound together by the sharing of two pairs of electrons, i.e. each oxygen atom contributes two electrons to the bond. This type of bond is called a *double covalent bond* or simply a *double bond*. It is represented by double lines between the two atoms involved in the bond, i.e. O = O.

Other substances in which there are double covalent bonds include the carbon(IV) oxide molecule and the ethene molecule. In the ethene molecule, there are four single covalent bonds between carbon and hydrogen atoms and one double covalent bond between the two carbon atoms.

Now, let us look at two substances in which there is a triple covalent bond, i.e. a bond formed by sharing three pairs of electrons. They are the nitrogen and the ethyne molecules.

By counting the electrons, including the shared electrons, each outer shell in the molecule of nitrogen has eight electrons. Each nitrogen atom is now stable and the molecule exists as a single unit. The nitrogen molecule can be written as N≡N indicating that three pairs of electrons are shared.

In the ethyne molecule, there are two C–H single bonds and one C≡C triple bond.

Covalent Compounds

The molecules of simple covalent compounds are not flat structures as shown in the figures discussed earlier. They are three-dimensional structures like the crystals of electrovalent compounds. The covalent bonds determine the shape of the covalent molecule. We shall now discuss the important characteristics of covalent compounds.

Structure

Covalent compounds consist of molecules which have a definite shape. Simple covalent compounds are often either gases or volatile liquids because their molecules, being electrically neutral, are not bound by strong

Fig. 4.19 Vaporization of an iodine crystal.

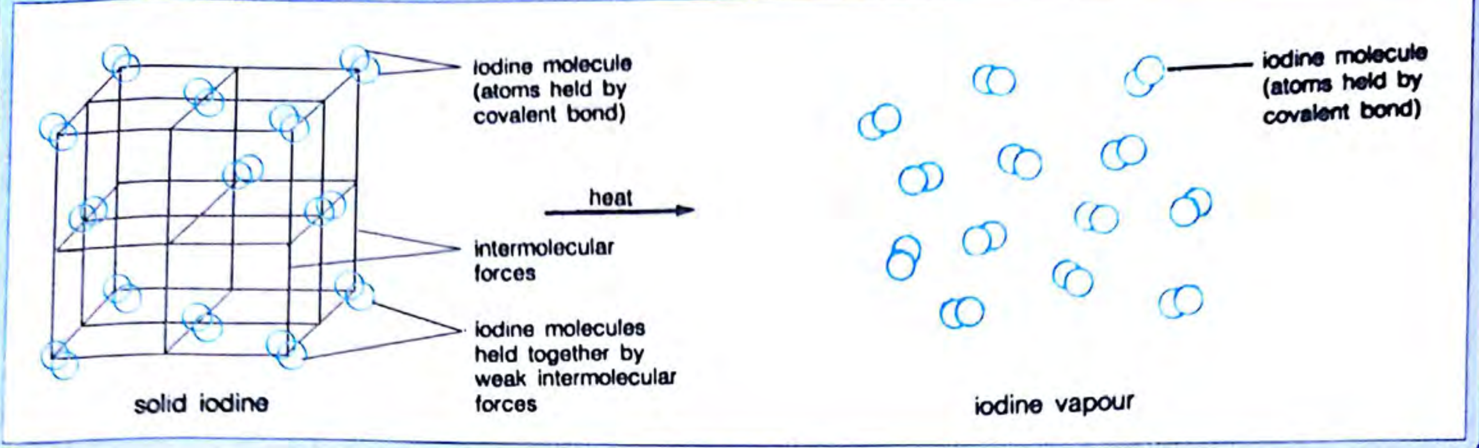
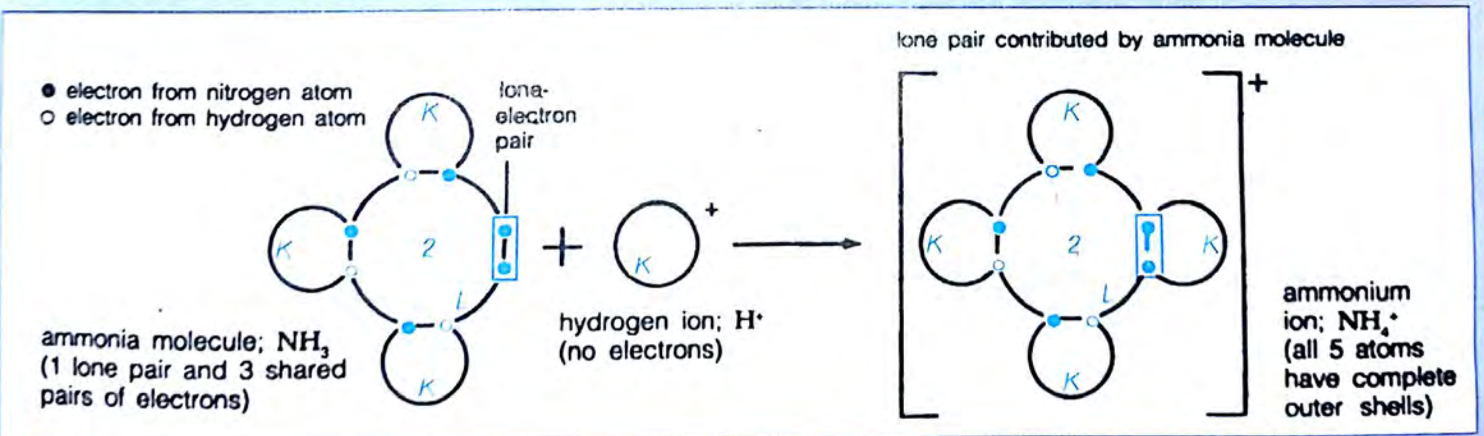


Table 4.14 Melting and boiling points of some ionic and covalent substances.

Substance	Nature of bonding	Melting point(°C)	Boiling point(°C)
Magnesium chloride	Electrovalent	712	1400
Magnesium oxide	Electrovalent	2800	3600
Sodium chloride	Electrovalent	800	1430
Ethene	Covalent	–169	–104
Ethane	Covalent	–183	–88
Water	Covalent	0	100
Ammonia	Covalent	–78	–33
Ethanol	Covalent	–115	79
Iodine	Covalent	–114	183

Fig. 4.20 Formation of the ammonium ion.



attractive forces. Carbon(IV) oxide, methane and ethanol are some examples. In more complex covalent compounds, the molecules are held together by weak intermolecular bonds such as hydrogen bonds and van der Waals forces to form liquids and crystals. Since such forces can easily be broken by a reasonably small amount of heat energy, these covalent compounds are usually volatile with low melting and boiling points.

From table 4.14, we see that ionic compounds have much higher melting and boiling points than covalent compounds. A greater amount of energy is required to separate the ions in an ionic compound than to separate the covalent molecules held together by weak intermolecular bonds in a solid or liquid covalent compound. Covalent bonds, however, are very strong and are not easily broken by heat.

Solubility

Covalent compounds usually dissolve in nonpolar solvents and not in polar solvents like water.

Non-electrolytes

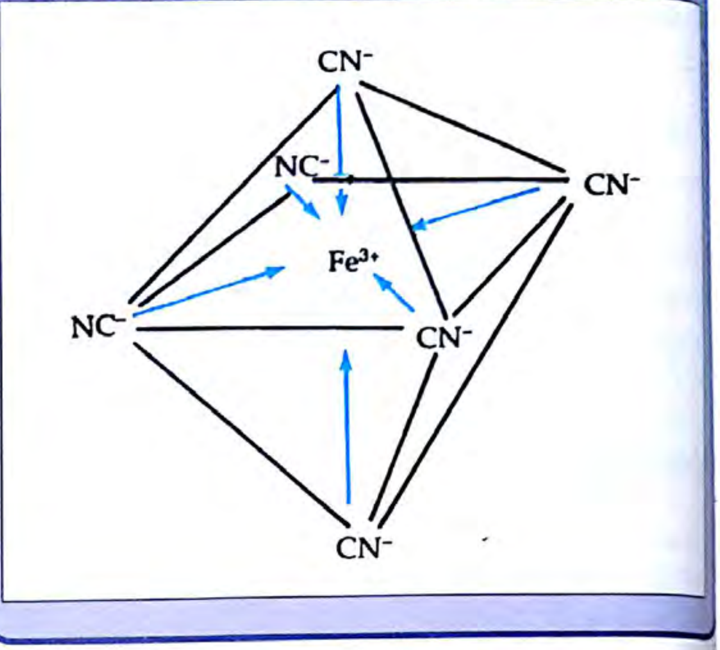
Most covalent compounds do not conduct electricity, i.e. they are not electrolytes. This is because covalent molecules do not contain charged particles. Some covalent compounds, like hydrogen chloride, exhibit a certain amount of ionic character. A solution of hydrogen chloride gas in water will conduct electricity, whereas a solution of dry hydrogen chloride gas in dry toluene (a non-polar solvent) will not.

Coordinate Covalent Combination

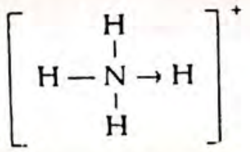
Coordinate covalent combination is also known as *dative covalent combination*. Like the ordinary covalent combination, there is a sharing of electrons. But, unlike the ordinary covalent bond in which the shared pair is contributed equally by the two participating atoms, the pair in the coordinate covalent bond is donated by only one of the participants. Such a pair of electrons is called the *lone pair*. Thus, one of the reactants in a coordinate covalent combination must have a lone pair.

Ammonia and water molecules possess lone pairs and so readily enter into coordinate covalent combinations. When ammonia reacts with hydrochloric acid, the hydrogen ion from the acid accepts the lone pair from the ammonia molecule, resulting in a coordinate covalent bond. This bond enables the hydrogen ion to acquire the stable duplet structure of helium, the nearest rare gas, and, at the same time, allows the nitrogen atom of the ammonia molecule to maintain the stable octet configuration. The positive charge on the hydrogen ion is carried over to give the positively charged ammonium ion, NH_4^+.

Fig. 4.22 The structure of hexacyanoferrate(III) ion.

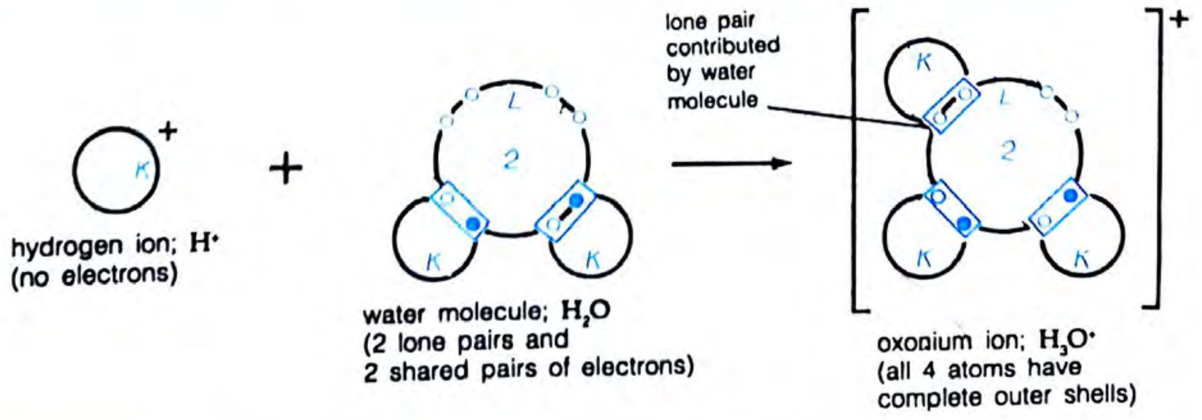


The coordinate covalent bond is represented conventionally by an arrow pointing from the donor atom to the acceptor atom.



$$\left[\begin{array}{c} H \\ | \\ H-N\rightarrow H \\ | \\ H \end{array}\right]^+$$

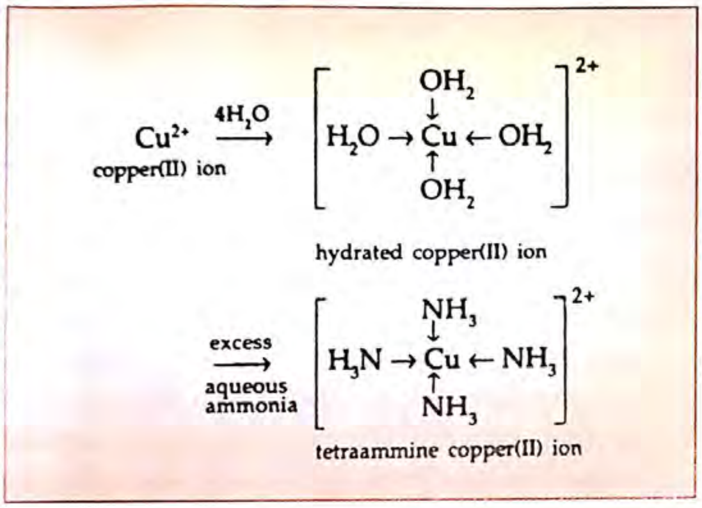
Fig. 4.21 Formation of the oxonium ion.



The oxonium ion is formed in a similar way.

The hydration of copper(II) ion is also due to the formation of coordinate covalent bonds. The copper(II) ion has no electrons in its outermost shell. It accepts four lone pairs of electrons from four water molecules (i.e. one lone pair from each water molecule). The blue hydrated ion that results is $[Cu(H_2O)_4]^{2+}$.

If excess aqueous ammonia is added to a solution of copper(II) ions, the ammonia molecules will replace the water molecules to form $[Cu(NH_3)_4]^{2+}$.



Other compounds with the coordinate covalent bonds are the hexacyanoferrate(II) and the hexacyanoferrate(III) ions. They have a central iron(II) or iron(III) ion surrounded by six cyano ions (CN^-). Four of the cyano ions are on the same plane as the iron(II) or iron(III) ion. One of the cyano ions is above and the other below the iron ion. In silver diammine ion, $[Ag(NH_3)_2]^+$, the lone pair of electrons in the ammonia molecule form a coordinate covalent bond as shown.

$$H_3N \rightarrow Ag^+ \leftarrow NH_3$$

Compounds containing coordinate and covalent bonds have properties which are very similar to purely covalent compounds. The presence of a coordinate bond, however, tends to make a compound less volatile.

Other Binding Forces

Besides the ionic and covalent forces, other attractive forces also bind atoms and molecules together. The most important of these are the *metallic bond*, the *van der Waals forces* and the *hydrogen bond*.

Metallic bond

Metal atoms are held together in crystal lattices by metallic bonds.

Van der Waals forces

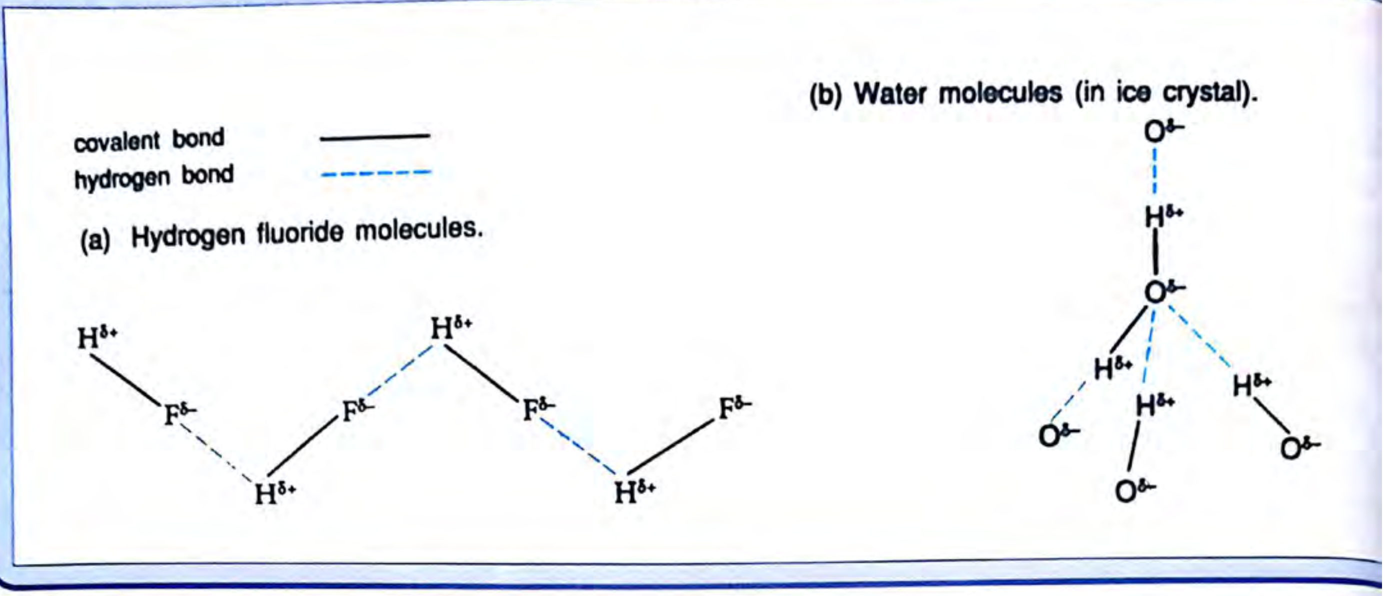
Weak attractive forces exist even between discrete molecules. They were first described by J. D. van der Waals, and are known as *van der Waals forces.* These forces are very weak when compared with ionic and covalent bonds, but they are important in the liquefaction of gases and in the formation of molecular lattices as in iodine and naphthalene crystals.

Hydrogen bond

The hydrogen bond is an intermolecular force which arises when hydrogen is covalently linked to elements like nitrogen, oxygen and fluorine. These latter elements are strongly *electronegative*, i.e. they have very strong affinity for electrons. They require only a few electrons to attain their octet configuration. They tend to pull the shared pair of electrons in the covalent bonds towards themselves, resulting in the formation of a *dipole* where the hydrogen atom is partially positive, while the nitrogen, oxygen or fluorine atom is partially negative. An electrostatic attraction between two dipoles is set up when the positive pole of one molecule attracts the negative pole of another. This attractive force is known as the *hydrogen bond.* Although this bond is weak, it has important effects on the physical properties of compounds like hydrogen fluoride and water.

The strongest hydrogen bonds are in hydrogen fluoride where the simple HF molecules are held together by hydrogen bonds to form larger aggregates of H_2F_2, H_3F_3, etc. Another common example is in ice crystals where the water molecules are held by hydrogen bonds of the type O–H- - -O–H. Even in the liquid state, for example in water, alkanols and some organic acids, transient aggregates of molecules may form as a result of hydrogen bonds.

Fig. 4.23 Association of molecules by hydrogen bonding.



MODIFICATIONS OF DALTON'S ATOMIC THEORY

1 *All elements are made up of small indivisible particles called atoms.* This statement has been proven wrong by Rutherford's discovery — the atom is built up of three main types of sub-particles: the proton, the electron and the neutron. It is not an indivisible solid piece.

2 *The atom can neither be created nor destroyed.* This statement still holds good for ordinary chemical reactions and is embodied in the basic Law of Conservation of Mass. During a nuclear reaction, such as the fission of uranium-235, the nucleus is broken up into smaller units which form simpler atoms while a tremendous amount of heat energy is released. These changes that occur during nuclear fission destroy the atoms of the element involved.

3 *The atoms of the same element are alike in ever aspect and differ from atoms of all other elements* The discovery of isotopes makes this statemen unacceptable. Chlorine, for example, has two different atoms or isotopes which differ in thei neutron content and hence in their relative atomic masses although they have the same atomic number and chemical activities.

4 *During a chemical reaction there is a combinatio of atoms in small whole numbers.* This statemen is generally true only for inorganic compound which usually contain a few atoms per molecule Carbon, however, forms very large organic molecules, such as proteins, fats and starch, which contain thousands of atoms. Even silicon, which is inorganic, forms some very complex trioxosilicates(IV) involving large numbers of atoms.

SUMMARY

- The atom is made up of three main sub-particles—electrons, protons and neutrons having the properties as shown.

Particle	Mass	Charge	Symbol
Electron	1/1 840 unit	−1 unit	*e*
Proton	1 unit	+1 unit	*p*
Neutron	1 unit	No charge	*n*

- Rutherford's atom consists of a positively charged core called the nucleus, where most of the mass of the atom is contained, and electrons, which move around the nucleus.
- When an electron of an atom in its ground state absorbs a quantum of energy (from light or radiation), it will jump to a level of higher energy. The electron is said to be excited. When the electron returns to its ground state, it emits the quantum of energy it absorbed, producing a line in the line emission spectrum.
- Bohr's model of an atom can be summarized as follows:

(a) The atom contains a minute nucleus consisting of protons and neutrons which contribute to most of the mass of the atom (similar to Rutherford's atom).

(b) The electrons revolve around the nucleus in circular orbits of definite quantun energy.

- The Wave Mechanics Model of the atom does not restrict electrons to definite regions around the nucleus as the Bohr's model does. Instead, it makes the electron elusive and indicates a region around the nucleus called an orbital where there is a possibility of finding an electron with a certain given amount of energy.
- The energy of an electron is characterized by four quantum numbers. They are the principal quantum number, n, the subsidiary quantum number, l, the magnetic quantum number, m, and the spin quantum number, s.
- The arrangement of electrons around the nucleus of an atom is determined by the four quantum numbers of each electron in the atom.
- The atomic number, A, of an element is the number of protons in one atom of that element. The atomic number is a basic property of an element.
- The mass number, Z, of an element is the sum of protons and neutrons in its atom.
- Isotopes of an element have the same number of proton(s) but different number of neutron(s).
- When elements are arranged in ascending order of atomic number, elements with similar chemical properties occur at regular periods. This is the basis for the arrangement of elements in the Periodic Table.
- The chemical stability of the rare gases is due to the duplet and octet electronic configurations in the outermost shells of their atoms. Other elements have a tendency to achieve these stable configurations through chemical combinations.
- There are two main types of chemical combinations.
  (a) *Electrovalent combination* There is a transfer of electron(s) from one atom to another resulting in an electrovalent bond between the ions.
  (b) *Covalent combination* Electron pairs are shared between two atoms resulting in an ordinary covalent bond (if each atom contributes one electron), or a coordinate covalent bond (if one atom donates both

electrons). Double and triple covalent bonds result when two and three pairs of electrons respective
are shared between the bonding atoms.

- Electrovalent or ionic compounds are composed of ions arranged in an orderly pattern to form crys lattices. They are hard, brittle solids with a high melting point. In the molten or aqueous state, they cond electricity. They are soluble in polar solvents like water.
- Simple covalent compounds are usually small molecules with a definite shape. They are often gases volatile liquids. If they are solids, they have low melting points. Covalent compounds are nonelectroly and are usually soluble in non-polar solvents.
- Van der Waals forces and the hydrogen bond are weak intermolecular bonds.

EXERCISES

1. An element belongs to a period in the periodic table because of
- A the number of electrons in its outer-most shell.
- B the shell number.
- C the electronic configuration in the azimuthal quantum number.
- D the size of the atom.

2. The major reason why chemical reaction occurs among elements is that they have the tendency to
- A attain the nearest noble gas structure.
- B become a metal.
- C become a non-metal.
- D become any noble element.

3. In electrovaleny most metallic atoms with few valence electrons to give out electrons because
- A they are unstable.
- B they require less energy to give away these electrons.
- C they require more energy to give away these electrons.
- D they need non-metals to operate.

4. In electrovalency, valence electrons are transferred and the atomic number is
- A also reduced.
- B stabilized.
- C unaffected.
- D destabilized.

5. Arrangement of ions in a regular pattern in solid crystal is called
- A configuration.
- B atomic structure.
- C lattice.
- D buffer.

6. If force is applied to an electrovalent crystal,
- A the shape will be deformed.
- B the shape will not be deformed.
- C the crystal will not be fractured
- D the shape and the crystal structure will b deformed.

7. The bond type in a diatomic nitrogen gas is
- A double covalent bond.
- B triple covalent bond.
- C single covalent bond.
- D double electrovalent bond.

8. The bond type between copper II ion and wate molecules is
- A electrovalent bond.
- B covalent bond.
- C active covalent bond.
- D hydrogen bond.

9. The bond between two iodine molecules is
- A co-ordinate bond.
- B electrovalent bond.
- C ionic bond.
- D van der Waal's forces.

10. Bonds between a highly electronegative atom and a hydrogen from another molecule is called

A hydrogen bond.
B covalent bond.
C inter molecular forces.
D ligand.

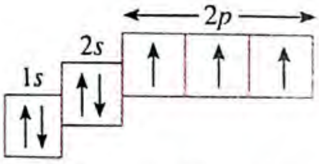
11. Rare gases are stable because they

A are monoatomic.
B are volatile gases.
C form ions easily.
D have duplet or octet electronic configurations in the outermost shells of their atoms.
E have no neutrons in their nucleus.

12. Which of these is the same in isotopes of an element?

A Mass number
B Number of neutrons
C Number of protons and neutrons
D Relative atomic mass
E Atomic number

13.



The above orbital diagram shows the electronic configuration of

A chlorine.
B nitrogen.
C calcium.
D neon.
E oxygen.

14. Which of these statements is not correct?
In going across Period 3 (from sodium to argon) of the Periodic Table, we notice that

A the melting point and boiling point increase gradually.
B the first ionization energy increases.
C the atomic size increases to the middle of the period and then decreases.
D there is a gradual change in their oxides from basic to acidic (argon does not form an oxide).
E there is a gradual decrease in electronegativity.

15. Which element has an electronic configuration of $1s^2 2s^2 2p^6 3s^1$?

A Calcium
B Chlorine
C Potassium
D Sodium
E Nitrogen

16. What contributions did the following scientists make towards elucidating the structure of the atom?

(a) J J Thomson
(b) Rutherford
(c) Millikan
(d) Chadwick

17. What are the three fundamental units of all matter? Give their relative masses and charges. Describe their relative positions to one another in an atom.

18. What did Thomas Young, Max Planck and Albert Einstein contribute towards the nature of light?

19. Explain simply how the lines in a hydrogen spectrum are obtained.

20. By means of orbital diagrams, write down the electronic configurations of these elements.

(a) Sodium
(b) Aluminium
(c) Phosphorus
(d) Chlorine
(e) Magnesium
(f) Silicon
(g) Sulphur
(h) Argon

21. Complete the table below and then answer the questions.

(a) Identify the elements, ions and isotopes.
(b) Which particles are iso-electronic (i.e. having the same number of electrons)?
(c) The electronic configuration of Na atom is 2, 8, 1. Give the electronic configurations of *C*, *D*, *G* and *H*.
(d) What type of chemical combination would *A*, *B*, *C* and *F* undergo?
(e) For each particle, give the name and formula of a compound it forms.

22. (a) Write briefly on the following, giving an illustrated example of each.
   (i) Electrovalent combination
   (ii) Covalent combination
   (iii) Coordinate covalent combination
   Compare the characteristics of compounds formed by electrovalent combination with those formed by covalent combination.
(b) What are the bond types present in each of the following compounds?
   (i) Carbon(IV) oxide
   (ii) Calcium oxide
   (iii) Methane
   (iv) Ammonium chloride

23. (a) What is the conductivity of metals due to?
(b) Why does solid sodium chloride not conduct electricity?

24. The following are the electronic configurations of five elements.

A	*B*	*C*	*D*	*E*
2, 8, 2	2, 8, 6	2, 8, 8	2, 8, 7	2, 3, 3

(a) Which element is unlikely to react with the others?
(b) Which elements will react to form covalent compounds?
(c) Which elements will react to form ionic solids? Give the common valency of the elements when they form ionic solids.
(d) Label the following as ionic or covalent.
CCl_4, KBr, CuS, CuO, HF, HCl, SO_2, PCl_3, HCl(aq).

25. (a) What are isotopes? Name any two elements that exhibit isotopy and give their respective isotopes.
(b) Explain why the relative atomic mass of chlorine is 35.5.
(c) The atomic number of sodium is 11 and its relative atomic mass is 22.99.
   (i) What is the mass number of a sodium atom?
   (ii) How many protons, neutrons and electrons are there in a sodium atom? What are the principal differences between these particles?

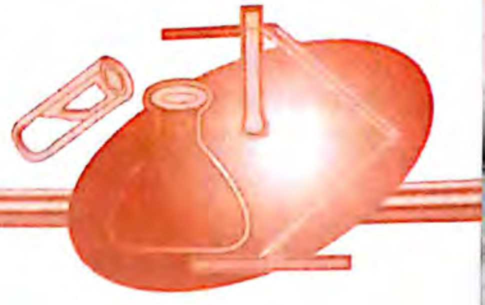
26. (a) State Dalton's theory about the atom.
(b) Outline in detail the modern atomic concept and show how it modifies Dalton's theory.
(c) The electronic configuration of the potassium atom is 2, 8, 8, 1. Explain this and show why potassium is a very reactive metal.

27. Write down the formula of the compound resulting from the combination of an element X of atomic number 20 with an element *Y* of atomic number 17.

Particle		Mass no.	Atomic no.	Protons	Neutrons	Electrons
A	Na		11		12	
B		37		17		17
C		16		8		10
D		27	13			10
E	Ne	20	10		10	
F			6		8	6
G	S^{2-}	32		16	16	
H			7		7	10

KINETIC THEORY OF MATTER 5

• GAS LAWS



KINETIC THEORY OF MATTER

We know that matter is made up of very tiny particles such as atoms, molecules and ions. *The kinetic theory of matter postulates that these particles are continually moving and so possess kinetic energy.* An increase in temperature causes an increase in the average kinetic energy of the particles. We say average kinetic energy because in any given sample of a substance, some particles are more energetic, i.e. they move faster, than others.

States of Matter

Matter exists in three states — as *solid*, *liquid* and *gas*. The fundamental difference between these three states of matter is the degree of movement of their particles.

Solid state

Various types of solids are formed by different chemical combinations. The molecules, atoms or ions in these solids are very closely packed, and are held firmly together by forces of cohesion. The forces of cohesion may be electrovalent, covalent, metallic or even the very weak van der Waals forces. The strength of any solid is determined by the type of bonds or forces holding the crystal structure together.

The cohesive forces holding the particles of a solid are strong enough to restrict their movement so that they are held in fixed positions. These particles can only vibrate and rotate about their fixed positions but they cannot *translate*, i.e. move from one place to another. As a result, solids have definite shapes and volumes, and are difficult to compress.

Liquid state

The particles in a liquid are slightly further apart than those in a solid. They have more kinetic energy and are no longer held in fixed positions. They can vibrate, rotate and translate. Although the particles can slide about randomly, they are still under the influence of the cohesive forces and their movements are restricted. A liquid, therefore, still possesses a fixed volume but has no definite shape or form. Instead, it assumes the shape of the container in which it is placed. A liquid is also hard to compress.

Fig. 5.1 The three states of matter.

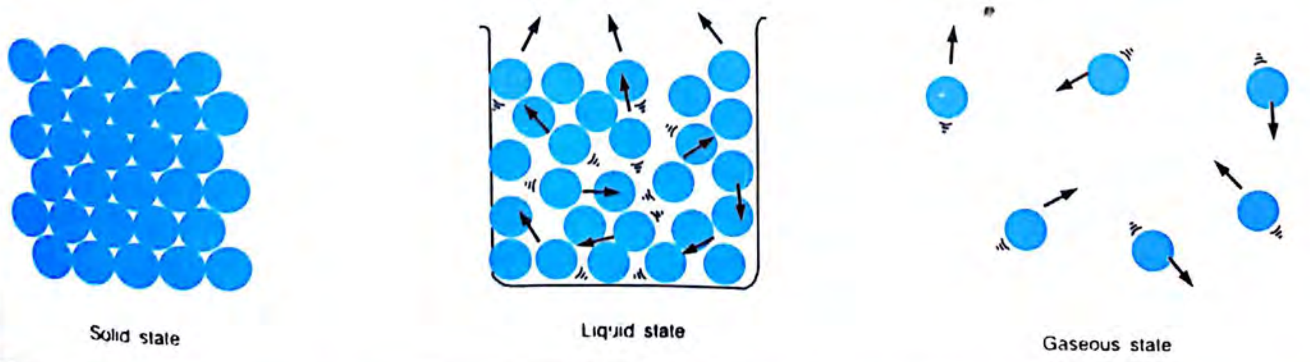


Table 5.1 Comparison of the properties of solids, liquids and gases.

Solid	Liquid	Gas
• Fixed mass.	Fixed mass.	Fixed mass.
• Particles vibrate and rotate about a fixed position.	Particles vibrate, rotate and move about within a restricted space.	Particles move about constantly at great speed and at random.
← Orderliness of particles increases from gas to solid.		
Random motion of particles increases from solid to gas. →		
Kinetic energy of particles increases from solid to gas. →		
• Fixed shape. • Fixed volume. • Incompressible. • Very dense.	No fixed shape. Fixed volume. Incompressible. Less dense.	No fixed shape. No fixed volume. Compressible. Least dense.

Gaseous state

In a gas, the particles have much more kinetic energy than those in a liquid. The cohesive forces in a gas are negligible and the particles are free to move about in all directions at great speed, restricted only by the walls of the container. A gas has no definite shape; it occupies the whole volume of its container. Gas particles are relatively far apart and may be readily compressed.

Change of State

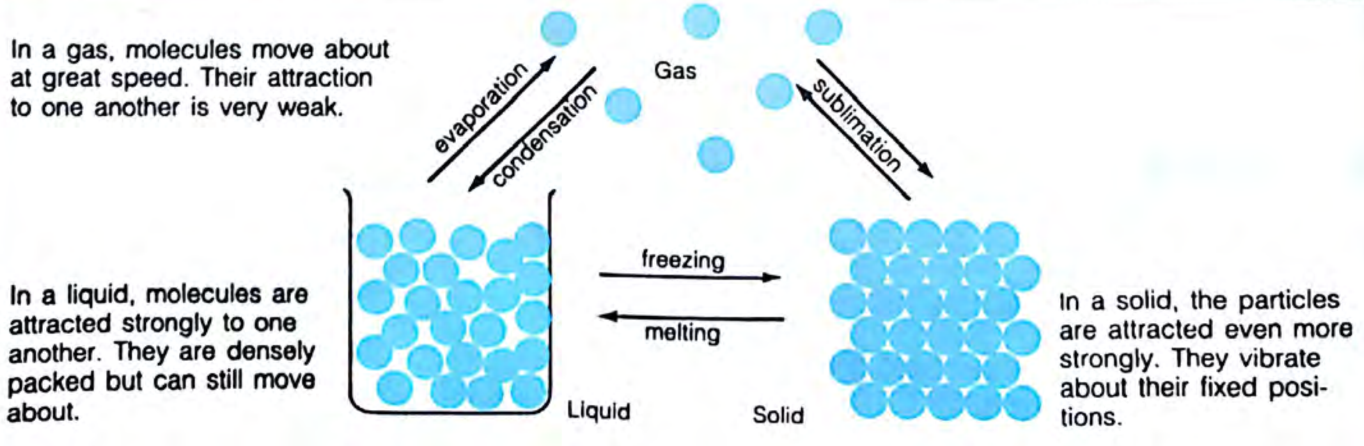
A given substance can exist as a solid, a liquid or a gas. Change of state is brought about by a change in temperature (i.e. heating or cooling). When a substance is heated, its particles acquire more kinetic energy. When cooled, they become less energetic.

We are familiar with the three states of matter. Candle wax readily changes into a liquid on heating, but decomposes on further heating.

Melting

When a solid is heated, the particles acquire more kinetic energy and vibrate more violently. Eventually, at a certain temperature called the *melting point* of the solid, the force of the vibrations overcomes the binding forces and the crystalline structure collapses suddenly. The particles are no longer held in fixed

Fig. 5.2 A substance can exist as a solid, a liquid or a gas.



In a gas, molecules move about at great speed. Their attraction to one another is very weak.

In a liquid, molecules are attracted strongly to one another. They are densely packed but can still move about.

In a solid, the particles are attracted even more strongly. They vibrate about their fixed positions.

positions, but instead are free to move about. We say the solids have melted or liquefied.

The presence of an impurity in the crystal will lower the melting point of a solid and may cause it to liquefy gradually instead of suddenly. In some cases, e.g. iodine, the molecules may break away from the crystal and change directly into the vapour state when the solid is heated. This is known as *sublimation*.

Evaporation

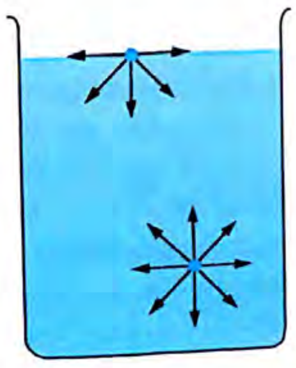
Particles in a liquid are attracted by neighbouring particles equally in all directions. Particles at the surface of a liquid body, however, are attracted only inwards and sideways by the neighbouring particles. The surface of the liquid is level and like a tightly-stretched skin. Such a liquid surface tends to prevent liquid molecules from escaping into the space above the liquid.

In a sample of a given substance, some particles are more energetic than others. When such energetic particles come near a liquid surface, they can break away from the attractive forces of the other nearby liquid molecules and escape into the space above, i.e. *vaporize*. When this happens we say the liquid *evaporates*.

Since evaporation results in the escape of energetic particles from the liquid body, the average kinetic energy of the liquid is lowered. This results in a drop in temperature of the liquid body.

Evaporation of a liquid occurs at all temperatures but, the rate of evaporation increases with increase in temperature. This is because the average kinetic energy of a liquid is greater at a higher temperature, so there are more particles with sufficient energy to vaporize.

Fig. 5.3 Attractive forces of liquid particles.



The rate of evaporation also depends on the type of liquid. Generally, the rate of evaporation is lower in electrovalent liquids than in covalent liquids. This is because the force of attraction is greater between the positive and negative ions in an electrovalent liquid than between the simple neutral molecules in a covalent liquid. More energy is needed for the particles in an electrovalent liquid to vaporize than for those in a covalent one. Thus, covalent liquids are said to be volatile.

Vapour pressure

When a liquid evaporates in a closed container, the escaped particles will gradually accumulate in the space above the liquid. Here the particles collide frequently with one another and with the walls of the vessel and consequently exert a pressure which is known as the *vapour pressure*. At the same time, some vapour molecules hit the liquid surface and re-enter the liquid, i.e. condense.

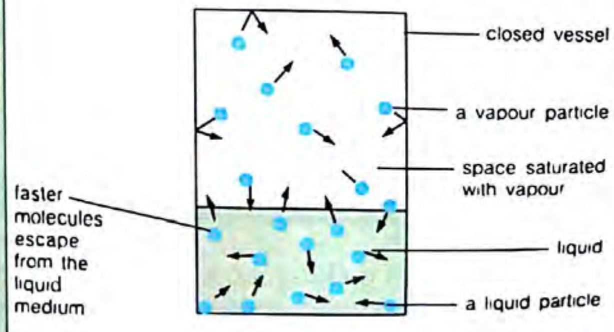
Condensation increases as the vapour pressure rises, i.e. as more and more liquid particles evaporate. Thus, two opposing forces are occurring in this system.

$$\textbf{Liquid particles} \underset{\text{condense}}{\overset{\text{evaporate}}{\rightleftharpoons}} \textbf{Vapour particles}$$

The vapour pressure continues to rise until a stage is reached when, at any given instant,

number of particles condensing into the liquid = number of particles evaporating from the liquid

Fig. 5.4 System at saturated vapour pressure.



When this happens, we say an equilibrium is established between evaporation and condensation. At equilibrium, the vapour pressure stops rising and remains constant. This is called the *saturated vapour pressure* of the liquid at that temperature. The vapour pressure of a liquid depends only on the temperature and the nature of the liquid, i.e. the type of cohesive forces holding the particles together.

Boiling

When a liquid is heated, the rate of evaporation increases. The saturated vapour pressure of the liquid also increases until a temperature is reached, at which it equals the prevailing atmospheric pressure. When this happens, bubbles of vapour form in the liquid and rise to the surface. The liquid is then said to *boil*, and the temperature at which this happens is known as the *boiling point* of the liquid, at the prevailing atmospheric pressure. The boiling point increases or decreases with a rise or fall in atmospheric pressure respectively. It also increases in the presence of impurities.

Freezing and condensation

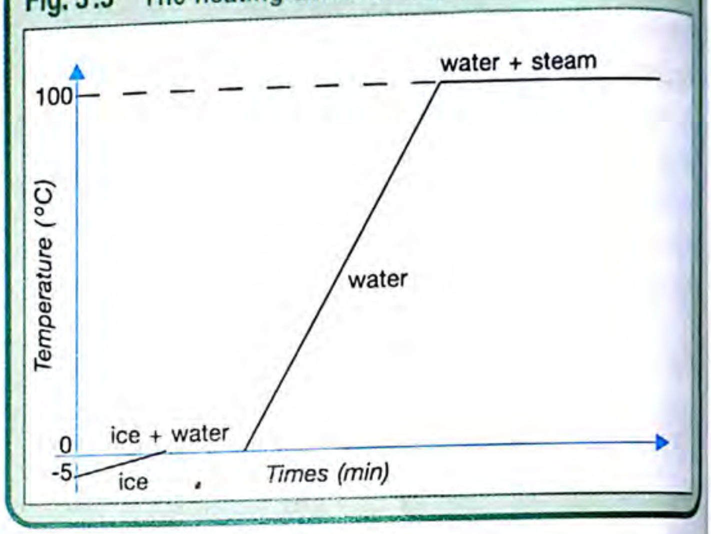
While heating causes melting and boiling, cooling causes *condensation* and *freezing*. Condensation is a process whereby a vapour loses some of its kinetic energy to a colder body and changes into the liquid state. This is what happens when a bottle of milk is taken out of the refrigerator and placed on a table at room temperature. Droplets of water can be seen on the outside surface of the milk bottle. The water vapour in the air around the bottle loses some of its energy to the bottle (cold body) and condenses as droplets of liquid water on the surface of the bottle.

When a liquid cools, it loses heat energy to its surroundings, causing its temperature to drop. If cooling is allowed to continue, the temperature of the liquid keeps on dropping until it reaches the freezing point of the liquid. At this temperature, the liquid changes into the solid state. The *freezing point* of a substance is the same as its melting point.

Latent heats of fusion and vaporization

During the process of melting, no temperature rise is observed even though heat energy is being supplied continuously. This is because the heat energy absorbed only performs the special function of weakening the cohesive forces which is not detectable by a thermometer. It is referred to as the latent (hidden) *heat of fusion*. Every solid has its own latent heat of fusion which depends on the strength of the cohesive forces. The heat energy required to overcome the cohesive forces during boiling is known as the *latent heat of vaporization*. It is not detectable by a thermometer because this energy is not used to increase the temperature of this system but to break the cohesive bonds between the particles of the liquid.

Fig. 5.5 The heating curve of water.



Phenomena Supporting Kinetic Theory

Nobody has seen the tiny particles which make up matter although scientists have managed to measure the velocities of molecules and detect their exact positions at definite times with the help of very sophisticated instruments. The fact that these particles are in constant motion is exhibited in some natural phenomena such as Brownian movement, diffusion and osmosis.

Brownian movement

Brownian movement was first observed by Brown, a botanist, in 1827, when he was examining a pollen grain suspended in a drop of water under a microscope. He noticed that the pollen grain was moving about all the time in a haphazard, zig-zag manner. This irregular movement was later found to be due to the bombardment of the suspended solid particle (in this case, the pollen grain) by the surrounding molecules of the liquid medium (in this case, water molecules). This phenomenon is called brownian movement or motion.

Diffusion

Diffusion describes the movement of solute particles through a medium, from a region of higher concentration to a region of lower concentration. In other words, the solute particles tend to move from a more crowded region to a less crowded region. Once the solute particles become evenly distributed throughout the medium, there will be no net diffusion in any particular direction.

Diffusion in gases Diffusion is fastest in gases because gas particles have more kinetic energy than particles in liquids and solids. The rate of diffusion of gases is affected by their densities (refer to experiment 5.3).

Diffusion in liquids Diffusion also takes place in liquids, though it is much slower than in gases. This is because liquid particles have less kinetic energy and are more restricted in their movement due to the cohesive forces between the particles.

Diffusion in solids Diffusion may also be observed in solids but the process is extremely slow. If a gold bar and a silver bar are tied together firmly and left for years, some gold particles will have diffused into the silver bar, and vice versa.

Diffusion is fastest in gases (in seconds). Their particles are far apart and the cohesive forces between them are negligible. It is slowest in solids (in years), where the particles are held in fixed positions by strong cohesive forces.

Osmosis

Osmosis is a special case of diffusion which involves the movement of water molecules, through a semi-permeable membrane, from a region where they are in higher concentration to one where they are in lower concentration. For example, if we place some dried bean seed in a beaker of water, they swell after some time because water molecules have moved through the semi-permeable skins into the seeds by osmosis. Thus, osmosis indicates movement of water molecules.

NOTE Osmosis occurs because the bean seeds contain sugar solution and placing them in water creates a situation where water molecules are in a lower concentration inside the seeds than on the outside.

Experiment 5.1 To demonstrate Brownian movement.

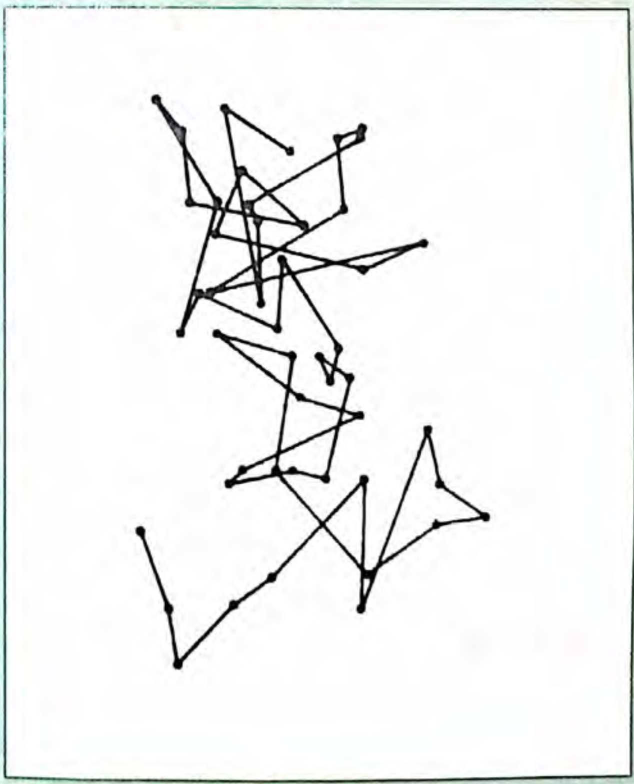
Method Add some powdered sulphur to water and stir. Then filter the suspended sulphur. Some of the sulphur particles are small enough to pass through the pores of the filter paper and, hence, stay in the filtrate as a colloidal suspension.

Put a drop of the filtrate on a slide and examine it under a powerful microscope.

Result The sulphur particles are observed to move about rapidly all the time in a random and zig-zag manner in the medium.

Conclusion The Brownian movement of the sulphur particles reflects the movement of the water molecules.

Fig. 5.6 Brownian movement.



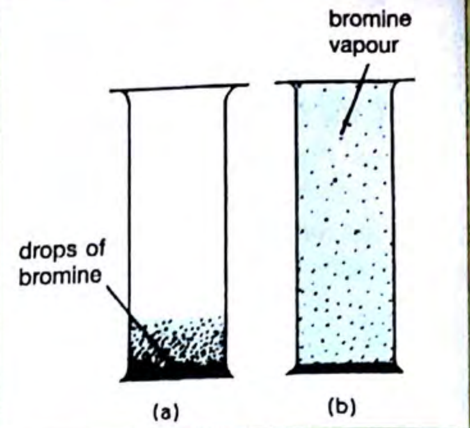
Experiment 5.2 To observe the diffusion of a gas.

Method Place a few drops of liquid bromine at the bottom of a gas jar. Cover the jar with a glass cover. Leave it to stand for some time.

Result After some time, the brown bromine vapour starts to spread upwards, in spite of the fact that bromine vapour is much denser than air. Eventually, the brown colour spreads evenly throughout the gas jar.

Conclusion The spread of the brown colour shows that the particles of bromine vapour have diffused in all directions to fill the whole jar.

Fig. 5.7 Diffusion of a vapour.



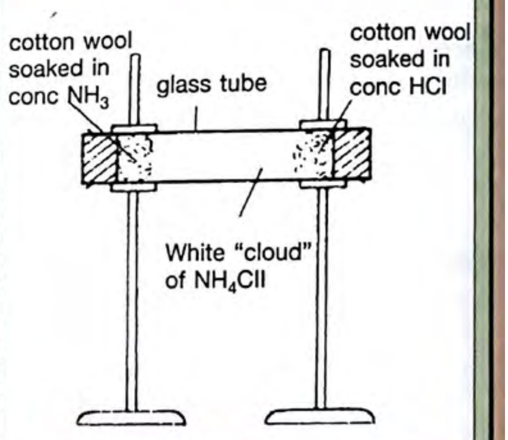
Experiment 5.3 To show the relative rates of diffusion of two gases of different densities.

Method Position a glass tube opened at both ends as shown. Soak a ball of cotton wool in concentrated aqueous ammonia, and another in concentrated hydrochloric acid. Stuff each ball, one at each end of the tube. Then close both ends with rubber or cork bungs.

Result After some time, a white "cloud" is seen in the tube at about one-third the length of the tube from the acid-soaked ball of cotton wool.

Conclusion The white "cloud" (which later settles down to form a ring around the tube) is actually solid ammonium chloride particles formed by the combination of ammonia gas and hydrogen chloride gas. Both these gases diffuse inwards and meet at a region closer to the acid end of the tube. This is because hydrogen chloride is a heavier gas and diffuses a shorter distance than ammonia in the same amount of time. The lighter or less dense ammonia particles diffuse faster than the denser hydrogen chloride gas particles.

Fig. 5.8 Diffusion of two gases.



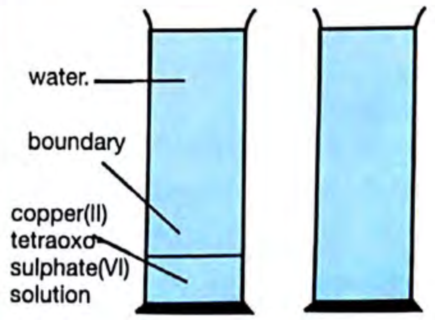
Experiment 5.4 To show diffusion in liquids.

Method Pour about 30 cm^3 of concentrated copper(II) tetraoxosulphate(VI) into a 100-cm^3 cylinder or tall jar. Use a water bottle with a fine jet and run water gently along the sides of the jar till about 50 cm^3 of clear water rests above the denser blue solution. Mark the line of separation between the two liquids and leave the jar undisturbed for a few days.

Result The blue copper(II) tetraoxosulphate(VI) spreads upwards, against gravity.

Conclusion Diffusion takes place in liquids, and it can overcome the force of gravity.

Fig. 5.9 Diffusion in liquids.



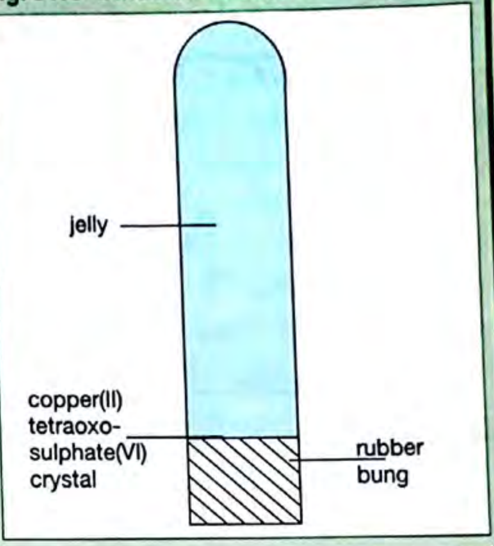
Experiment 5.5 To show diffusion in solids.

Method Dissolve some jelly crystals in water. Pour the solution into a test-tube and place it in a refrigerator for the jelly to solidify. When the jelly has set, insert a crystal of copper(II) tetraoxosulphate(VI) just under the surface of the jelly. Close the mouth of the test-tube with a rubber bung and let the tube stand upside down as shown.

Result There is a gradual upward movement of the blue colour throughout the jelly.

Conclusion The spread of the blue colour indicates that the particles of copper(II) tetraoxosulphate(VI) have diffused through the jelly, even overcoming the force of gravity.

Fig. 5.10 Diffusion in solids.



STUDY OF GASES

Matter in the gaseous state has different characteristics from that in the solid and liquid states. Thus, the behaviour of gases is expected to differ from that of solids and liquids. This was investigated by many of the early scientists like Boyle, Charles, Graham and Dalton. They studied the physical behaviour of gases. Their important findings are now named after them. The chemical behaviour of gases was studied by Gay-Lussac.

Kinetic Theory of Gases

The gas laws which explain the physical behaviour of gases can be explained by the Kinetic Theory of gases. This theory describes the behaviour of an *Ideal* or *Perfect Gas*. It states the following:

1. *The gas molecules move randomly in straight lines*, colliding with one another and with the walls of the container. As a result, the speeds of the various molecules differ widely and are constantly changing. The collisions of the gas molecules on the walls of the container constitute the gas pressure exerted in this container.
2. *The collisions of the gas molecules are perfectly elastic*. When two molecules collide, their individual energies may change, and one may move faster while the other slows down, but their total kinetic energies remain the same, i.e. no kinetic energy is converted to heat. When the molecules collide with the walls of the container, they rebounce like elastic balls without any loss of energy.
3. *The actual volume occupied by the gas molecules themselves is negligible* relative to the volume of the container. The gas molecules are also small in relation to the distances between them.
4. *The cohesive forces between the gas molecules are negligible.*
5. *The temperature of the gas is a measure of the average kinetic energy of the gas particles.*

In the above theory, certain assumptions have been made to simplify the description of the behaviour of gases. Real gases, however, show deviations in behaviour as given in this theory.

Pressure Exerted by Gases

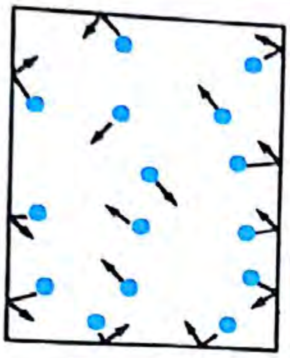
The particles of a gas contained in a vessel move randomly at high speeds, often colliding with one another and with the walls of the vessel. Each time a gaseous particle hits or collides with the wall of the vessel it exerts a very small force on it. Since the gas particles are numerous and evenly distributed, their collisions exert a constant force on the walls of the vessel. This force that the gaseous particles exert per unit area of the wall is known as the gas pressure. It will be constant in every unit area of the walls of the vessel in which the gas is enclosed.

Gas pressure is commonly measured in atmospheres (atm) or mm Hg. The SI unit for measuring pressure is the pascal (Pa), i.e. newtons per square metre (N m^{-2}).

The relationship between these units is:

1 atm = 760 mm Hg = 101 325 N m^{-2}

Fig. 5.11 Gas pressure is exerted by gaseous particles hitting the walls of the vessel.



Boyle's Law

The relationship between volume and pressure of a gas was first stated by Robert Boyle in 1662.

Boyle's law states that the volume of a given mass of gas is inversely proportional to its pressure, provided that the temperature remains constanr.

According to Boyle's Law, volume of a gas increases as the pressure decreases and vice versa. This relationship is independent of the nature of the gas and it can be expressed mathematically as:

$$V \propto \frac{1}{p}$$

$$\therefore \quad V = \frac{k}{p}$$

$$\text{or} \quad pV = k$$

(where V = volume at pressure p,
k = a mathematical constant).

For a given mass of gas, the product of its pressure and its volume is always a constant. If the pressure of a given mass of gas increases, its volume will decrease by a similar proportion, and vice versa, as long as the temperature remains constant. This relationship can also be expressed mathematically as:

$$p_1V_1 = p_2V_2$$

(where V_1 = volume at pressure p_1,
V_2 = volume at pressure p_2).

Boyle's Law can be re-stated in the following way: *The pressure of a given mass of gas is inversely proportional to its volume, provided the temperature remains constant.*

How Kinetic Theory explains Boyle's Law

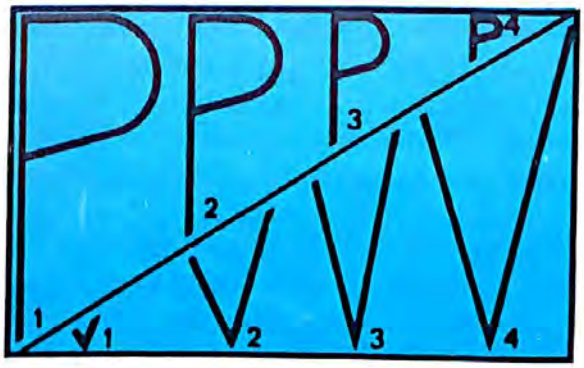
Let us consider a given mass of gas enclosed in a vessel with a movable piston, which is kept stationary by placing a suitable weight on it. At constant temperature, the average velocity of the gas molecules is constant, so the number of collisions they make with per unit area of the wall of the vessel is also constant, i.e. the gas exerts a certain constant pressure p, on the walls of the vessel.

If the weight on the piston is replaced with a lighter one such that the piston moves up and the original volume, V, of the gas is doubled, then the gas molecules will be spread out. As a result, the number of collisions the gas molecules make per unit area of the wall is halved, i.e. the gas exerts only half its original pressure, p. Hence, at constant temperature, volume of a gas increases as pressure decreases.

On the other hand, if the weight on the piston is replaced with a heavier one such that the piston moves down and the original volume, V, of the gas is halved, then the gas molecules will be packed more closely. As a result, the number of collisions the gas molecules make per unit area of the wall is doubled, i.e. the gas exerts double its original pressure, p. Hence, at constant temperature, as the volume of a gas decreases pressure it exerts increases.

Figure 5.13 shows diagrammatically how the Kinetic Theory of Matter explains Boyle's Law, which states that volume of a gas is inversely proportional to its pressure.

Fig. 5.12 A representation of Boyle's Law.



EXAMPLE

375 cm³ of a gas has a pressure of 770 mm Hg. Find its volume if the pressure is reduced to 750 mm Hg.

$$p_1V_1 = p_2V_2 \quad \text{BOYLE'S LAW}$$

$p_1 = 770$ mm Hg $V_1 = 375$ cm³

$p_2 = 750$ mm Hg $V_2 =$ new volume of gas

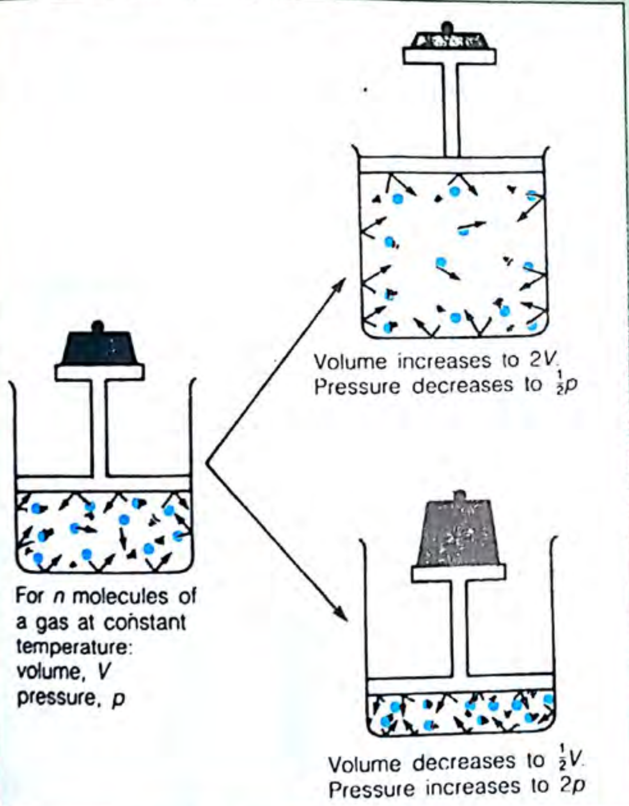
$$\therefore V_2 = \frac{p_1V_1}{p_2}$$

$$= \frac{770 \times 375}{750}$$

$$= 385 \text{ cm}^3$$

The volume will be 385 cm³.

Fig. 5.13 Boyle's Law and the Kinetic Theory.



Kelvin Temperatures

Temperature affects the volume of matter. The effect is most pronounced on gases. Charles, a French scientist, discovered that the volume of a given mass of gas will increase or decrease by 1/273 of its volume at 0 °C for every 1 °C rise or fall in the temperature, provided that the pressure remains constant. Thus, if a gas has a volume of 273 m³ at 0 °C, its volume would be 272 m³ at –1 °C, 271 m³ at –2 °C and 0 m³ at –273 °C, i.e. the gas would vanish completely at –273 °C. In actual practice this is not possible because all gases liquefy above this temperature and hence Charles' Law would no longer apply. But this temperature, at which the volume of a gas would be theoretically reduced to zero, is significant because it is the lowest possible temperature that can be reached. Earlier scientists described this temperature of –273 °C as the *absolute zero.*

The kelvin temperature scale has –273 °C as its starting point. (The Celsius or Centigrade temperature scale uses the freezing point of water, 0 °C, as its starting point.) Before we can apply the gas laws in our calculations, we must convert all the temperature readings involved to the kelvin scale. The kelvin temperatures are also called the *absolute temperatures*. The temperatures on this scale are measured in K units (with no degree sign). A general kelvin scale temperature is represented by the symbol *T*.

Temperature conversions

The equivalent temperatures on the Celsius and kelvin scales which should be remembered are as follows:

0 °C = 273 K, –273 °C = 0 K

To convert a Celsius temperature (0 °C) to a kelvin temperature (K), add 273 to the former, i.e.

K = °C + 273

Conversely, a kelvin temperature can be converted to a Celsius temperature by subtracting 273 from the kelvin temperature, i.e.

°C = K – 273

EXAMPLES

1 *Convert the following Celsius temperatures to kelvin temperatures.*
(a) 148 °C (b) 0 °C (c) –132 °C
Formula to be used: K = °C + 273
(a) 148 °C = (148 + 273) K = 421 K
(b) 0 °C = (0 + 273) K = 273 K

Experiment 5.6 To verify Boyle's Law.

Method Connect the open end of a burette to a rubber tubing. Push an open glass tube into the other en of the tubing and mount the apparatus as in fig. 5.14.

Open the tap of the burette and fill the apparatus with mercury through the mouth of the open glass tube. When the mercury has reached a reasonable level inside the burette, close the tap to trap some air above the mercury inside the burette. Arrange the mercury levels in the two arms to be equal by adjusting the height of the arms. The trapped air is exactly at atmospheric pressure now. Note the barometric reading (B) for the atmospheric pressure, and note the volume (V) of the trapped air in the burette.

Increase(or decrease) the pressure(p) of the trapped air. To do this,

(a) raise (or lower) the mercury level in the glass tube;
(b) measure the difference(D) between the two mercury levels;
(c) add(or subtract) the difference(D) to the barometric reading(B).

This value is the new pressure(p_1) of the trapped air. Next, measure the corresponding new volume(V_2) of the trapped air. Obtain several sets of reading by varying the pressure of the trapped air.

Result Record the readings in the table below.

Volume of trapped air (V cm^3)	Difference in mercury levels (D mm)	Pressure of trapped air (p mm Hg) $p=B\pm D$	Product of pressure and volume of trapped air (pV
V_1	D_1	$p_1=B\pm D_1$	$P_1V_1=k$
V_2	D_2	$p_2=B\pm D_2$	$P_2V_2=k$
V_3	D_3	$p_3=B\pm D_3$	$P_3V_{3=}k$
V_4	D_4	$p_4=B\pm D_4$	$p_4v_4=k$

Similar experiments have shown that,
$pV = k$ (where k is a mathematical constant)

$$\therefore\ p = \frac{k}{V} \text{ or } V = \frac{k}{p}$$

$$\therefore\ p \propto \frac{1}{V} \text{ or } V \propto \frac{1}{p}$$

Thus, the volume of a mass of gas is inversely proportional to its pressure, i.e. volume of a gas is directly proportional to the reciprocal of the corresponding pressure, and vice versa.

By plotting the values of the various volumes (V_1, V_2, V_3, etc.) against the reciprocals of the corresponding pressures ($\frac{1}{p_1}$, $\frac{1}{p_2}$, $\frac{1}{p_3}$, etc.), or vice versa, we obtain straight line graphs passing through the origins.

Conclusion Boyle's Law is verified since the volume of a given mass of gas is inversely proportional to its pressure provided the temperature remains constant.

Fig. 5.14 Verifying Boyle's Law.

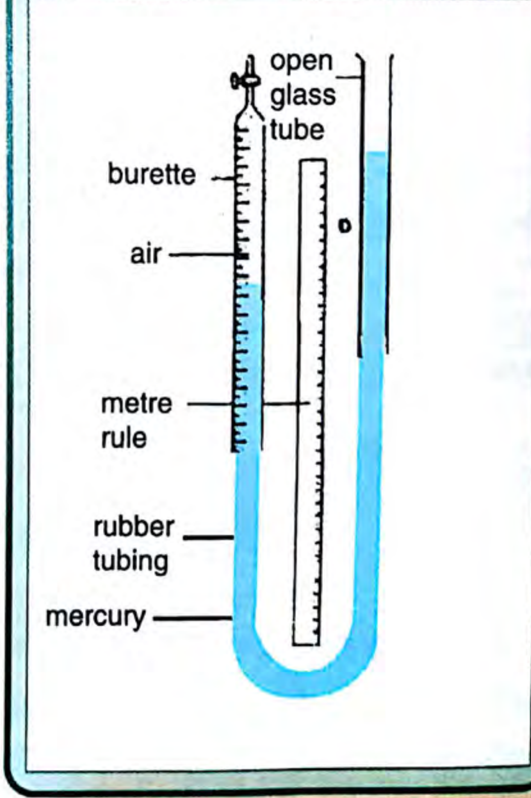
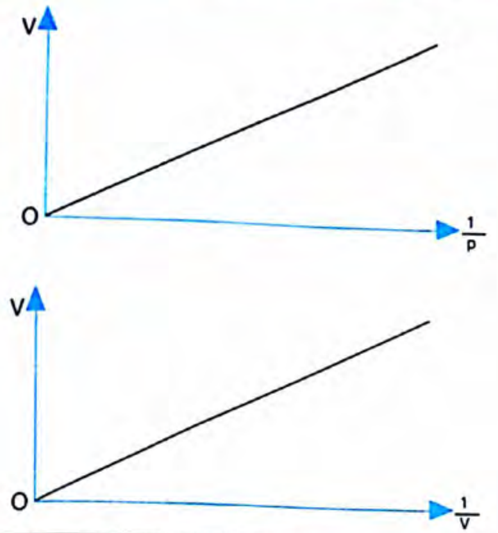


Fig. 5.15 Graphical representations of Boyle's Law.



(c) −132 °C = (−132 + 273) K = 141 K

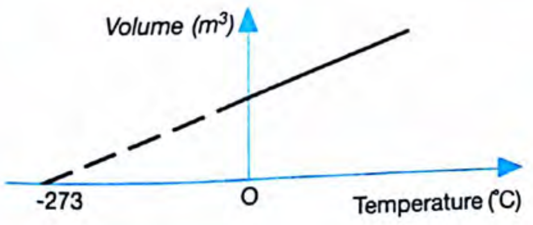
2 *Convert the following kelvin temperatures to Celsius temperatures.*
(a) 125 K *(b) 405 K* *(c) 298 K*

Formula to be used: 0 °C = K − 273
(a) 125 K = (125 − 273) °C = −148 °C
(b) 405 K = (405 − 273) °C = 132 °C
(c) 298 K = (298 − 273) °C = 25 °C

Charles' Law

The effect of temperature changes on the volume of a given mass of gas at a constant pressure is described by *Charles' Law.*

Fig. 5.16 Graphical representation of Charles' Law.



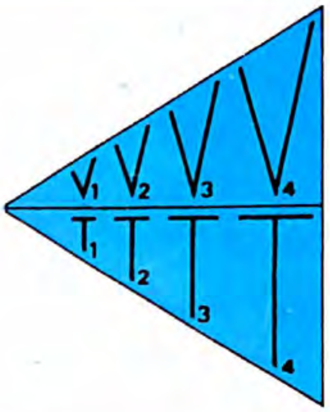
Charles' Law states that the volume of a given mass of gas is directly proportional to its temperature in kelvin, provided that pressure remains constant.

The volume of the gas decreases as the temperature decreases and increases as the temperature increases. Mathematically, the law can be expressed as:

$$V \propto T$$
$$\therefore \quad V = kT$$
$$\text{or} \quad \frac{V}{T} = k$$

(where V = volume,
T = kelvin temperature,
k = a mathematical constant)

Fig. 5.17 A representation of Charles' Law.



If we divide the varying gas volumes by the corresponding temperatures in kelvin, the result would always be a constant. This relationship can also be expressed in another form.

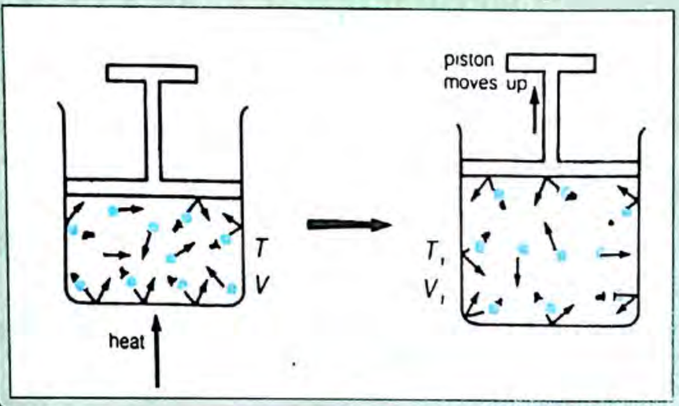
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
$$\therefore \quad V_2 = \frac{T_2 V_1}{T_1}$$

(where V_1 is the volume at temperature T_1,
V_2 is the volume at temperature T_2).

How Kinetic Theory explains Charles' Law

Let us consider a given mass of a gas confined in a vessel with a movable piston. If the gas is heated, the molecules acquire more kinetic energy, move faster and collide more often with the walls of the vessel, thereby increasing the pressure they exert. To maintain the same number of collisions on the walls of the vessel (i.e. to remain at constant pressure), the piston moves up so that the volume of the gas is increased. Hence, at a constant pressure, the volume of a given mass of gas is directly proportional to the temperature.

Fig. 5.18 Charles' Law and the Kinetic Theory.



For n molecules of a gas, if temperature increases from T to T_1, the volume V must also increase proportionally from V to V_1 to keep the number of collisions on per unit area of the walls of the vessel (the pressure) the same.

EXAMPLE

At 17 °C, a sample of hydrogen gas occupies 125 cm³. What will the volume be at 100 °C, if the pressure remains constant?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{CHARLES' LAW}$$

$V_1 = 125\ \text{cm}^3$ $\qquad T_1 = (17 + 273)\ \text{K} = 290\ \text{K}$

$V_2 = \text{new volume of gas}$ $\qquad T_2 = (100 + 273)\ \text{K} = 373\ \text{K}$

$$\therefore \quad V_2 = \frac{V_1 T_2}{T_1}$$

$$= \frac{125 \times 373}{290}\ \text{cm}^3$$

$$= 161\ \text{cm}^3$$

The new volume will be 161 cm³.

General Gas Equation

From the gas laws, we know that the volume of a gas depends on both its temperature and pressure. The relationship between the three variables, i.e. volume, temperature and pressure, can be summed up as follow:

If $\quad V \propto \frac{1}{p} \quad$ (Boyle's Law — at constant temperature)

and $\quad V \propto T \quad$ (Charles' Law — at constant pressure)

then $\quad V \propto \frac{1}{p} \times T \quad$ (both temperature and pressure may vary)

or $\quad \frac{pV}{T} = k \quad$ where k is a constant for a fixed mass of gas.

The above equation $\frac{pV}{T} = k$ is often known as the *General Gas Equation*. It simply states that for a fixed mass of gas under any set of conditions of V, p and T, the value of $\frac{pV}{T}$ must remain constant.

If, for a fixed mass of gas, V_1 is the volume at pressure p_1 and absolute temperature T_1, and V_2 is the volume at pressure p_2 and absolute temperature T_2, it follows that:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

The General Gas Equation can be used to find the volume of a gas when both its pressure and temperature change. Thus,

$$V_2 = \frac{p_1 V_1 T_2}{p_2 T_1}$$

Standard temperature and pressure (s.t.p.)

The volumes of gases change markedly with changes in temperature and pressure. If two chemists, one in a temperate country, like England, and the other in a tropical country, like Nigeria, were carrying out identical investigations on gases, their gas volumes would differ markedly because of the temperature difference between the two countries. Scientists, therefore, decided that 0 °C or 273 K and 760 mm Hg or $1.01 \times 10^5\ \text{N m}^{-2}$ (in S.I. units) should be the *standard temperature and pressure (s.t.p.)* at which gas volumes are given.

Experiment 5.7 To verify Charles' Law.

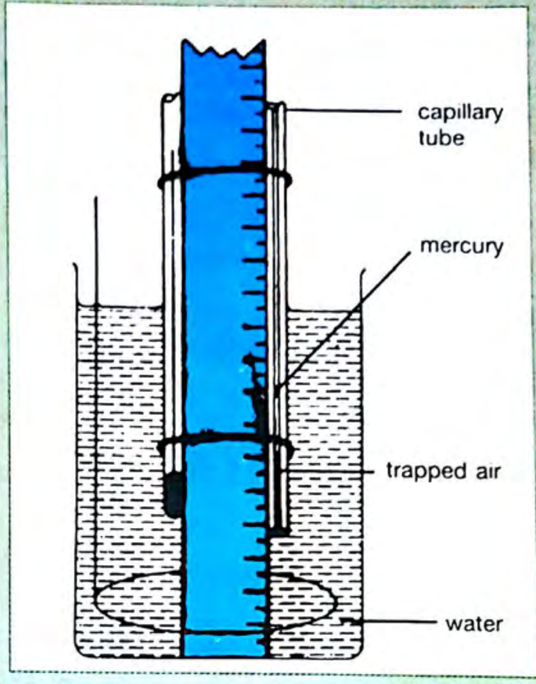
Method Tie a capillary tube, sealed at one end with some dry air trapped in it by a pellet of mercury, to a half-metre rule and a thermometer as shown. The length of the enclosed column of air can be read off from the ruler and can be taken to be equivalent to its volume.

Note The capillary tube acts as a cylinder, while the mercury pellet acts as an almost frictionless piston. This allows for the expansion of the trapped air while keeping the pressure acting on it almost constant.

Add ice shavings to the water in the beaker, stirring all the time, until the thermometer reads 0 °C. Note the volume of the trapped air.

Heat the water to raise the temperature by about 15 °C. Then remove the flame and stir the water. Record the highest temperature reached and the volume of the air at that temperature. Repeat this procedure five or six times and record your readings as shown. Then plot a graph of volume of air against temperature in kelvin.

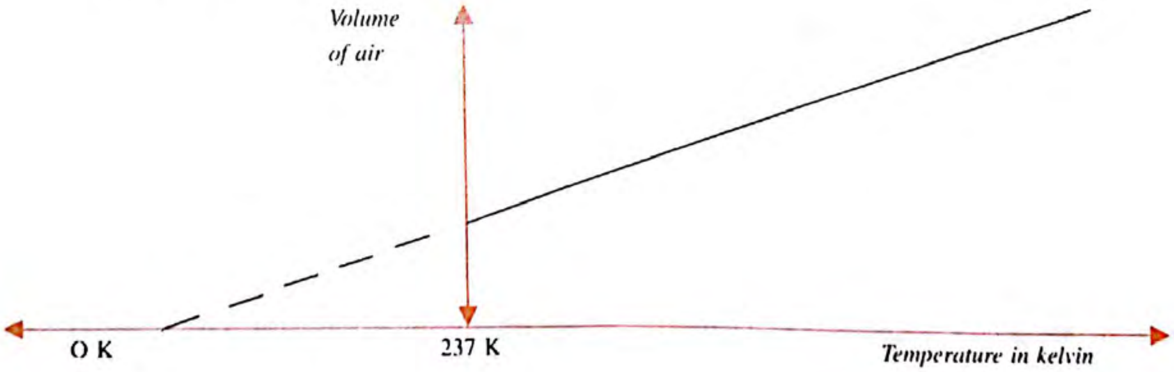
Fig. 5.19 Verification of Charles' Law.



Result

Volume of trapped air (V mm)	Temperature of trapped air	
	q °C	T K

The graph of volume of air against temperature in kelvin is a straight line which passes through the origin when extended.



Conclusion **The straight line graph shows that the volume of a fixed mass of air (or any gas) is directly proportional to its temperature in kelvin, i.e.**

$$V \propto T$$

EXAMPLES

1 *At s.t.p., a certain mass of gas occupies a volume of 790 cm³.* Find the temperature at which the gas occupies 1 000 cm³ and has a pressure of 726 mm Hg.

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \quad \text{GAS EQUATION}$$

p_1 = s.p. = 760 mm Hg $\qquad V_1 = 790\ \text{cm}^3$
T_1 = s.t. = 273 K
p_2 = 726 mm Hg $\qquad V_2 = 1\,000\ \text{cm}^3$
T_2 = new temperature of the gas

$$\therefore T_2 = \frac{p_2V_2T_1}{p_1V_1}$$

$$= \frac{726 \times 1\,000 \times 273}{760 \times 790} = 330.1\ \text{K}$$

The new temperature of the gas is 330.1 K.

2 *A given mass of a gas occupies 850 cm³* at 320 K and 0.92×10^5 N m^{-2} pressure. Calculate the volume of the gas at s.t.p..

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \quad \text{GAS EQUATION}$$

$p_1 = 0.92 \times 10^5\ \text{N m}^{-2}$ $\qquad T_1 = 320$ K
$V_1 = 850\ \text{cm}^3$
p_2 = s.p. = $1.01 \times 10^5\ \text{N m}^{-2}$ $\qquad T_2$ = s.t. = 273 K
V_2 = new volume of gas

$$\therefore \quad V_2 = \frac{p_1V_1T_2}{p_2T_1}$$

$$= \frac{0.92 \times 10^5 \times 850 \times 273}{1.01 \times 10^5 \times 320}$$

$$= 660.5\ \text{cm}^3$$

The volume of the gas at s.t.p. is 660.5 cm³.

Dalton's Law of Partial Pressures

The law of partial pressures states that if there is a mixture of gases which do not react chemically together, then the total pressure exerted by the mixture is the sum of the partial pressures of the individual gases that make up the mixture.

According to Dalton's Law, the total pressure o a mixture of gases is the sum of the pressures whic each individual gas would exert if it were confine alone in the volume occupied by the mixtur Mathematically, this can be expressed as:

$$p_{\text{total}} = p_A + p_B + p_C + \ldots..$$

where p_{total} = total pressure of the mixture, and p_A, p_B, p_C are the partial pressures exerted separately b the individual gases *A*, *B*, *C* that make up the mixture.

If a gas is collected over water, it is likely to b saturated with water vapour, and the total pressure becomes:

$$p_{\text{total}} = p_{\text{gas}} + p_{\text{water vapour}}$$

The effective pressure of the dry gas itself can be calculated by subtracting the saturated vapour pressure of water at that particular temperature and pressure from the total gas pressure.

EXAMPLE

A certain mass of hydrogen gas collected over water at 6 °C and 765 mm Hg pressure has a volume o 35 cm³. Calculate the volume when it is dry at s.t.p. (S.V.P. of water at 6 °C = 7 mm Hg.)

The true pressure of the hydrogen gas
= (765 – 7) mm Hg = 758 mm Hg

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \quad \text{GAS EQUATION}$$

p_1 = 758 mm Hg $\qquad V_1 = 35\ \text{cm}^3$
T_1 = (6 + 273) K = 279 K
p_2 = s.p. = 760 mm Hg $\quad V_2$ = volume of gas at s.t.p.
T_2 = s.t. = 273 K

$$\therefore \quad V_2 = \frac{p_1V_1T_2}{p_2T_1}$$

$$= \frac{758 \times 35 \times 273}{760 \times 279} = 34.2\ \text{cm}^3$$

The volume of the gas at s.t.p. is 34.2 cm³.

Table 5.2 Saturated vapour pressure (S.V.P.) of water at various temperatures.

Temperature (°C)	0	1	2	3	4	5	6	7	8	9	10	11	12
S.V.P. (mm Hg)	4.6	4.9	5.3	5.7	6.1	6.5	7.0	7.5	8.0	8.6	9.2	9.8	10.5
Temperature (°C)	13	14	15	16	17	18	19	20	21	22	23	24	25
S.V.P. (mm Hg)	11.2	11.9	12.7	13.5	14.0	15.0	16.0	17.0	18.0	19.0	20.5	22.5	23.5

Ideal Gas Equation

Four quantities are important in all experimental work, measurements or calculations involving gases. They are

- volume,
- pressure,
- temperature, and
- number of moles or mass.

Three of these parameters appear in the General Gas Equation:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

This equation states that for an ideal gas pV/T is a constant. It has also been proven experimentally that equal volumes of all gases at the same temperature and pressure contain the same number of molecules, and that one mole of any gas at s.t.p. occupies a volume of 22.4 dm³. This fact, together with Boyle's and Charles' laws, leads to another equation:

$$pV = RT$$

where R is a constant termed as the molar gas constant. The equation is called the Ideal Gas Equation and holds true for all gases. The above equation applies only to one mole of gas. For n moles of gas, we get the general form of the equation:

$$pV = nRT$$

where p is in atm, V in dm³, T in K, n = no. of moles of gases

At s.t.p., for 1 mole of gas,

$$R = \frac{pV}{nT}$$

$$= \frac{(1 \text{ atm})\ (22.4 \text{ dm}^3)}{(1 \text{ mol})\ \ (273 \text{ K})}$$

$$= 0.082 \text{ atm dm}^3 \text{ K}^{-1}\text{mol}^{-1}$$

EXAMPLES

1 *A certain amount of gas occupies 5.0 dm³ at 2 atm and 10 °C. Calculate the number of moles present. (R = 0.082 atm dm³ K⁻¹ mol⁻¹)*

From the ideal gas equation $pV = nRT$, we get

$$n = \frac{pV}{RT}, \qquad \text{where } p = 2 \text{ atm } V = 5.0 \text{ dm}^3$$

$$T = 10\ °\text{C} = 10 + 273 = 283 \text{ K}$$

$$R = 0.082 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$\therefore n = \frac{2 \times 5.0}{0.082 \times 283} = 0.431 \text{ mole}$$

2 *2.0 moles of an ideal gas are at a temperature of −13 °C and a pressure of 2 atm. What volume in dm³* will the gas occupy at that temperature? (R = 0.082 atm dm³ K⁻¹ mol⁻¹)

Using the ideal gas equation, $pV = nRT$, we get

$$V = \frac{nRT}{p}, \qquad \text{where } p = 2 \text{ atm } n = 2.0 \text{ moles}$$

$$T = -13\ °\text{C} = -13 + 273 = 260 \text{ K}$$

$$V = \frac{2.0 \times 0.082 \times 260}{2} = 21.32 \text{ dm}^3$$

3 *Under a pressure of 3 000 N m⁻²*, a gas has a volume of 250 cm³. What will its volume be if the pressure is changed to 100 mm Hg at the same temperature?
(760 mm Hg = 101 325 N m⁻²)

$$3\ 000 \text{ N m}^{-2} = \frac{3000}{101\ 325} \times 760 = 22.5 \text{ mm Hg}$$

Using the formula,

$$\frac{p_1V1}{T_1} = \frac{p_2V_2}{T_2}, \qquad \text{we get}$$

$$V_2 = \frac{p_1 V_1}{p_2}, \quad \text{where } p_1 = 22.5 \text{ mm Hg}$$

$$p_2 = 100\text{mm Hg} \quad V_1 = 250 \text{ cm}^3$$

$$V_2 = \text{volume of gas at } 100 \text{ mm Hg}$$

$$V_2 = \frac{22.5 \times 250}{100} = 56.25 \text{ cm}^3$$

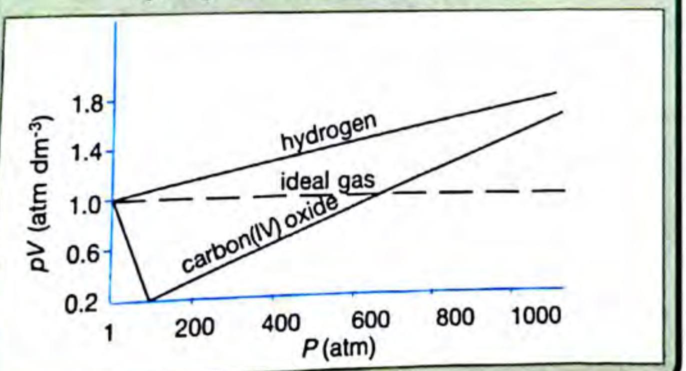
Deviations from the gas laws

Ideal gases do not exist. The behaviour of real gases deviates from those depicted by the gas laws. The main reasons for the deviation are that, unlike ideal gases, the molecules of real gases occupy space and there are forces of attraction between them. When pressure rises and temperature falls, the molecules of the gas will be made to come closer together, and they will also slow down. This makes the volume of the individual molecule less negligible – as opposed to what is assumed in the Kinetic Theory of gases. Intermolecular forces will be stronger and better felt — also contrary to the Kinetic Theory.

When gaseous molecules do not behave according to the Kinetic Theory, they no longer conform to Boyle's and Charles' Laws. For example, Boyle's Law states that pV = constant, which means that the graph of pV against p should be a horizontal line. This is not true for many gases. According to Charles' Law, an ideal gas never liquefies. This is not true as real gases do liquefy when the temperature drops. In fact, condensation of a gas to a liquid is one of the major differences between a real gas and an ideal gas.

Gas laws and equations can still be used for real gases especially in conditions of low pressure and high temperature. Under normal laboratory conditions, most gases obey the gas laws with less than 1% deviation.

Fig. 5.20 pV against p graph for an ideal gas, hydrogen and carbon(IV) oxide.



Gay-Lussac's Law

Gay-Lussac's Law describes the combining volume of gases that react together. In his experiments, a temperatures and pressures were kept constant.

Steam Gay-Lussac observed that two volumes o hydrogen reacted with one volume of oxygen to yiel two volumes of steam.

	hydrogen	+	oxygen	→	steam
Volume	2		1		2
Ratio	2	:	1	:	2

Hydrogen chloride gas One volume of hydroge combined with one volume of chlorine to yield tw volumes of hydrogen chloride gas.

	hydrogen	+	chlorine	→	hydrogen chlorid
Volume	1		1		2
Ratio	1	:	1	:	2

Gay-Lussac noticed that the combining volumes as well as the volumes of the products, if gaseous were related by simple ratios of whole numbers. He proposed the *Law of Combining Volumes or Gaseous Volumes*.

> *Gay-Lussac's Law of Combining Volumes states that when gases react, they do so in volumes which are simple ratios to one another and to the volumes of the products, if gaseous, provided that the temperature and the pressure remain constant.*

EXAMPLES

1 *What is the volume of oxygen required to burn completely 45 cm³ of methane* (CH_4)?

Equation of reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

By Gay-Lussac's Law,
1 volume of methane requires 2 volumes of oxygen,
i.e. 1 cm³ of methane requires 2 cm³ of oxygen
∴ 45 cm³ of methane require 90 cm³ of oxygen

2 *20 cm^3 of carbon(II) oxide are sparked with 20 cm^3* of oxygen. If all the volumes of gases are measured at s.t.p., calculate the volume of the residual gases after sparking.

Equation of reaction: $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

Combining volumes: 2 1 2
Volumes before sparking: 20 cm^3 2 0
cm^3 –
Reacting volumes: 20 cm^3 10 cm^3 2 0
cm^3
Volumes after sparking: – 1 0
cm^3 20 cm^3

Residual gases = unreacted oxygen + carbon(IV) oxide formed

Volume of residual gases = 10 cm^3 + 20 cm^3
= 30 cm^3

Avogadro's Hypothesis

Avogadro (1776–1856), an Italian professor, put forward a hypothesis that explained Gay-Lussac's Law satisfactorily.

Avogadro's Hypothesis states that equal volumes of all gases at the same temperature and pressure contain the same number of molecules.

In recent years, Avogadro's Hypothesis was confirmed and is now known as *Avogadro's Law*.

Avogadro's Law and Gay-Lussac's Law

By applying Avogadro's Law, the volume of gases can be converted into the relative number of molecules they contain. This helps to explain Gay-Lussac's Law. The experimentally observed Gay-Lussac's Law can be re-stated as follows: *When gases react, they do so in small whole numbers of molecules of reactants to produce small whole numbers of molecules of products*. This is also what Dalton had suggested. The following examples show how Avogadro's Law explains that Gay-Lussac's Law is in agreement with the equations of reaction (at constant temperature and pressure).

Steam

Reaction	hydrogen	+	oxygen	→	steam
Volume	2		1		2
Gay-Lussac's ratio	2	:	1	:	2
Avogadro's proposal	2 molecules	:	1 molecule	:	2 molecules

This agrees with the equation of the reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

i.e. 2 molecules of hydrogen combine with 1 molecule of oxygen to yield 2 molecules of water.

Hydrogen chloride

Reaction	hydrogen	+	chlorine	→	hydrogen chloride
Volume	1		1		2
Gay-Lussac's ratio	1	:	1	:	2
Avogadro's proposal	1 molecule	:	1 molecule	:	2 molecules

This agrees with the equation of the reaction,

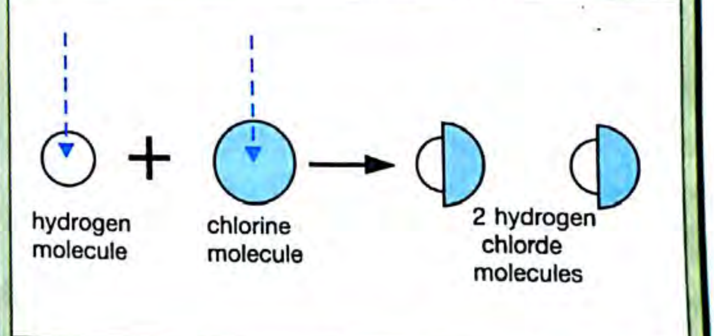
$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

i.e. 1 molecule of hydrogen combines with 1 molecule of chlorine to yield 2 molecules of hydrogen chloride.

Nature of the molecule

In the reaction between hydrogen and chlorine, one molecule of hydrogen reacts with one mulecule of chlorine to yield two molecules of hydrogen chloride. This is in accordance with Avogadro's Law. Since only whole atoms can take part in a chemical combination (Atomic Theory), the molecule of hydrogen and the molecule of chlorine that combine to yield two molecules of hydrogen chloride must contain more than one atom each. Otherwise, there would be a halving of each atom which is contrary to the Atomic Theory.

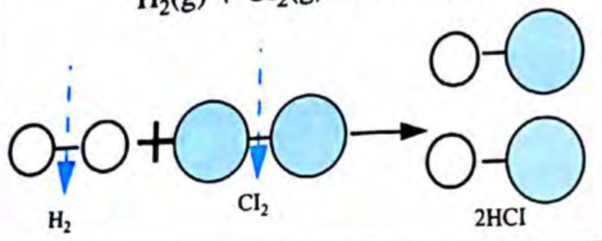
Fig. 5.21 Formation of hydrogen chloride molecules (contrary to the Atomic Theory).



If the hydrogen and the chlorine molecules are assumed to contain two atoms each, the formation of the two molecules of hydrogen chloride is possible without having to halve the atoms.

Fig. 5.22 Formation of hydrogen chloride molecules (in agreement with the Atomic Theory).

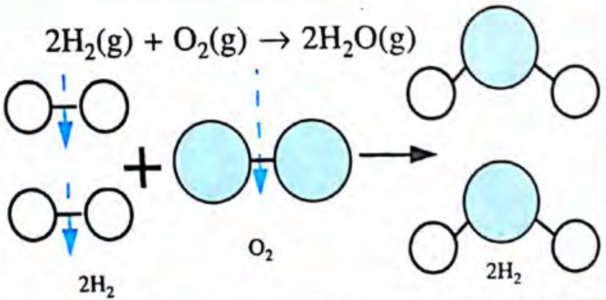
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$



A similar explanation can be given for the formation of steam.

Fig. 5.23 Formation of water molecules.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$



Mole, Avogadro number, molar volume

The mole is the unit used for measuring amount (in terms of number of particles) of matter.

The number of specified particles contained in a mole of any substance is equal to 6.02×10^{23}. This is known as the *Avogadro Number* or *Constant*.

The Avogadro Number is the number of carbon atoms in 12 g of carbon–12 and is numerically equal to 6.02×10^{23}.

By experiment, it has been found that 1 dm^3 of hydrogen gas has a mass of 0.09 g at s.t.p. The molar mass of hydrogen gas is 2.016 g. This mass of hydrogen occupies $\frac{2.016}{0.09}$ dm^3 or 22.4 dm^3 at s.t.p. Applying Avogadro's Law, the molar mass of any gas will occupy a volume of 22.4 dm^3 at s.t.p. The volum 22.4 dm^3, at s.t.p. is known as the *molar volume* o gases.

The molar volume of any gas is the volume occupied by one mole of that gas at s.t.p., and is equal numerically to 22.4 dm^3.

1 mole of	Mass	Volume at s.t.p	Number of particles
Chlorine, Cl_2	71 g	22.4 dm^3	6.02×10^{23} molecules
Carbon(IV) oxide, CO_2	44 g	22.4 dm^3	6.02×10^{23} molecules

EXAMPLES

1 *Calculate the volumes of (a) 2.5 moles of oxygen, (b) 25.5g of ammonia, at s.t.p. (Molar volume of a gas is 22.4* dm^3, *molar mass of* NH_3 *is 17 g)*

(a) 1 mole of oxygen occupies 22.4 dm^3 at s.t.p.
∴ 2.5 moles of oxygen occupy (22.4×2.5)
$= 56.0$ dm^3 at s.t.p.

(b) Molar mass of ammonia = 17 g
17 g of ammonia = 1 mole
25.5 g of ammonia = 1.5 moles
1.5 moles of ammonia occupy (1.5×22.4)
$= 33.6$ dm^3 at s.t.p.

2 *If 0.8 g of gas Z occupies 0.56* dm^3 *at s.t.p., calculate its relative molecular mass. (Molar volume of gas is 22.4* dm^3.*)*

0.56 dm^3 of gas Z has a mass of 0.8 g.

22.4 dm^3 of gas Z has a mass of $\frac{22.4}{0.56} \times 0.8$
$= 32$ g.

∴ relative molecular mass of gas Z is 32.

Relative Vapour Density of Gases

The vapour density of a gas (or vapour) is expressed as the number of times a given volume of the gas (or vapour) is as heavy as the same volume of hydrogen at a particular temperature and pressure.

The vapour density (V.D.) of a gas or vapour can be expressed as follows:

$$\begin{array}{c}\text{V.D.}\\\text{of a gas}\end{array} = \frac{\text{Mass of a given volume of the gas / vapour}}{\text{Mass of an equal volume of hydrogen}}$$

(The temperature and pressure must be constant.)

Vapour density and relative molecular mass

$$\begin{array}{c}\text{Vapour density}\\\text{of gas / vapour}\end{array} = \frac{\text{Mass of } x \text{ volumes of gas / vapour}}{\text{Mass of } x \text{ volumes of hydrogen}}$$

By applying Avogadro's Law,

$$\text{V.D.} = \frac{\text{Mass of } x \text{ molecules of gas / vapour}}{\text{Mass of } x \text{ molecules of hydrogen}}$$

$$= \frac{\text{Mass of 1 molecule of gas / vapour}}{\text{Mass of 1 molecule of hydrogen}}$$

But the molecule of hydrogen is diatomic,

$$\therefore \quad \text{V.D.} = \frac{\text{Mass of 1 molecules of gas / vapour}}{\text{Mass of 2 atoms of hydrogen}}$$

$$2\text{xV.D.} = \frac{\text{Mass of 1 molecule of gas / vapour}}{\text{Mass of 1 atom of hydrogen}}$$

On the hydrogen scale,

$$\frac{\text{Mass of 1 molecule of gas / vapour}}{\text{Mass of 1 atom of hydrogen}} = \begin{array}{c}\text{Relative molecular}\\\text{mass of gas / vapour}\end{array}$$

$$\therefore 2 \times \text{V.D.} = \begin{array}{c}\text{Relative molecular}\\\text{mass of gas / vapour}\end{array}$$

or,

$$\boxed{\therefore \ \text{V.D.} = \frac{1}{2} \times \begin{array}{c}\text{Relative molecular}\\\text{mass of the gas / vapour}\end{array}}$$

In the earlier days, this relationship was used frequently to determine the relative molecular masses of gases and vapours. This method has since been replaced by other more accurate methods.

Graham's Law of Diffusion of Gases

In 1833, Graham, an English chemist, discovered that a less dense gas can diffuse through a medium much faster than a denser gas. He carried out an experiment to examine the relationship between the rate of diffusion of a gas and its density.

Graham's Law of Diffusion states that at a constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density.

From Graham's Law,

$R \propto \dfrac{1}{\sqrt{\rho}}$ where R is the rate of diffusion and ρ (ρ is the Greek letter rho) is the density of the gas.

Where 2 gases are involved, gases 1 and 2,

$\dfrac{R_1}{R_2} = \sqrt{\dfrac{\rho_2}{\rho_1}}$ where R_1 and R_2 are the rates of diffusion and ρ_1 and ρ_2 the densities of the two gases.

The density of a given gas is found to be directly proportional to its molecular mass. Graham's law can be re-defined as follows:

At a constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its relative molecular mass, i.e.

$R \propto \dfrac{1}{\sqrt{M}}$ where R is the rate of diffusion and M, the relative molecular mass of the gas.

$\therefore \dfrac{R_1}{R_2} = \sqrt{\dfrac{M_2}{M_1}}$ where R_1 and R_2 are the rates of diffusion and M_1 and M_2, the relative

EXAMPLES

1 *If 280 cm*^{3} of hydrogen diffuses in 40 seconds, how long will it take for 490 cm^3 of a gas, X, whose vapour density is 25, to diffuse under the same conditions? (Relative molecular mass of hydrogen = 2).

Let

R_x = rate of diffusion of the gas X in cm^{3}s^{-1}

R_H = rate of diffusion of hydrogen = $\dfrac{280 \text{ cm}^3}{40 \text{ s}}$

ρ_x = vapour density of gas X = 25

ρ_H = vapour density of hydrogen

$$\text{V.D.} = \frac{1}{2} \times \text{relative molecular mass of the gas}$$

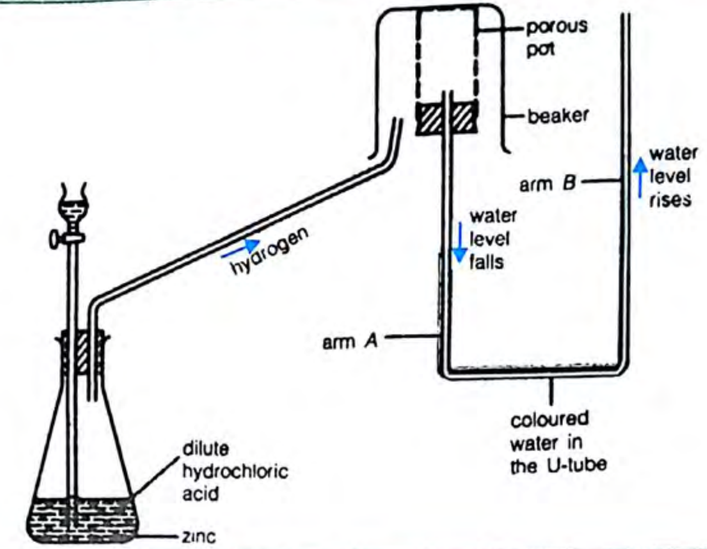
$$\rho_H = \frac{1}{2} \times M_r \text{ of hydrogen} = \frac{1}{2} \times 2 = 1$$

$$\frac{R_x}{R_H} = \sqrt{\frac{\rho_H}{\rho_x}} \qquad \text{GRAHAM'S LAW}$$

Experiment 5.8 To show that hydrogen, a less dense gas, diffuses through a medium at a faster rate than air, a mixture of denser gases.

Method Set up the apparatus as shown. Cover the porous pot with a large beaker and note the levels of the coloured water in the U-tube. Add some dilute hydrochloric acid to the zinc in the conical flask and direct the hydrogen gas formed into the beaker through a glass delivery tube. Note the levels of the coloured water in the U-tube. Cut the hydrogen supply after some time and note the water levels again.

Fig. 5.24 Hydrogen diffuses at a much faster rate than air.



Result For the sake of clarity, divide the experiment into three stages.

Stage 1 Before the hydrogen gas is introduced into the beaker.
Stage 2 When the hydrogen gas is introduced into the beaker.
Stage 3 After the hydrogen supply is cut and the beaker is removed.

Stage 1 it is observed that the levels of the coloured water in the two arms of the U-tube are the same. This indicates that the pressure acting on the two surfaces are equal. They are both at atmospheric pressure (i.e. pressure exerted by air alone).

Stage 2 The water level in arm *A*, which is connected to the porous pot, is lower than the level in arm *B*, which is exposed to the atmosphere. This higher pressure inside the porous pot indicates that it contains many more gas particles now than before. This is caused by the hydrogen diffusing into the porous pot at a faster rate than that at which the air inside the pot is diffusing out.

Stage 3 The water level in arm *A* rises above that in arm *B*, showing that the pressure inside the pot has become less than atmospheric pressure. This is because the hydrogen inside the porous pot is diffusing out at a faster rate than that at which air is entering it, so that there is a great reduction in the amount of gas particles inside the porous pot.

Conclusion Hydrogen, a less dense gas, diffuses at a faster rate than the denser air.

$$\therefore R_x = R_H\sqrt{\frac{\rho_H}{\rho_x}} = \frac{280}{40}\sqrt{\frac{1}{25}}$$

$$= 7\times\frac{1}{5} = 1.4\ \text{cm}^3\ \text{s}^{-1}$$

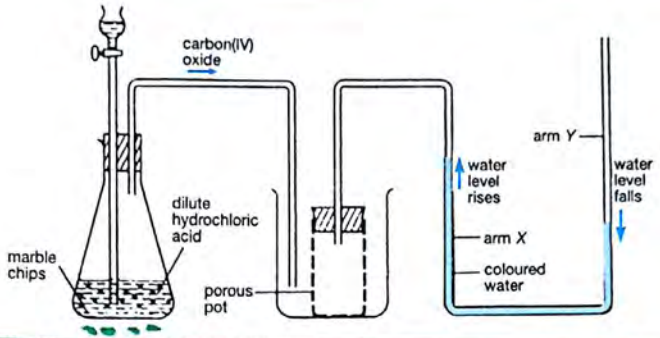
$\therefore$ 490 cm^3 of X would diffuse in

$$\frac{490}{1.4} = 350 \text{ seconds}$$

Experiment 5.9 To show that carbon(IV) oxide, a denser gas, diffuses through a medium at a slower rate than air.

Method Set up the apparatus as shown. Connect the porous pot to the U-tube containing coloured water and put it inside a large beaker. Note the levels of the coloured water in the U-tube. Add some dilute hydrochloric acid to the marble chips in the conical flask and deliver the carbon(IV) oxide produced into the beaker. Note the levels of the water in the U-tube. After some time, cut the carbon(IV) oxide supply and remove the beaker. Note the water levels again.

Fig. 5.25 Carbon(IV) oxide diffuses at a much slower rate than air.



Result Again divide the experiment into three stages as before.

Stage 1 Before the carbon(IV) oxide is introduced into the beaker.
Stage 2 When the carbon(IV) oxide is introduced into the beaker.
Stage 3 After the carbon(IV) oxide supply is cut and the beaker is removed.

Stage 1 The water levels in the two arms of the U-tube are equal as they are both at atmospheric pressure.

Stage 2 The water level in arm *X* rises above that in arm *Y*. The reduced pressure inside the porous pot is due to the air inside the porous pot diffusing out at a faster rate than at which carbon(IV) oxide is diffusing into it.

Stage 3 The water level in arm *Y* rises above that in arm *X*, i.e. the pressure inside the pot has become greater than the atmospheric pressure. This is because the air outside is diffusing into the pot at a faster rate than that at which the carbon(IV) oxide inside is diffusing out. Hence, the inside of the porous pot contains a larger number of carbon(IV) oxide and air molecules than before.

Conclusion Carbon(IV) oxide, a denser gas, diffuses at a slower rate than air which is less dense.

2 *Under the same conditions of temperature and pressure, hydrogen diffuses 8 times as fast as a gas, Y. Calculate the relative molecular mass of Y. (Relative molecular mass of hydrogen = 2)*

$$\frac{R_Y}{R_H} = \sqrt{\frac{M_H}{M_Y}}$$

where R_Y and R_H are the rates of diffusion of the gas *Y* and hydrogen respectively, and M_Y and M_H are the relative molecular masses of the gas *Y* and hydrogen respectively.

$$\frac{1}{8} = \sqrt{\frac{2}{M_Y}}$$

$$\left(\frac{1}{8}\right)^2 = \frac{2}{M_Y}$$

$$\frac{1}{64} = \frac{2}{M_Y}$$

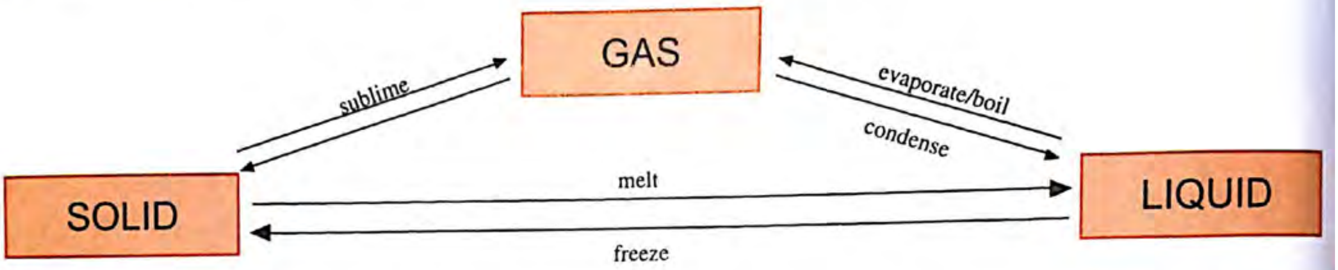
$$\therefore \quad M_Y = 2 \times 64$$

$$= 128$$

The relative molecular mass of gas *Y* = 128.

SUMMARY

- The Kinetic Theory of Matter states that all matter is made up of very tiny particles which are in constan motion and possess kinetic energy.
- Matter exists in three states: solid, liquid and gaseous.
  (a) In solids, the cohesive forces between the particles are very strong. The particles only vibrate an rotate about a fixed position, and possess very little energy.
  (b) In liquids, the cohesive forces between the particles are weaker than those in solids. The particle move about randomly, but only within a restricted space only. They possess more kinetic energy tha the particles in solids.
  (c) In gases, the cohesive forces between the particles are negligible. The particles move about freely at random and at high speeds. Of all the three states, the particles in the gaseous state possess the greatest amount of energy.
- A substance can exist as a solid, a liquid or a gas. Change of state is brought about by a change i temperature. As a substance changes from a gas to a liquid, then to a solid, its particles become les energetic and lose their random motion gradually to finally get arranged in an orderly pattern.



- The phenomena supporting the Kinetic Theory of Matter are osmosis, diffusion, dialysis and Brownian movement.
- Boyle's Law states that the volume, V, of a given mass of gas is inversely proportional to its pressure, p, provided that the temperature remains constant.

$$V \propto \frac{1}{p} \quad \text{or} \quad Vp = k \text{ (where } k \text{ is a constant)}$$

- The kelvin temperature scale has –273 °C as its starting point. This is known as the absolute zero.
- Charles' Law states that the volume, V, of a given mass of gas is directly proportional to its temperature, T, in kelvin, provided that the pressure remains constant.

$$V \propto T \quad \text{or} \quad \frac{V}{T} = k \text{ (where } k \text{ is a constant)}$$

- The General Gas Equation gives the relationship between volume, V, pressure, p and temperature, T, of a gas.

$$\frac{pV}{T} = k \quad \text{or} \quad \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

- Standard temperature and pressure or s.t.p. is at 0 °C or 273 K and 760 mm Hg or 1.01×10^5 N m^{-2}.
- Dalton's Law of Partial Pressures states that if there is a mixture of gases which do not react chemically

together, then the total pressure exerted by the mixture is the sum of the partial pressures of the individual gases that make up the mixture.

- The Ideal Gas Equation describes the relationship between volume, V, pressure, p, temperature, T, and number of moles, n, for a given mass of gas.

  $pV = nRT$ (where R is the molar gas constant)

  This equation is true for all gases at low pressures and high temperatures.
- Gay-Lussac's Law of Combining Volumes states that when gaseous reactants combine together to give gaseous products, they do so in simple ratios of their volumes, provided that the temperature and pressure remain constant.
- Avogadro's Law states that gases with similar volumes contain the same number of molecules at a certain temperature and pressure.
- Avogadro number or Constant is equal to 6.02×10^{23} particles (i.e. molecules, atoms, electrons, ions, etc.).
- The Molar Volume of any gas is the volume occupied by one mole of that gas at s.t.p. and is equal to 22.4 dm^3.
- One Mole of any substance, be it an element, compound or ion, contains 6.02×10^{23} particles and if gaseous, occupies a volume of 22.4 dm^3 at s.t.p.
- The Vapour Density of a gas (or vapour) is expressed as the number of times a given volume of the gas (or vapour) is as heavy as the same volume of hydrogen at a particular temperature and pressure.
- Graham's Law of Diffusion states that at a constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density.

EXERCISES

1. Water (H_2O) exists as a solid, liquid and gas respectively because
A water is colourless.
B water is electrovalent.
C water in any state posseses a certain degree of motion in the molecules.
D water is molecular.

2. Which of the three states of matter has no fixed shape, no fixed volume and least dense.
A Gas B Liquid
C Solid D Crystals

3. Presence of sodium chloride in ice will
A decrease or lower the boiling point of sodium chloride.
B increase the melting point of sodium chloride.
C make sodium chloride impure.
D lower the freezing point of sodium chloride.

4. The escape of molecules with more than average kinetic energy of the molecules is called
A melting. B freezing.
C evaporation. D efflorescence.

5. The phenomenon whereby the atmospheric pressure equals the saturated vapour pressure is called
A freezing.
B latent heat.
C boiling.
D normal pressure.

6. Which of these does not support the phenomenon of kinetic theory.
A Brownian motion
B Diffusion
C Osmosis
D Linear expansivity

7. $P_1V_1 = P_2V_2$ supports
- A Charle's law
- B Boyle's law
- C Graham's law
- D Avogadro's law

8. Kelvin temperature can be converted into Celsius temperature by
- A $°C = K - 273$
- B $K + 273$
- C $\frac{°C + 273}{K}$
- D $\frac{K + 273}{°C}$

9. What will be the new volume (V) if the new pressure is halved and the initial pressure remain the same.
- A $2P_1V_1 = P_2V_2$
- B $P_1V_1 = 2P_2V_2$
- C $\frac{P_1V_1}{2} = \frac{P_2V_2}{2}$
- D $P_1V_1 = \frac{P_2V_2}{2}$

10. From ideal gas equation, PV = nRT, the unit of *n* is
- A atm dm^3
- B atm dm^3 K^{-1}
- C moles
- D K^{-1} $mole^{-1}$

11. How many atoms are contained in 2 g of hydrogen gas. (H = 1)
- A 6.02×10^{23} atoms
- B 6.02×10^{23} molecules
- C 12.04×10^{23} atoms
- D 12.04×10^{23} molecules

12. How many molecules of oxygen gas are contained in 0.2 mole of oxygen gas. (O = 16)
- A 0.20×10^{23} molecules
- B 1.204×10^{23} molecules
- C 2.40×10^{23} molecules
- D 1 molecule

13. If 10^3 of hydrogen gas were sparked with 20 c of oxygen, calculate the volume(s) of resid gas(es) after cooling.
- A 25 cm^3 of O_2
- B 5 cm^3 of O_2
- C 15 cm^3 of O_2
- D 10 cm^3 of water

14. 400 cm^3 of a gas *x* diffused through a porous p in 2 minutes. Calculate the rate at which diffuses.
- A 6.3 cm^3 s^{-1}
- B 20 cm^3 s^{-1}
- C 200 cm^3 s^{-1}
- D 3.33 cm^3 s^{-1}

15. The pressure exerted by a gas is a result of
- A the continuous random motion of it particles.
- B bombardment of the walls of the container by its molecules.
- C the expansion of the gas molecules.
- D the elastic nature of the gas molecules.
- E the collision between the gas molecules.

16. The closer the molecules of a gas are in the liquid state
- A the more accurately it will follow the Ideal Gas Equation.
- B the more it will deviate from the Ideal Gas Equation.
- C the more random is the movement of its molecules.
- D the more kinetic energy it will possess.
- E the greater is the pressure it exerts on the walls of the container.

17. State the Kinetic Theory of Matter and outline three natural phenomena which support it.

18. (a) What happens to the particles of a solid at its melting point?

(b) Why does a given gas occupy all the available space in a container?

(c) Explain the latent heat of fusion.

(d) How does evaporation occur and why does it cause cooling?

19. (a) A given mass of nitrogen is 0.12 dm^3 at 60 °C and 1.01×10^5 N m^{-2}. Find its pressure at the same temperature if its volume is changed to 0.24 dm^3.

(b) A sample of nitrogen occupies a volume of 1 dm^3 at 500 K and 1.01×10^5 N m^{-2}. What will its volume be at 2.02×10^5 N m^{-2} and 400 K?

(c) To what temperature must a given mass of nitrogen at 0 °C be heated so that both its volume and pressure will be doubled?

20. In a certain experiment, two pads of cotton wool, one soaked in concentrated ammonia solution and the other in concentrated hydrochloric acid, are used to plug up the opposite ends of a horizontal glass tube. When the two gases meet inside the tube, white fumes of ammonium chloride are formed. Show, with explanations, in which of the following positions the fumes are formed.

(a) In the middle
(b) Nearer to ammonia
(c) Nearer to hydrochloric acid

Which gas diffuses faster and by what ratio? (N = 14, H = 1, Cl = 35.5)

21. 130 cm^3 of a gas at 20 °C exerts a pressure of 750 mm Hg. Calculate its pressure if its volume is increased to 150 cm^3 at 35 °C.

22. What do you understand by the term *standard temperature and pressure* (s.t.p.)? Calculate the volume of hydrogen produced at s.t.p. when 25 g of zinc are added to excess dilute hydrochloric acid at 31 °C and 778 mm Hg pressure. (H = 1, Zn = 65, Cl = 35.5, molar volume of a gas at s.t.p. = 22.4 dm^3)

23. The combustion of butane in oxygen (air) is represented in the equation below.

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 10H_2O(g) + 8CO_2(g)$$

Calculate the volume of oxygen at s.t.p. needed to burn 30 cm^3 of the butane. What will be the volume of the oxygen if it is measured at 13 °C and 284 mm Hg pressure?

24. (a) State Dalton's Law of Partial Pressures. In a gas jar containing a gas and water, what is the total pressure composed of?

(b) 272 cm^3 of carbon(IV) oxide were collected over water at 15 °C and 782 mm Hg pressure. Calculate the volume of the dry gas at s.t.p. (S.V.P. of water at 15 °C is 12 mm Hg)

25. State how the volume of a given mass of gas alters with:

(a) the change in pressure when the temperature is maintained at a constant value,

(b) the change in temperature when the pressure is maintained at a constant value.

Outline how each of the above behaviour is explained by the Kinetic Theory.

26. (a) State the laws attributable to Gay-Lussac and Avogadro respectively.

(b) How does Avogadro's law explain Gay-Lussac's Law? Use the formation of steam or ammonia to illustrate your answer.

(c) Why is Avogadro's Law sometimes referred to as a hypothesis?

27. A given amount of gas was collected over water at 302 K where the vapour pressure of water was 4.0 kN m^{-2}. Calculate the pressure of the dry gas if the atmospheric pressure at the same temperature was 101.3 kN m^{-2}.

28. If 465 cm^3 of sulphur(IV) oxide, can diffuse through porous partition in 30 seconds, how long will **(a)** an equal volume, **(b)** 620 cm^3 of hydrogen sulphide take to diffuse through the same partition? (H = 1, S = 32, O = 16)

29. (a) Describe an experiment to show that a lighter gas diffuses faster than a heavier one.

(b) If a gas *A* is 9 times as heavy as hydrogen, which will diffuse faster, and by what factor?

6

ACIDS • BASES • SALTS

ACIDS

Acids have long been associated with the sour taste of some fruits such as lime and lemon. Their ability to change litmus solution (a vegetable dye) from blue to red is also well-known.

There are two classes of acids – *organic acids* and *mineral* or *inorganic acids*. The former occur as natural products in plant or animal materials while the latter can be prepared from mineral elements or inorganic matter.

Table 6.1 *Some organic and inorganic acids.*

Organic acid		**Source**
Ethanoic acid		Vinegar
Lactic acid		Milk
Citric acid		Lime, lemon
Amino acids		Proteins
Fatty acids		Fats and oils
Ascorbic acid (vitamin C)		Oranges
Tataric acid		Grape.
Inorganic acid	**Formula**	**Constituents**
Hydrochloric acid	HCl	Hydrogen, chlorine
Tetraoxo-sulphate(VI) acid	H_2SO_4	Hydrogen, sulphur, oxygen
Trioxonitrate(V) acid	HNO_3	Hydrogen, nitrogen, oxygen

Acids in Solution

Acids dissolve in water to produce hydrogen ions, H^+, as the only positive ions, together with the corresponding negative ions. This process is known as *ionization.*

An acid is a substance which produces hydrogen ions (or protons) as the only positive ion when dissolved in water.

The characteristic properties of an acid in solution are due to the presence of these hydrogen ions. This is seen when dry hydrogen chloride gas is dissolved in water and in methyl benzene.

- In water, it forms hydrogen ions and behaves like a typical acid.
- In methyl benzene, it does not form hydrogen ions and does not show any acidic properties.

Thus, an acid has at least one ionizable hydrogen atom in its molecule.

Strong acids ionize completely in water to give hydrogen ions and anions. The concentration of hydrogen ions is very high in such acid solutions. Following are examples of strong acids.

Hydrochloric acid $HCl \rightarrow H^+ + Cl^-$

Trioxonitrate(V) acid $HNO_3 \rightarrow H^+ + NO_3^-$

Tetraoxosulphate(VI) acid $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

Weak acids are only partially ionized in water. Such acid solutions have a low concentration of hydrogen ions. For example, ethanoic acid has only 0.4% ionization in water, i.e. only four out of every thousand acid molecules will ionize in water. Other examples of weak acids include trioxocarbonate(IV) acid, tetraoxophosphate(V) acid and most organic acids.

Trioxocarbonate(IV) acid $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

Tetraoxophosphate(V) acid $H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$

Ethanoic acid $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Trioxosulphate(IV) acid $H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$

If a large amount of water is added to a small amount of acid, the resulting acid solution is *dilute.*

amount of acid, the solution will be *concentrated*. A solution made by adding 5 moles of a pure acid to 1·000 cm^3 (or 1 dm^3) of water is more concentrated than another made by adding 2 moles of the same acid to the same amount of water.

Basicity of an Acid

All acids in an aqueous solution yield hydrogen ions which can be replaced by metallic ions. The number of such hydrogen ions present in one molecule of an acid is known as the *basicity* of this acid.

> *The basicity of an acid is the number of replace-able hydrogen ions, H^+, in one molecule of the acid.*

Table 6.2 Basicity of some common acids.

Acid	Ions produced	Basicity
HCl	H^+, Cl^-	1 or monobasic
H_2SO_4	$2H^+$, SO_4^{2-}	2 or dibasic
H_3PO_4	$3H^+$, PO_4^{3-}	3 or tribasic

Not all the hydrogen atoms in a molecule of an acid are replaceable by a metal. Ethanoic acid, CH_3COOH, for instance, has four hydrogen atoms per molecule of acid, but only one of these is replaceable by a metal. Ethanoic acid is, therefore, monobasic.

$CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H^+(aq)$
ethanoic acid ethanoate ion hydrogen ion

$CH_3COOH(aq) + NaOH(aq)$
ethanoic acid sodium hydroxide
$\rightarrow CH_3COONa(aq) + H_2O(l)$
sodium ethanoate water

Physical Properties of Acids

- Dilute acids have a sour taste. The sour taste of unripe fruit, vinegar and rancid milk is due to the presence of acids in them.
- Acids turn blue litmus red.
- The concentrated forms of strong acids like hydrochloric acid, trioxonitrate(V) acid and tetraoxosulphate(VI) acid are corrosive.

CAUTION Never add water directly to concentrated tetraoxosulphate(VI) acid. The hot acid solution may splatter onto your body and face, and may cause serious burns. Always add acid to water.

Chemical Properties of Acids

Reaction with metals

Acids react with some metals like zinc, iron and magnesium to liberate hydrogen gas. Such reactions are due to the displacement of the hydrogen ions in the acids by the metals. Dilute trioxonitrate(V) acid, however, is an exception to this rule.

acid + metal → salt + hydrogen

$$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$
$$H_2SO_4(aq) + Mg(s) \rightarrow MgSO_4(aq) + H_2(g)$$

Reaction with bases

Acids react with insoluble bases and alkalis to form salts and water as the only products. Such a reaction is known as *neutralization*.

acid + base → salt + water

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$
$$2HCl(aq) + CaO(s) \rightarrow CaCl_2(aq) + H_2O(l)$$

Reaction with trioxocarbonates(IV)

Acids react with trioxocarbonates(IV) to liberate carbon(IV) oxide.

acid + trioxocarbonate(IV)
→ salt + water + carbon(IV) oxide

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

$$H_2SO_4(aq) + K_2CO_3(aq) \rightarrow K_2SO_4(aq) + H_2O(l) + CO_2(g)$$

The three chemical properties listed above are characteristic properties of acids.

Preparation of Acids

An outline of the general methods for the preparation of acids is given here.

Dissolving an acid anhydride in water

1 Carbon(IV) oxide dissolves in water to form a weak acid, trioxocarbonate(IV) acid.

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

2 Sulphur(IV) oxide dissolves to form trioxosulphate(IV) acid in water.

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

3 Sulphur(VI) oxide dissolves to form tetraoxosulphate(VI) acid in water.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

These non-metallic oxides which dissolve in water to produce various acids are known as *acid anhydrides*. For example, carbon(IV) oxide is the acid anhydride of trioxocarbonate(IV) acid.

Combination of constituent elements

1 Burning hydrogen in chlorine, in the presence of activated charcoal as the catalyst, yields hydrogen chloride gas which dissolves readily in water to give hydrochloric acid.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{activated charcoal}} 2HCl(g)$$

2 Heating hydrogen gas and bromine vapour, the presence of platinum as the catalyst, produ hydrogen bromide gas, which dissolves read in water to form hydrobromic acid.

$$H_2(g) + Br_2(g) \xrightarrow{\text{platinum}} 2HBr(g)$$

Using a strong acid to displace a weak acid or volatile acid from its salt

A strong acid may be used to displace a more volat acid or a weaker acid from its salt.

1 Concentrated tetraoxosulphate(VI) acid displac the more volatile trioxonitrate(V) acid from trioxonitrate(V) salt. The salt, e.g. sodiu trioxonitrate(V), must be in excess.

$$2NaNO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2HNO_3($$

2 A chloride yields the volatile hydrogen chlori gas when heated with concentrate tetraoxosulphate(VI) acid. The volatile hydroge chloride dissolves readily in water to giv hydrochloric acid.

$$2KCl(s) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2HCl($$

3 Dilute hydrochloric acid which is a strong aci displaces the weak trioxocarbonate(IV) acid fro trioxocarbonates(IV). The trioxocarbonate aci breaks down to evolve carbon(IV) oxide, the aci

Table 6.3 Uses of some inorganic and organic acids.

Name	Uses
Hydrochloric acid	• Needed by industries to make chemicals. • Used to remove rust.
Tetraoxosulphate(VI) acid	• Needed by industries to make chemicals. • Used as a drying and dehydrating agent. • Used as an electrolyte in lead-acid accumulators. • Required in oil refineries.
Trioxonitrate(V) acid	• Needed by industries for making fertilizers, explosives, etc.
Boric acid	• Used as a mild antiseptic or germicide.
Tartaric acid	• Used in making baking soda, soft drinks and health salts.
Acetic acid (ethanoic acid)	• Used in preserving food. • Used in dyeing silk and other textiles.
Citric acid	• Used in making fruit juice.
Fatty acids (e.g. palmitic and stearic acids)	• Used in the manufacture of soap. The process is known as saponification. Fatty acid + caustic soda → soap + water

anhydride. The weak acid is reformed by dissolving the carbon(IV) oxide in water.

$$\begin{aligned}&2HCl(aq) + CaCO_3(s)\\ &\quad\rightarrow CaCl_2(aq) + H_2CO_3(aq)\\ &\quad\rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)\end{aligned}$$

Uses of Acids

Acids are extremely useful chemicals which are used in many industries to make other consumer chemicals such as fertilizers, detergents and drugs. They are used in industrial processes as drying agents, oxidizing agents and catalysts.

BASES AND ALKALIS

The term *base* was originally used to describe substances that turned red litmus blue and neutralized the properties of acids in aqueous solutions.

Most oxides and hydroxides of metals are bases. Common examples of basic oxides are sodium oxide, Na_2O, potassium oxide, K_2O, and magnesium oxide, MgO. They are formed when these metals burn in air or oxygen, e.g.

$$4Na(s) + O_2(g) \rightarrow \underset{\text{sodium oxide}}{2Na_2O(s)}$$

Most of these metallic oxides are insoluble in water. Some, however, dissolve in water to form hydroxides. For example,

$$Na_2O(s) + H_2O(l) \rightarrow \underset{\text{sodium hydroxide}}{2NaOH(aq)}$$

$$K_2O(s) + H_2O(l) \rightarrow \underset{\text{potassium hydroxide}}{2KOH(aq)}$$

A soluble hydroxide is known as an *alkali*. Many basic hydroxides like copper hydroxide, $Cu(OH)_2$, and aluminium hydroxide, $Al(OH)_3$, are insoluble in water. The few soluble hydroxides like the hydroxides of sodium, potassium and calcium are economically important.

An alkali is a basic hydroxide which is soluble in water.

Like acids, alkalis may be *strong* or *weak*. Sodium and potassium hydroxides are strong alkalis that ionize completely in aqueous solutions to produce negatively charged hydroxide ions, OH^-, and positively charged metallic ions. Calcium oxide, CaO, reacts with water to give a hydroxide which is only slightly soluble in water. A calcium hydroxide solution produces relatively few ions. It is a weak alkali.

$$CaO(s) + H_2O(l) \rightarrow \underset{\text{calcium hydroxide}}{Ca(OH)_2(aq)}$$

$$Ca(OH)_2(aq) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

Another common alkali is aqueous ammonia, formed when ammonia is bubbled through water.

$$\underset{\text{ammonia}}{NH_3(g)} + \underset{\text{water}}{H_2O(l)} \rightarrow \underset{\text{aqueous ammonia}}{NH_3.H_2O(aq)}$$

Aqueous ammonia will ionize to a limited extent in solution to liberate ammonium ions, NH_4^+, and hydroxide ions, OH^-. Hence, aqueous ammonia is also a weak alkali.

$$NH_3H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Neutralization

An acid turns blue litmus red and an alkali turns red litmus blue. If an acid such as hydrochloric acid is gradually added to an alkali such as sodium hydroxide, there will come a stage when the solution becomes completely neutral to litmus (i.e. the litmus becomes purplish), indicating that the solution is neither acidic nor alkaline. Only a salt (in this case, sodium chloride) and water are formed during an acid-alkali reaction or *neutralization*.

acid + **alkali (base)** → **salt** + **water**

e.g. $HCl(aq) + NaOH(aq) \rightarrow Na^+Cl^-(aq) + H_2O(l)$

During the reaction, the hydrogen ion, H^+, from the acid is neutralized by the hydroxide ion, OH^-, from the alkali to form the water molecule, H_2O.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Neutralization is a process in which an acid reacts completely with an appropriate amount of an alkali (or any other base) to produce a salt and water only.

or

Neutralization is the combination of hydrogen ions, H^+, and hydroxide ions, OH^-, to form water molecules, H_2O. A salt is formed at the same time.

Based on this definition of neutralization, a base may be defined as follows:

A base is a substance which will neutralize an acid to yield a salt and water only.

Oxonium ion

Experiments indicate that in an aqueous solution, the hydrogen ion, H^+, becomes associated with a water molecule to form the oxonium ion, H_3O^+. The bonding formed is an example of a coordinate covalent combination.

$$H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$$

During neutralization, an oxonium ion reacts with a hydroxide ion to produce water.

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

Neutralization may also be defined as *the combination of oxonium ions,* H_3O^+, *and hydroxide ions,* OH^-, *to form water molecules,* H_2O. *A salt is formed at the same time.*

The existence of the oxonium ion modifies the earlier definition of an acid. *Thus, an acid is also defined as a substance which in aqueous solution produces oxonium ions,* H_3O^+, *as the only positive ions.* The ionization of acids is represented more correctly as follows:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
$$H_2SO_4(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$$
$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Similarly, the neutralization and acid-trioxocarbonate(IV) reactions may be represented in the ionic form as follows:

Neutralization reactions

$$\underset{\text{hydrochloric acid}}{H_3O^+Cl^-(aq)} + \underset{\text{potassium hydroxide}}{K^+OH^-(aq)} \rightarrow \underset{\text{potassium chloride}}{K^+Cl^-(aq)} + \underset{\text{water}}{2H_2O(l)}$$

$$\underset{\text{tetraoxosulphate(VI) acid}}{(H_3O^+)_2SO_4^{2-}(aq)} + \underset{\text{sodium hydroxide}}{2(Na^+OH^-)(aq)}$$
$$\rightarrow \underset{\text{sodium tetraoxosulphate(VI)}}{(Na^+)_2SO^{2-}{}_4(aq)} + \underset{\text{water}}{4H_2O(l)}$$

Acid-trioxocarbonate(IV) reactions

$$\underset{\text{hydrochloric acid}}{2(H_3O^+Cl^-)(aq)} + \underset{\text{sodium trioxocarbonate(IV)}}{(Na^+)_2CO_3^{2-}(aq)}$$
$$\rightarrow \underset{\text{sodium chloride}}{2(Na^+Cl^-)(aq)} + \underset{\text{water}}{3H_2O(l)} + \underset{\text{carbon(IV oxide}}{CO_{2}(g}$$

Since the sodium ions, Na^+, and the chloride ions, Cl^-, remain dissociated in solution, the reaction ca be simplified as follows:

$$2H_3O^+(aq) + CO_3^{2-}(aq) \rightarrow 3H_2O(l) + CO_2(g)$$

Physical properties of Alkalis

1 Alkalis have a bitter taste.
2 Alkalis are soapy to the touch.
3 Alkalis turn red litmus blue.
4 Concentrated forms of the two caustic alkalis, sodium hydroxide and potassium hydroxide, are corrosive.

Chemical properties of Bases/Alkalis

Reaction with acids

All bases react with acids to form salts and water only.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$
$$MgO(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2O(l)$$
$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$

Reaction with ammonium salts

Alkalis react with ammonium salts, in the presence of heat, to generate ammonia gas. This reaction can be used as a test for alkalis.

$$Ca(OH)_2(aq) + 2NH_4Cl(aq)$$
$$\rightarrow CaCl_2(aq) + 2H_2O(l) + 2NH_3(g$$

$$NaOH(aq) + NH_4NO_3(aq)$$
$$\rightarrow NaNO_3(aq) + H_2O(l) + NH_3(g$$

Table 6.4 *Uses of some alkalis*

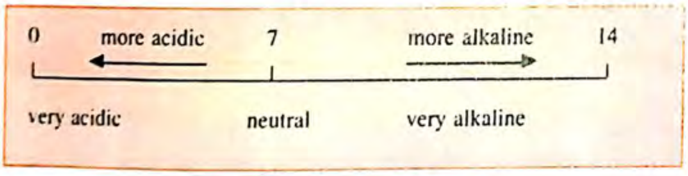
Name	Uses
Sodium hydroxide	• Used in the manufacture of soap, sodium salts and plastics. • Used in petrol refining.
Potassium hydroxide	• Used in the manufacture of liquid soap. • Used in dyeing and electroplating.
Calcium hydroxide	• Used in the manufacture of mortar, cement and plaster. • Used in neutralizing acidic soils.
Magnesium hydroxide	• Used in the manufacture of toothpaste. • Used as a laxative.
Aqueous ammonia	• Used for bleaching cloth. • Used as a detergent.

Uses of Alkalis

Alkalis are important substances used in industries concerned with the manufacture of glass, soap, paper and rayon. Some alkalis are also used to soften hard water.

MEASUREMENT OF ACIDITY AND ALKALINITY

pH scale



The acidity and alkalinity of susbtances are measured using a scale of numbers from 0 to 14, called the *pH scale*. A solution with a pH value of 7 is neutral, i.e. neither acidic nor alkaline. A solution with a pH value less than 7 is acidic, while one with a value more than 7 is alkaline. Acidity increases with decreasing pH values, while alkalinity increases with increasing pH values.

Table 6.5 *Approximate pH values of some substances.*

Substance	pH values
Stomach acid	1.0
Lemons, limes	2.4
Pineapples	3.6
Tomatoes	3.9
Bananas	4.6
Urine	4.8–8.0
Milk	6.5
Plasma	7.4
Sea-water	8.2
Milk of magnesia	10.5

Importance of pH pH values play an important role in our daily life. In our body, an acidic medium is required for digestion of food in the stomach while an alkaline medium is needed for digestion in the small intestine. The pH of normal human blood is about 7.4. For our bodies to function properly, the body fluids must be maintained at the correct pH values. Deviations from these values indicate ill health.

Soil has pH values varying from 4 to 9. Most plants grow well in soils with a pH of 7 to 8. A farmer has to ensure that the soil has the correct pH requirements for the crop he intends to plant. Usually, acidic soils are treated with slaked lime (a base) to neutralize its acidity.

pH values are also important in pharmacy, medicine, water purification, sewage treatment and several other industrial processes.

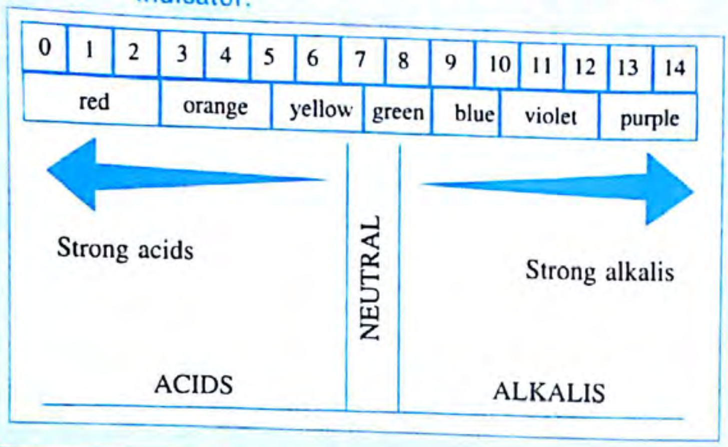
Acid-base Indicators

Acid-base indicators are dyes which change colour according to the pH of the medium (see pages 150 and 239). Litmus is a common indicator which is red in acid and blue in alkali. It changes from red to purple to blue over a pH range of 5.0 to 8.0. Each indicator has its own specific pH range over which it changes colour.

Table 6.6 *Colour changes of some indicators.*

Indicator	*Methyl orange*	*Litmus*	*Phenolphthalein*
pH range for colour change (colour in this range)	3.1–4.6 (Orange)	5.0–8.0 (Purple)	8.3–10.0 (Pale pink)
Acidic medium	Red	Red	Colourless
Alkaline medium	Yellow	Blue	Pink

Fig. 6.1 pH range and colour changes of a universal indicator.



Measuring pH of a solution The pH of a solution may be measured by

- universal indicators, and
- pH meters.

A universal indicator is made up of a mixture of various indicators which work at different pH ranges. By a series of successive colour changes, it can indicate pH values from about 3 to 11. These pH changes can be easily determined by comparing the colour obtained with that of the standards given. This method of measuring the pH is not very accurate.

The pH of a solution can be measured accurately by using a pH meter. It can even measure the pH of very dilute solutions as well as that of coloured and opaque liquids.

Use a universal indicator to compare the pH of 1.0 M solutions of the following:

- Strong acid, e.g. hydrochloric acid
- Weak acid, e.g. ethanoic acid
- Strong alkali, e.g. sodium hydroxide solution
- Weak alkali, e.g. aqueous ammonia
- Pure distilled water

We will notice that strong acids and alkalis have pH values at the extremes of the pH scale, while weak acids and alkalis have pH values close to 7. For pure distilled water, the pH value is 7.

Next, find the pH of some common substances such as lemon juice, milk, well-water, sea-water, saliva and urine.

SALTS

Pillars of salt in the Dead Sea, whose water is nine times saltier than of any ocean.

In everyday language, *salt* refers to common table salt or sodium chloride. In scientific language, *salt* means more than sodium chloride. In fact, sodium chloride is just one of the numerous salts. In science, *salt* refers to a chemical compound formed by replacing the hydrogen ions in an acid with metallic or ammonium ions. It is the only other product formed, besides water, when an acid reacts with a base. Thus, a salt is composed of an aggregation of positively charged metallic or ammonium ions and negatively charged ions. The salt has a net charge of zero since the opposite charges are balanced.

A salt is the compound formed when all or part of the ionizable hydrogen of an acid is replaced by metallic or ammonium ions.

Types of Salts

There are five main types of salts: normal salts, acid salts, basic salts, double salts and complex salts.

Normal salts

Normal salts are formed when all the replaceable hydrogen ions in the acid have been completely replaced by metallic ions.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
$$H_2SO_4(aq) + ZnO(s) \rightarrow ZnSO_4(aq) + H_2O(l)$$

Table 6.7 *Some examples of acids and their corresponding normal salts*

Acid	Replacing metal	Corresponding normal salt
Hydrochloric acid, HCl	Sodium, Na	Sodium chloride, NaCl
Trioxonitrate(V) acid, HNO_3	Potassium, K	Potassium trioxonitrate(V), KNO_3
Tetraoxosulphate(VI) acid, H_2SO_4	Zinc, Zn	Zinc tetraoxosulphate(VI), $ZnSO_4$

Normal salts are neutral to litmus. However, a few normal salts such as sodium trioxocarbonate(IV), aluminium chloride and sodium sulphide will undergo hydrolysis in water to give an acidic or alkaline medium.

Acid salts

Acid salts are formed when the replaceable hydrogen ions in acids are only partially replaced by a metal. They are produced only by acids containing more than one replaceable hydrogen ion. Acids with two replaceable hydrogen ions can form only one acid salt, while acids with three replaceable hydrogen ions can form two different acid salts.

Acid salts result when there is an insufficient supply of metallic ions to replace all the replaceable hydrogen ions in the acid. For example,

$$\underset{}{H_2SO_4(aq)} + KOH(aq) \rightarrow \underset{\text{acid salt}}{KHSO_4(aq)} + H_2O(l)$$

An acid salt still contains replaceable hydrogen ions and has acidic properties, e.g. it will turn blue litmus red. In the presence of excess metallic ions, the remaining replaceable hydrogen ions in the acid become replaced, converting the acid salt to a normal salt.

$$\underset{\text{acid salt}}{KHSO_4(aq)} + \underset{\text{alkali}}{KOH(aq)} \rightarrow \underset{\text{normal salt}}{K_2SO_4(aq)} + \underset{\text{water}}{H_2O(l)}$$

Basic salts

Basic salts contain the hydroxide ion, OH^-. They occur when there is an insufficient supply of acid which is needed for the complete neutralization of the base. Basic salts have the properties of a base. For example, a basic salt will turn red litmus blue and will react with excess acid to form a normal salt and water in the following way.

$$\underset{\text{basic salt}}{Zn(OH)Cl(aq)} + \underset{\text{acid}}{HCl(aq)} \rightarrow \underset{\text{normal salt}}{ZnCl_2(aq)} + \underset{\text{water}}{H_2O(l)}$$

Double salts

Double salts are salts which ionize to produce three different types of ions in solution. Usually two of these are positively charged (metallic or ammonium ions), while the other is negatively charged.

Complex salts

Complex salts contain complex ions, i.e. ions consisting of a charged group of atoms.

- Sodium tetrahydroxozincate(II), and
- potassium hexacyanoferrate(II)

are complex salts which ionize as follows:

$$Na_2Zn(OH)_4(aq) \rightleftharpoons 2Na^+(aq) + [Zn(OH_4]^{2-}(aq)$$
$$K_4Fe(CN)_6(aq) \rightleftharpoons 4K^+(aq) + [Fe(CN)_6]^{4-}(aq)$$

Uses of Salts

Salts are used in the manufacture of many industrial, agricultural and consumer substances like chlorine gas, fertilizers and laxatives. They are also used as food preservatives, drying agents and antifreeze.

Preparation of Salts

Several general methods are available for preparing salts. The method chosen for preparing a particular salt depends largely on

- its solubility in water, and
- its stability to heat.

Preparation of Soluble Salts

Salts that are soluble in water may be prepared by various methods. The salts formed are in aqueous solutions and so must be recovered from these solutions by evaporation or crystallization.

Table 6.8 Some examples of acid, basic and double salts.

Acid	Acid salt	Normal salt
Tetraoxosulphate(VI) acid, H_2SO_4	Sodium hydrogen-tetraoxosulphate(VI), $NaHSO_4$	Sodium tetraoxosulphate(IV), Na_2SO_4
Trioxocarbonate(IV) acid, H_2CO_3	Sodium hydrogen-trioxocarbonate(IV), $NaHCO_3$	Sodium trioxocarbonate(IV), Na_2CO_3
Tetraoxophospate(V) acid, H_3PO_4	Sodium dihydrogen-tetraoxophospate(V), NaH_2PO_4 Sodium hydrogen-tetraoxophospate(V), Na_2HPO_4	Sodium tetraoxophospate(V), Na_3PO_4
Basic hydroxide	**Basic salt**	**Normal salt**
Zinc hydroxide, $Zn(OH)_2$	Zinc chloride hydroxide, $Zn(OH)Cl$	Zinc chloride, $ZnCl_2$
Magnesium hydroxide, $Mg(OH)_2$	Magnesium hydroxide trioxonitrate(V), $Mg(OH)NO_3$	Magnesium trioxonitrate(V), $Mg(NO_3)_2$
Bismuth(III) hydroxide, $Bi(OH)_3$	Bismuth(III) dihydroxide trioxonitrate(V), $Bi(OH)_2NO_3$	Bismuth(III) trioxonitrate(V), $Bi(NO_3)_3$
Double salt	**Positively charged ion**	**Negatively charged ion**
Ammonium iron(II) tetraoxosulphate(VI)-hexahydrate, $(NH_4)_2Fe(SO_4)_2.6H_2O$	Iron(II) ion, Fe^{2+} Ammonium ion, NH_4^+	Tetraoxosulphate(VI) ion, SO_4^{2-}
Potash alum or aluminium potassium tetraoxosulphate(VI)-duodecahydrate, $KAl(SO_4)_2.12H_2O$	Potassium ion, K^+ Aluminium ion, Al^{3+}	Tetraoxosulphate(VI) ion, SO_4^{2-}
Chrome alum or chromium(III) potassium tetraoxosulphate(VI)-dodecahydrate, $KCr(SO_4)_2.12H_2O$	Potassium ion, K^+ Chromium(III) ion, Cr^{3+}	Tetraoxosulphate(VI) ion, SO_4^{2-}

Dilute acid and metal

A salt may be prepared by the direct displacement of the hydrogen ion in an acid by a metal more reactive than hydrogen, e.g. calcium, magnesium, zinc and iron.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$
$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

Alkali and acid

A salt may be prepared by titrating an alkali against an appropriate acid. A suitable indicator is used to determine when the neutralization reaction is complete.

$$KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$$

Sodium chloride is used in the glazing of pottery
overcome porosity

Table 6.9 Salts and their uses.

Name	Uses
Ammonium chloride	• Used in washing powders and as electrolyte in dry cells
Calcium trioxocarbonate(IV)	• Used as a medicine to neutralize acidity in the stomach
Calcium chloride	• Used as an antifreeze
Fused calcium chloride	• Used as a drying agent
Calcium tetraoxosulphate(VI)	• Used for making plaster of Paris
Copper II tetraoxosulphate(VI)	• Used in dyeing and calico printing
Magnesium tetraoxosulphate(VI)	• Used as a laxative
Potassium trioxonitrate(V)	• Used for making gunpowder and matches and as soil fertilizers
Sodium chloride	• Used for preserving food and in glazing pottery
Zinc chloride	• Used in petroleum refining

Table 6.10 Examples of soluble and insoluble salts.

Soluble	Insoluble
All sodium. potassium and ammonium salts.	
All trioxonitrates(V).	
All chlorides except ...	lead II chloride and silver chloride. (Lead II chloride is soluble in hot water.)
All tetraoxosulphates (VI) except ...	lead (II) tetraoxosulphate (VI) and barium tetraoxosulphate (VI). Calcium tetraoxosulphate (VI) is only slightly soluble in water.
Trioxocarbonates(IV) of sodium, potassium and ammonium.	All other trioxocarbonates (IV).

Dilute acid and insoluble base

The dilute acid is heated and the base is added a little t a time, until no more base can dissolve. The excess ase is then filtered off, leaving the salt formed in the olution.

$$H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$$

Dilute acid and trioxocarbonate(IV)

n acid will act on a trioxocarbonate(IV) to produce salt, water and carbon(IV) oxide.

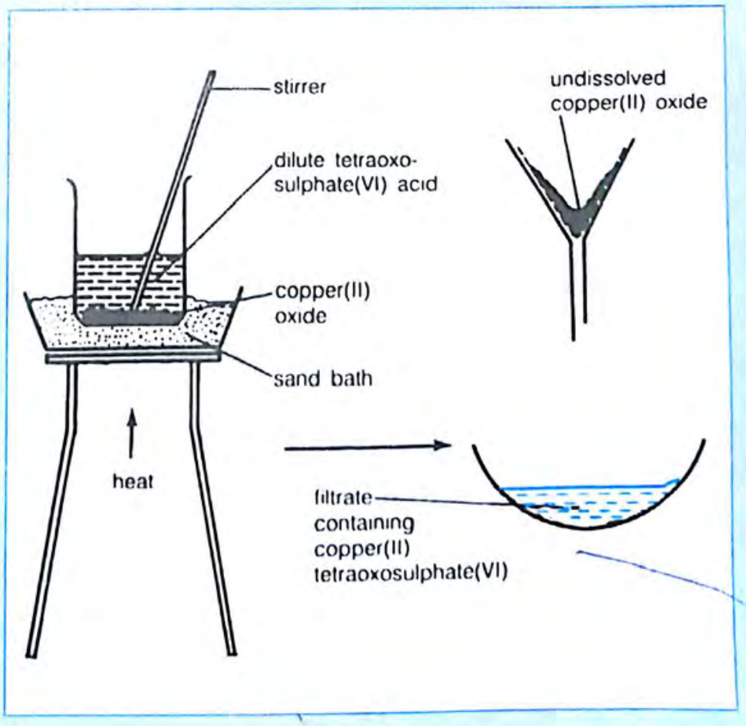
$$_2SO_4(aq) + CuCO_3(s) \rightarrow CuSO_4(aq) + H_2O(l) + CO_2(g)$$

Where the trioxocarbonate(IV) is soluble, it is rated against the acid using a suitable indicator. An soluble trioxocarbonate(IV) is added in excess to the acid and the soluble salt formed is obtained by filtering off the excess trioxocarbonate(IV). This method is not used if the trioxocarbonate(IV) and the salt are both insoluble because the salt formed will precipitate on the unchanged trioxocarbonate(IV) and stop the reaction.

Recovering soluble salts from solution

Heating to dryness This method is used only when the soluble salt can withstand dry heating. Most chlorides, except zinc and iron(III) chlorides, are recovered from solution by this method. The salt solution is usually put in an evaporating dish and heated slowly to dryness to produce the salt in the solid crystalline form.

Fig. 6.2 Preparing copper(II) tetraoxosulphate(VI).



Crystallization This method is used when a salt can be destroyed or decomposed by dry heating. Trioxonitrate(V) and tetraoxosulphate(VI) salts are usually recovered by the crystallization method.

The salt solution is first boiled to drive away some of the water. On cooling the concentrated solution, crystals of the salt will begin to appear in the solution. Sometimes, a speck of the salt in question is added to the solution as a seed to induce crystallization. Scratching the inside of the container with a glass rod may also induce crystallization of the salt. The crystals of the salts obtained can be washed with distilled water and then dried between filter papers.

Preparation of Insoluble Salts

Salts which are insoluble in water can be prepared in the laboratory by the following methods.

Double decomposition

In this method, usually two soluble compounds, one containing the metallic radical and the other the acidic radical of the required insoluble salt, are mixed together. During double decomposition, there is an exchange of ionic radicals resulting in the precipitatio of the required salt, which is then obtained by filtratio

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(a$$

soluble	soluble	insoluble white precipitate	soluble

$$BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(a$$

soluble	soluble	insoluble white precipitate	soluble

Other salts prepared by this method includ lead(II) chloride, lead(II) iodide and calciu trioxocarbonate(IV).

Combination of constituent elements

Some metallic salts, such as chlorides and sulphides, may be prepared by the direct combination of the elements which make up the salt. This method of salt preparation is confined to binary salts, i.e. salts made up of two elements only.

$$Fe(s) + S(s) \rightarrow FeS(s)$$
$$2Fe(s) + 3Cl_2(s) \rightarrow 2FeCl_3(s)$$

Experiment 6.1 To prepare copper(II) tetraoxosulphate(VI)-pentahydrate crystals by the addition of dilute tetraoxosulphate(VI) acid to copper(II) oxide (an insoluble base).

Method Place about 40 cm³ of tetraoxosulphate(VI) acid, which is about twice the concentration of bench tetraoxosulphate(VI) acid, in a beaker and heat it. Add some black copper(II) oxide powder to the acid, stirring gently all the time with a glass rod, until no more copper(II)oxide dissolves. Filter the mixture and collect the residue.

Heat the filtrate on a sand-bath until it is reduced to about one-fifth of its original volume. Place the beaker in cold water to allow the solution to cool and crystallize. If no crystals form, add a few crystals of blue copper(II) tetraoxosulphate(VI) to the solution to serve as seeds. Filter, wash and dry the crystals formed.

Result A blue solution of copper(II) tetraoxosulphate(VI) is formed when the oxide dissolves in the acid. On concentrating and cooling this solution, blue crystals of copper(II) tetraoxosulphate(VI)-pentahydrate are formed.

$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$
$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$$

Conclusion Blue copper(II) tetraoxosulphate(VI)-pentahydrate can be prepared by the action of dilute tetraoxosulphate(VI) acid on the insoluble base, copper(II) oxide.

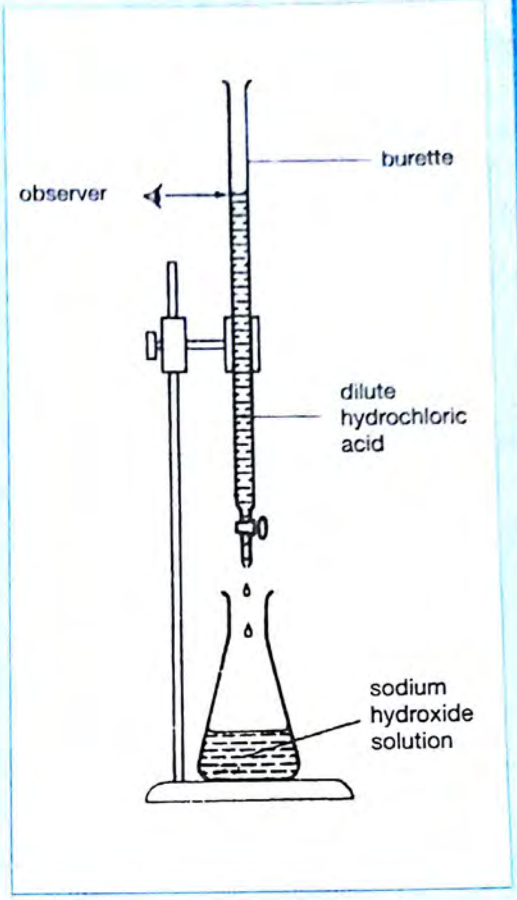
Experiment 6.2 To prepare crystals of sodium chloride (common salt) by neutralization.

Method Put about 25 cm^3 of bench sodium hydroxide solution into a conical flask. Add a few drops of litmus solution into the flask. What do you notice? Fill a burette with dilute hydrochloric acid solution and read the acid level. Now, run the acid slowly into the alkali in the flask, shaking it frequently to obtain a homogeneous solution, until the litmus solution just turns purple. Read the new acid level and calculate the exact volume of acid needed to neutralize the known volume of the alkali. This will enable you to repeat the experiment to obtain a neutral solution of sodium chloride which is free of litmus. Now, evaporate the neutral solution to dryness on a sand-bath. Wash the crystals two or three times with a small amount of cold distilled water and then dry them between filter papers.

Result Sodium chloride solution is left in the flask after neutralization is completed. It is evaporated to obtain white crystals of salt.

Conclusion Sodium chloride can be prepared by neutralizing sodium hydroxide solution with hydrochloric acid.

Fig. 6.3 Preparing sodium chloride by neutralization.



Experiment 6.3 To prepare a sample of insoluble lead(II) chloride by double decomposition.

Method Add lead(II) trioxonitrate(V) solution to sodium chloride solution and stir with a glass rod. Filter the resultant solution and wash the residue on the filter paper with cold distilled water before drying it.

Result A white precipitate of lead(II) chloride is obtained.

Conclusion Lead(II) chloride can be precipitated by mixing solutions of lead(II) trioxonitrate(V) and sodium chloride together.

WATER OF CRYSTALLIZATION

Many salts combine chemically with water to form *hydrates*. For example, copper(II) tetraoxosulphate(VI) combines with water to form a hydrate in the following way:

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$$

The five molecules of water associated with a molecule of copper(II) tetraoxosulphate(VI) are known as *water of crystallization*. The water molecules are loosely bound to the salt molecule and are easily dissociated from it by heating. The residual salt that is left behind on heating a hydrate is said to be *anhydrous* and *amorphous* (shapeless). This implies that water provides colour and shapes to such salts.

EXAMPLE

7.47 g of blue copper(II) tetraoxosulphate(VI) crystals, $CuSO_4.5H_2O$, were heated in a crucible to a constan mass, first at a temperature of 110 °C, and then at 130 °C. The residue that was obtained at 110 °C weighe 5.31 g and that obtained at 130 °C weighed 4.77 g. Calculate the stages of dehydration reached at 110 °C an 130°C respectively.

Mass of blue $CuSO_4.5H_2O$ crystals = 7.47 g
Mass of dehydrated crystals at 110 °C = 5.31 g
∴ mass of H_2O driven off at 110 °C = (7.47–5.31) g
= 2.16 g

If the number of molecules of H_2O driven off is x, then the mass of x molecules of H_2O = 2.16 g

Mass of the dehydrated crystals at 130 °C = 4.77 g
∴ mass of H_2O driven off at 130 °C = (7.47–4.77) g
= 2.70 g

If the number of molecules of H_2O driven off is y, then the mass of y molecules of H_2O = 2.70 g

Dehydration reached at 110 °C

Mass of H_2O driven off at 110 °C = 2.16 g

$$\frac{xH_2O}{CuSO_4.5H_2O} = \frac{2.16}{7.47}$$
$$\frac{18x}{249.5} = \frac{2.16}{7.47}$$
$$x = \frac{2.16 \times 249.5}{7.47 \times 18}$$
$$= 4.008$$

∴ number of molecules of H_2O driven off = 4
∴ copper(II) tetraoxosulphate(VI) exists as *$CuSO_4.H_2O$ at 110 °C.*

Dehydration reached at 130 °C

Mass of H_2O dnven off at 130 °C = 2.70 g

$$\frac{yH_2O}{CuSO_4.5H_2O} = \frac{2.70}{7.47}$$
$$\frac{18y}{249.5} = \frac{2.70}{7.47}$$
$$y = \frac{2.70 \times 249.5}{7.47 \times 18}$$
$$= 5.01$$

∴ number of molecules of H_2O driven off = 5
copper(II) tetraoxosulphate(VI) exists as $CuSO_4$ at 130 °C

Table 6.11 Examples of salts with and without water of crystallization.

Salts with water of crystallization	Salts without water of crystallization
Blue copper(II) tetraoxosulphate(VI)-pentahydrate, $CuSO_4.5H_2O$	Sodium chloride, NaCl
Iron(II) tetraoxosulphate(VI)-heptahydrate, $FeSO_4.7H_2O$	Potassium trioxonitrate(V), KNO_3
Zinc tetraoxosulphate(VI)-heptahydrate, $ZnSO_4.7H_2O$	Potassium tetraoxomanganate(VII), $KMnO_4$
Sodium trioxocarbonate(IV)-decahydrate, $Na_2CO_3.10H_2O$	Ammonium tetraoxosulphate(VI), $(NH_4)_2SO$
Copper(II) trioxonitrate(V)-trihydrate, $Cu(NO_3)_2.3H_2O$	Potassium tetraoxosulphate(VI), K_2SO_4
Magnesium tetraoxosulphate(VI)-heptahydrate, $MgSO_4.7H_2O$	Lead(II) trioxonitrate(V), $Pb(NO_3)_2$
Zinc trioxonitrate(V)-hexahydrate, $Zn(NO_3)_2.6H_2O$	Silver trioxonitrate(V), $AgNO_3$

Experiment 6.4 To find the water of crystallization of copper(II) tetraoxosulphate(VI) crystals.

Method Weigh a clean dry crucible with its lid. Place a few grams of blue copper(II) tetraoxosulphate(VI) crystals in it and weigh again. Heat the crucible and its contents to drive away any water of crystallization. Cool the anhydrous salt in a desiccator. Weigh the whole crucible together with the lid and the contents. Heat again to make sure that all the water of crystallization has been driven away, then cool as before and weigh again. Repeat the heating, cooling and weighing process until a constant mass is obtained, indicating that there is no more water of crystallization in the salt.

Calculation

Mass of hydrated copper(II) tetraoxosulphate(VI) $= x$ g
Mass of anhydrous copper(II) tetraoxosulphate(VI) residue $= y$ g
Mass of water driven away $= z$ g

Formula of the anhydrous copper(II) tetraoxosulphate(VI) is $CuSO_4$.

Formula of the hydrated copper(II) tetraoxosulphate(VI) is $CuSO_4.nH_2O$, where n = number of molecules of water of crystallization.

Mass of $CuSO_4$ $= x$ g
Mass of nH_2O $= z$ g

$$\therefore \quad \frac{nH_2O}{CuSO_4} = \frac{z}{x}$$

Molar mass of $CuSO_4$ = 159.5 g
Molar mass of nH_2O = $18n$ g

$$\therefore \quad \frac{18n}{159.5} = \frac{z}{x}$$

n can now be found by solving the equation.

Conclusion The number of molecules of water of crystallization in the hydrated copper(II) tetraoxosulphate(VI) is obtained by calculations based on the mass difference between the hydrated and the anhydrous forms of the salt.

Hydrated salts have a definite chemical composition, i.e. a definite number of water molecules are always associated with one formula mass of a given hydrated salt.

Hydrates can be crystallized out of solution by cooling the saturated solutions of the salts. There are also some salts which crystallize out without any water of hydration. Thus, although all hydrates are crystalline, not all crystalline salts are hydrates.

EFFLORESCENT, DELIQUESCENT AND HYGROSCOPIC SUBSTANCES

When certain compounds are exposed to air, they either lose their water of crystallization or they absorb moisture from their surroundings. The terms efflorescent, deliquescent and hygroscopic are used to describe such compounds.

Get the following substances: pellets of sodium hydroxide, washing soda crystals (from an airtight container), quicklime and concentrated tetraoxosulphate(VI) acid. Place small amounts of each substance on a watch glass and note their appearances carefully. Leave the substances in the open air for some time. Then note any changes in their appearances.

Efflorescence

Some crystalline salts will lose part or all of their water of crystallization when they are exposed to the atmosphere to form a lower dehydrate or the anhydrous salt. This phenomenon is known as *efflorescence* and the salt is said to be *efflorescent*. An example is the washing soda molecule which loses nine out of its ten molecules of water of crystallization when exposed to the atmosphere.

$$Na_2CO_3.10H_2O(s) \rightarrow Na_2CO_3.H_2O(s) + 9H_2O(g)$$

Deliquescence

Some compounds tend to absorb a large amount of water on exposure to the atmosphere so that they eventually turn into solutions. This phenomenon is known as *deliquescence* and the substances are said to be *deliquescent*. Examples of these substances are

- sodium hydroxide,
- iron(III) chloride,
- potassium hydroxide,
- calcium chloride,
- magnesium chloride, and
- phosphorus(V) oxide.

Hygroscopy

Hygroscopic substances also absorb moisture on exposure to the atmosphere. If they are solids, they will not form solutions but merely become sticky or moist. A hygroscopic liquid like concentrated tetraoxosulphate(VI) acid will absorb water from the air, usually diluting itself up to about three times its original volume. Other examples of hygroscopic substances include

- sodium trioxonitrate(V),
- copper(II) oxide, and
- quicklime.

Hygroscopic substances are commonly employed as drying agents in the laboratory.

Drying agents

Drying agents are substances that have a strong affinity for moisture or water. They may be either hygroscopic or deliquescent. They are usually used to dry gases in the laboratory. They are also commonly used in desiccators. A drying agent cannot be used if it reacts with the substance to be dried. For example, concentrated tetraoxosulphate(VI) acid cannot be used to dry ammonia since they react to form ammonium tetraoxosulphate(VI).

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

Table 6.12 Common drying agents

Drying agents	Gases
Concentrated tetraoxosulphate(VI) acid	All gases except ammonia and hydrogen sulphide.
Fused calcium chloride	All gases except ammonia
Calcium oxide (quicklime)	Suitable for ammonia in particular.
Phosphorus(V) oxide	All gases except ammonia
Silica gel	All gases.

IONIC REACTIONS AND EQUATIONS

Compounds such as acids, alkalis, salts and trioxocarbonates(IV) that dissolve in water tend to exist in solution as ions. These ions are in constant motion. Reactions between these compounds may occur when the individual positive and negative ions collide with one another. Most reactions involving these compounds are ionic reactions, and can be represented in the ionic form.

For the neutralization of hydrochloric acid with sodium hydroxide, the molecular equation for the reaction is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

In the ionic form, the equation for the reaction is as follows:

$$H^+Cl^-(aq) + Na^+OH^-(aq) \rightarrow Na^+Cl^-(aq) + H_2O(l)$$

Since the Na^+ and Cl^- ions appear on both sides of the equation, they are cancelled out, so that the ionic equation for the reaction becomes:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

For the neutralization of calcium hydroxide with trioxonitrate(V) acid, we have,

$$Ca^{2+}2OH^-(aq) + 2H^+2NO_3^-(aq)$$
$$\rightarrow Ca^{2+}2NO_3^-(aq) + 2H_2O(l)$$

or simply, $2OH^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l)$

These reactions represent the essential feature of neutralization which is the formation of unionized molecules of water from hydrogen and hydroxide ions. Thus, ionic equations provide a better understanding of ionic reactions.

Rules for writing ionic equations

The following arbitrary rules should be observed when writing ionic equations.

1. Do not break up gases, insoluble substances and weakly ionized substances, like water or weak acids and bases, into ions but represent them as molecules.
2. Cancel out of the equation, any ions which are exactly the same on both sides.
3. When balancing ionic equations, the number of atoms of each element and the net charge must be the same on both sides of the equation.

Equation 1

$$Zn(s) + Cu^{2+}SO_4^{2-}(aq) \rightarrow Zn^{2+}SO_4^{2-}(aq) + Cu(s)$$

or simply, $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Equation 2

$$Ag^+NO_3^-(aq) + Na^+Cl^-(aq) \rightarrow AgCl(s) + Na^+NO_3^-(aq)$$

or simply, $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

In the reaction in *equation* 2, the association of silver ions, Ag^+, and chloride ions, Cl^-, produces an insoluble substance, silver chloride, AgCl, which precipitates out of the solution.

The net charges of the ions on both sides of the equation are +2 for *equation 1* and 0 for *equation* 2.

Water as a reactant

Pure water, which often participates in chemical reactions, does not exist completely as molecules but is ionized into oxonium ions, H_3O^+, and hydroxide ions, OH^-, to a limited extent. It is these ions which often take part in ionic reactions. The ionization of water can be written as follows:

$$2H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$$

or simply, $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$

CONDUCTANCE OF ACIDS, BASES AND SALTS

Most acids, bases and salts are electrolytes. They tend to exist in solution as ions, which are the carriers of electricity. Not all electrolytes, however, can conduct electricity to the same extent. This is because different electrolytes have different degrees of ionization. Strong electrolytes, which include all the strong acids and alkalis as well as most salts, ionize completely or almost completely in solution to produce high concentration of ions. These compounds have much higher conductance than weak electrolytes, which ionize only slightly in solution, producing very low concentration of ions.

Pure distilled water, the most common solvent for acids, bases and salts, is a weak electrolyte as its degree of ionization is very low. For every molecule of water that is ionized to give one hydrogen ion, H^+, and one hydroxide ion, OH^-, there are 6×10^8 molecules of water that are not ionized. If by electrical or chemical action, the hydrogen or hydroxide ions are removed, more water molecules can ionize. So, although the hydrogen and hydroxide ion concentrations in pure water are very small, water has the capacity to yield more of these ions. Such a situation arises when water is acidified with a few drops of tetraoxosulphate(VI) acid. Thus, acidified water exhibits a higher conductance than pure water.

Experiment 6.5 To compare the conductance of 1.0 M solutions of some electrolytes.

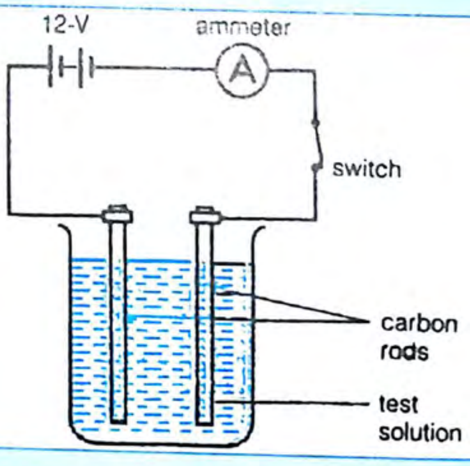
Requirements Beakers, 12-volt lead accumulator, ammeter, two carbon rods, copper wires, a switch and the following 1.0 M solutions of various compounds.

Strong acids	(i) Trioxonitrate(V) (ii) Hydrochloric acid	63 g dm^{-3} 36.5 g dm^{-3}
Weak acids	(i) Ethanoic acid (ii) Tetraoxophosphate(V) acid	60 g dm^{-3} 98 g dm^{-3}
Weak alkalis	(i) Calcium hydroxide solution (lime water) (ii) Aqueous ammonia	74 g dm^{-3} 35 g dm^{-3}
Highly ionized salts	(i) Sodium chloride (ii) Potassium trioxonitrate(V)	58.5 g dm^{-3} 101 g dm^{-3}
Weakly ionized salts	(i) Ammonium chloride (ii) Magnesium tetraoxosulphate(VI)	53.5 g dm^{-3} 120 g dm^{-3}
Pure distilled water		
Acidified distilled water	Distilled water with a few drops of tetraoxosulphate(VI) acid.	

Method Prepare the above solutions by dissolving each of the specified masses of the solutes in 1 dm^3 of distilled water. Then place 100 cm^3 of each solution in a beaker.

Using copper wires, connect the two carbon rods in series with the lead accumulator, the ammeter and the switch. Partially immerse the two carbon rods (which act as electrodes) into the solution to be tested and close the switch. If a current flows across the solution between the two electrodes, the ammeter will show a reading. A higher ammeter reading would mean that more current is passing through due to the greater conductance of the solution used. Thus, the conductance of the various solutions is reflected by the ammeter reading.

Fig. 6.4 Testing the conductance of some electrolytes.



Result Record your readings in the table below.

Electrolyte	Ammeter reading (Conductance)

Conclusion The strong electrolytes, i.e. the strong acids and alkalis, the highly ionized salts and the acidified distilled water have a much higher conductance than the other solutions which are weak electrolytes.

SUMMARY

- An acid is a substance which produces hydrogen ions, H^+, as the only positively charged ion in aqueous solution. Strong and weak acids differ in the concentration of hydrogen ions they can produce in solution.

- The basicity of an acid is the number of replaceable hydrogen ions, H^+, in one molecule of the acid.

- Acids
  (a) taste sour, turn blue litmus red and are corrosive when they are concentrated,
  (b) react with most metals to liberate hydrogen,
  (c) neutralize bases, and
  (d) release carbon(IV) oxide from trioxocarbonate(IV) and hydrogen trioxocarbonate(IV).

- A base is a substance which will neutralize an acid to give a salt and water only.

- An alkali is a soluble basic hydroxide. In aqueous solution, an alkali produces negatively charged hydroxide ions, OH^-.

- Alkalis
  (a) taste bitter, turn red litmus blue, are soapy and corrosive when concentrated,
  (b) neutralize acids, and
  (c) release ammonia gas from ammonium salts.

- Neutralization is a process in which an acid reacts completely with an appropriate amount of an alkali (or any other base) to produce a salt and water only.

- The pH scale with units ranging from 0 to 14 measures the acidity and alkalinity of substances. A neutral solution has a pH of 7. Acidic solutions have pH values less than 7, while alkaline solutions have values greater than 7.

- Indicators are compounds which change colour in accordance with the pH of the medium.

- A salt is the compound formed when all or part of the ionizable hydrogen of an acid is replaced by metallic or ammonium ions.

- Salts which combine chemically with water are said to be hydrated. For a given hydrated salt, a definite number of molecules of water, known as water of crystallization, is associated with one formula mass of the salt.

- Efflorescent compounds lose their water of crystallization to the surroundings. Hygroscopic and deliquescent compounds absorb moisture from their surroundings. While hygroscopic compounds absorb water to become sticky or moist, deliquescent compounds absorb large amounts of water to become solutions. Drying agents may be either hygroscopic or deliquescent.

- Soluble salts may be prepared by
  (a) action of dilute acid on a metal,
  (b) neutralization of an alkali by an acid,
  (c) action of a dilute acid on an insoluble base, and
  (d) action of a dilute acid on a trioxocarbo-nate(IV).
  Salts are then recovered from solution by evaporation or crystallization.

- Insoluble salts are formed by
  (a) double decomposition, and
  (b) direct combination of two elements.

- All acids, bases and salts are electrolytes as they tend to exist in solution as ions, which are the carriers of electricity.

EXERCISES

1. What is common to both hydrochloric acid and trioxonitrate V acid?
- A Both are used for fountain experiment.
- B Both are monobasic.
- C Both are used to prepare hydrogen from zinc granules.
- D Both attack rubber.

2. A strong dilute H_2SO_4 ionizes
- A slowly but contains more water than acid.
- B fast but contains more water than acid.
- C fast but contains more acid than water.
- D slowly but contains more acid than water.

3. Acid anhydride is the same as
- A dry acid.
- B acid that increase its volume when exposed to air.
- C acid made by drying the reactants first.
- D acid made from oxides of non-metals.

4. Drop the odd one out from $Cu(OH)_2$, $Al(OH)_3$, $Mg(OH)_2$ and $Zn(OH)_2$.
- A $Cu(OH)_2$
- B $Mg(OH)_2$
- C $Zn(OH)_2$
- D $Al(OH)_3$

5. $H^+_{aq} + OH^-_{aq} \rightarrow H_2O\ (l)$
The above equation represents
- A hydrolysis.
- B hydration.
- C neutralization.
- D electron affinity.

6. An oxonium ion is
- A H_3O
- B H_3O^+
- C H_3O^-
- D $2[H^+ OH^-]$

7. pH of a 0.001 m acid is
- A 2
- B 3
- C 4
- D 1

8. A solution whose pH cannot be easily alter due to accidental addition of acid or base is call
- A plasma.
- B annotated solution.
- C buffer solution.
- D deionized water.

9. The main difference between the salt in the De Sea and salt in the school lab is that
- A salt in the Dead Sea is saltier.
- B salt in the Dead Sea is iodized while that o the lab is uniodized.
- C salt in the Dead Sea is sodium chloride whil that of the lab has its hydrogen replaced.
- D salt in the Dead Sea is sodium chloride whil salt in the lab is either soluble or insolubl in water.

10. These are types of salts except
- A normal salt, acid salt, and basic salt, comple salt and double salt.
- B normal salt, double salt, acid salt.
- C complex salt, basic salt, acid salt, hydrolyse salts.
- D double salt, basic salt, complex salt.

11. Which of these is not recovered through dr heating (evaporation).
- A $NaCl3^2$
- B $NH_4\ NO_3$
- C $CuHSO_4$
- D $NaHCO_3$

12. Water in crystalline salts provides
- A hydrated bonds and colour.
- B colour and solubility base.
- C colour and shape.
- D shape and crystal lattice.

13. Which of these is not a hygroscopic salt?
A Calcium oxide
B Magnesium chloride
C Copper II oxide
D Sodium trioxonitrate V

14. All common gases are dried using P_2O_5 except
A NO_2 B NH_3
C SO_2 D H_2S

15. Which of the following substances is not a salt?
A Sodium hydrogentrioxosulphate(IV)
B Lead(II) trioxonitrate(V)
C Basic zinc chloride
D Aluminium oxide
E Washing soda

16. Which pH value indicates a basic solution?
A −1   C 3   E 9
B 0   D 7

17. All of the following acids are monobasic except
A hydrofluoric acid.
B hydrochloric acid.
C trioxonitrate(V) acid.
D ethanoic acid.
E tetraoxosulphate(VI) acid.

18. Sodium hydroxide is added drop by drop to some hydrochloric acid in a beaker. Which of the following occurs in the beaker?
A The pH of the solution decreases.
B The concentration of hydrogen ions increases.
C The concentration of hydroxide ions increases.
D The solution turns pink.
E Sodium chloride crystals form.

19. (a) Define an acid. Give the natural sources of the following organic acids.
(i) Lactic acid
(ii) Ascorbic acid
(iii) Amino acid
(b) How would you prove that a given colourless liquid is an acid?
(c) Sulphur(IV) oxide is described as an acid anhydride. Elaborate on this statement.
(d) Give three uses of any acid you know.

20. (a) Give the definition of a base or an alkali.
(b) Using equations, show the formation of hydroxonium ions in an aqueous solution of tetraoxosulphate(VI) acid.
(c) Define the term neutralization reaction. Using an ionic equation, show how an aqueous solution of hydrochloric acid containing the hydroxonium ion neutralizes a potassium hydroxide solution.
(d) How would you prove that sodium hydroxide is a base without using litmus paper to test? Give the equation for the reaction.

21. (a) Define a salt. Potash alum is a double salt. Explain this statement using the chemical formula of the alum.
(b) The basicity of tetraoxosulphate(VI) acid is 2. Explain this statement with an equation showing the reaction between the acid and potassium hydroxide.

22. (a) Give four general methods of preparing salts. Give equations for the examples.
(b) What product is always obtained in the neutralization reaction?
(c) How would you prepare pure dry crystals of potassium trioxonitrate(V)?

23. (a) Explain and give an example each of
(i) Hygroscopic substance
(ii) Efflorescent substance
(iii) Deliquescent substance
(b) What substances are used in desiccators?

24. How would you determine experimentally the water of crystallization of a sample of hydrated copper(II) tetraoxosulphate(VI)? How would you do the calculation?

25. The following pairs of solutions are mixed. Which mixtures produce a precipitate?
(a) Calcium chloride and potassium trioxocarbonate(IV).
(b) Sodium hydroxide and hydrochloric acid.
(c) Sodium chloride and lead trioxonitrate(V).
(d) Silver trioxonitrate(V) and hydrochloric acid.
(e) Aqueous ammonia and sodium tetraoxosulphate(VI).

7 CARBON AND ITS COMPOUNDS

CARBON

Carbon is a non-metal known to people for a long time under the names charcoal, soot and diamond. It occurs naturally as *diamond* and *graphite*. Carbon also occurs in an impure form as *coal* and in the combined state as *petroleum*, *wood* and *natural gases*. These carbon compounds form an important source of fuels. They are burnt to release heat and light, which may be converted to other forms of energy. Other sources that contain carbon are mineral deposits of metallic trioxocarbonates(IV), especially calcium trioxocarbonate(IV) (*limestone*) and magnesium trioxocarbonate(IV) (*dolomite*), and the carbon(IV) oxide in the air and water around us. Carbon is also an essential constituent of all living things.

Carbon is naturally present in many compounds. In addition, new useful carbon compounds are being synthesized all the time. Thus, their numbers are continually increasing.

The chemistry of carbon compounds is known as *organic chemistry*. However, the study of some of its compounds such as the oxides, sulphides, metallic carbides, trioxocarbonates(IV) and hydrogentrioxocarbonates(IV), is usually included in *inorganic chemistry*. In this chapter, we shall confine our study to that of carbon itself and its inorganic compounds.

Allotropes of Carbon

The ability of carbon to exist in various forms in the same physical state is known as *allotropy*. Diamond and graphite are two allotropic forms of crystalline carbon. The others like coal, coke, charcoal, lampblack, sugar charcoal and animal charcoal are amorphous or non-crystalline forms of carbon.

Diamond

Diamonds are found naturally in Africa, Brazil, India, the Republic of Guyana, Siberia and Venezuela. The world's main supply of diamonds comes from south-western Africa.

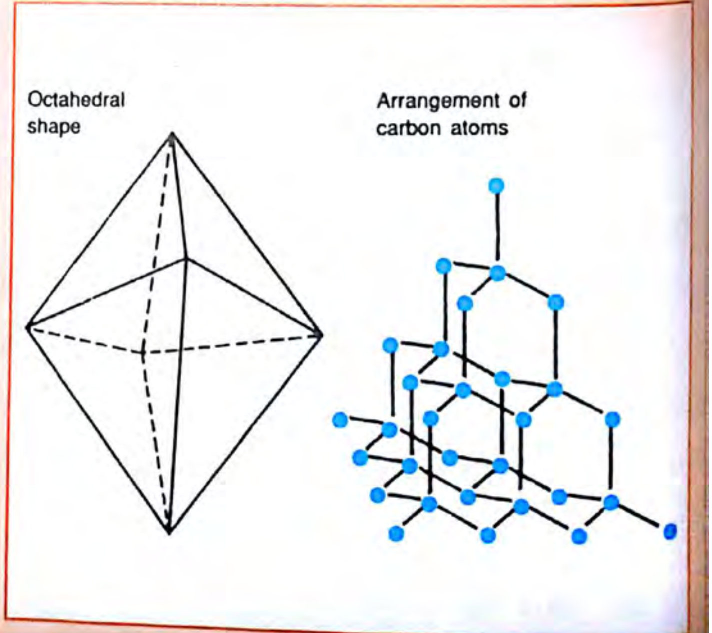
Diamonds are the purest form of naturally occurring carbon. They are found as colourless lustreless solids which can be transformed into brilliant gems. Sometimes, they are coloured by slight traces of impurities.

The diamond crystal is octahedral in shape. It is actually a giant molecule in which the carbon atoms are closely packed and held together by strong covalent bonds.

Properties

The diamond is the hardest substance known. As a result only a diamond can cut a diamond. It has a high melting point. It is very dense and resistant to high temperatures and chemical attack. It is a non-conductor of electricity because there are no free valence electrons in the diamond crystal, as all of them are used in bond formation.

Fig. 7.1 Structure of the diamond crystal.



Uses

Since diamonds are dense and hard, they are used industrially in drills for mining, as abrasives to sharpen very hard tools, and for cutting glass and metals. They are also used as pivot supports in precision instruments and as dies for drawing wires. Its high refractive index and dispersion power give it a sparkling brilliance when it is cut and polished, making it valuable as jewellery.

Artificial diamond

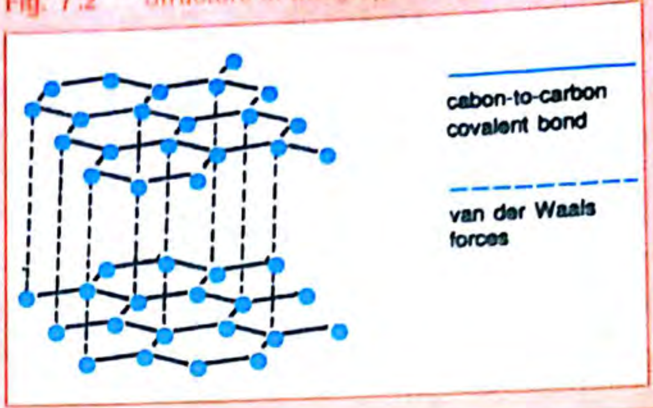
Artificial diamonds, suitable only for certain industrial applications, became commercially available in 1957. They are made by subjecting graphite to very high pressures and temperature for several hours, in the presence of a catalyst such as nickel or rhodium.

Graphite

Graphite occurs naturally as *plumbago*, an opaque black solid. It is mined mainly in Austria, China, West Germany, Republic of Korea, Madagascar, Mexico, Siberia and Sri Lanka. Like diamond, it is probably formed by the action of volcanic heat on coal deposits.

The carbon atoms in graphite form flat layers. These layers are arranged in parallel, one above the other, to form a crystal lattice.

Fig. 7.2 Structure of the graphite crystal



Properties

Graphite is soft and flakes easily because of its layered crystalline structure. It has a high melting point but is less dense than diamond. It is relatively inert chemically but can be oxidized to six-carbon atom organic compounds under suitable conditions. Unlike diamond, graphite is a good conductor of electricity because of the presence of mobile electrons in the crystal lattice. Mobile electrons exist since only three of the four valence electrons of each carbon atom in the graphite crystal are involved in bond formation.

Uses

Graphite is an excellent dry lubricant. This is because its layered structure allows one layer to slide over another easily. Unlike oil, it is non-volatile and not sticky. It is usually used on bicycle chains and for the bearings of some motor cars. Sometimes, it is mixed with oil to form a high-temperature lubricant. As graphite is a good conductor of electricity and relatively inert, it is often used as electrodes in

Table 7.1 Properties of diamond and graphite.

	Diamond	Graphite
Appearance	Colourless transparent solid; sparkles when cut and polished.	Black opaque solid, with a metallic lustre.
Crystalline structure	Octahedral crystal; 3-dimensional lattice based on tetrahedral units, with no planes of weakness.	Basic 2-dimensional hexagonal units forming parallel layers; layers are held together by weak van der Waals forces, and can easily slide over one another.
Density	3.5 g cm^{-3}	2.3 g cm^{-3}
Hardness	Hardest natural substance known.	One of the softest minerals; marks paper.
Electrical conductivity	Non-conductor.	Good conductor.
Chemical activity	Very inert, but burns in air at about 900 °C to form carbon(IV) oxide, and combines with fluorine at about 700 °C.	More reactive; burns at about 700 °C to form carbon(IV) oxide; reacts with oxidizing agents to form oxides; reacts with fluorine and tetraoxosulphate(VI) acid.

electroplating and in dry cells. A non-conductor may be made conductive by coating it with graphite.

Since graphite can withstand high temperatures, it is used to line crucibles used for making high-grade steel and other alloys. A mixture of graphite and clay is used as 'lead' in pencils. Graphite is used as a black pigment in paint, and as a neutron moderator in atomic piles.

Industrial preparation

There is a great demand for graphite. It is produced industrially by heating coke in an electric furnace to a very high temperature for about 20 to 30 hours. Air is excluded by covering the coke with sand. The graphite produced is very pure and free from grit. This process, called the *Acheson process*, requires a lot of energy, and is only feasible in countries with cheap electricity.

Amorphous Carbon

From X-ray studies, we know that amorphous forms of carbon consist of minute crystals of graphite bound together by impurities. Thus, they are not considered as true allotropes of carbon. With the exception of coal, which is mined from natural deposits, the other amorphous forms can be prepared in various ways.

Coal

Coal was formed from the vegetation of the *Carboniferous Era* which was protected from complete decay by overlying water-washed earth deposits. Decomposition occurred gradually under pressure and in the absence of air. Carbon(IV) oxide, methane and water were liberated, leaving behind a material that contained a very high percentage of carbon. During this process of *carbonization*, the vegetable material was converted in stages into *peat*, *lignite* (or brown coal), *bituminous* (or soft) *coal*, and, finally, *anthracite* (or hard coal) which is about 95% pure carbon. Impurities present may include nitrogen, sulphur and phosphorus.

Coal is used mainly as a fuel to generate power for steam engines, factories and electric plants. It is also used for making various chemicals.

In Nigeria, large amounts of coal are mined in Udi and the Milken hills of Enugu State every year. There are also extensive lignite deposits in Onitsha and Asaba.

Coal being transported in wagons in a coal mine.

Coke

Coke is obtained by heating bituminous coal to very high temperatures (about 1300 °C) in the absence of air to drive away all the volatile constituents. This process is known as the *destructive distillation* of coal. Coke is used mainly as a fuel. It burns with practically no smoke and leaves very little residue. It is a very important industrial reducing agent, and is used in the extraction of metals, especially iron, from their ores. It is also used in the production of gaseous fuels, like water gas and producer gas and for the manufacture of graphite, calcium carbide, silicon carbide and carbon(IV) sulphide.

Carbon black (soot)

Carbon black or soot is finely divided carbon particles produced by burning carbonaceous materials in a limited supply of air. *Lamp-black* is obtained from vegetable or lamp oils, while *carbon black* is obtained from coal gas, natural gas or fuel oils. Carbon black is used in manufacturing rubber tyres, black shoe polish, printer's ink, typewriting ribbons and carbon paper.

Charcoal

Charcoal can be made by heating wood, nut shells, bones, sugar and even blood.

Wood charcoal is the most common. It is prepared by heating wood in a limited supply of air. It contains impurities such as *sulphur*.

Sugar charcoal is formed when sugar is dehydrated (i.e. the hydrogen and oxygen it contains are removed in the form of water) either by burning

Experiment 7.1 To investigate the ability of wood charcoal to adsorb gases.

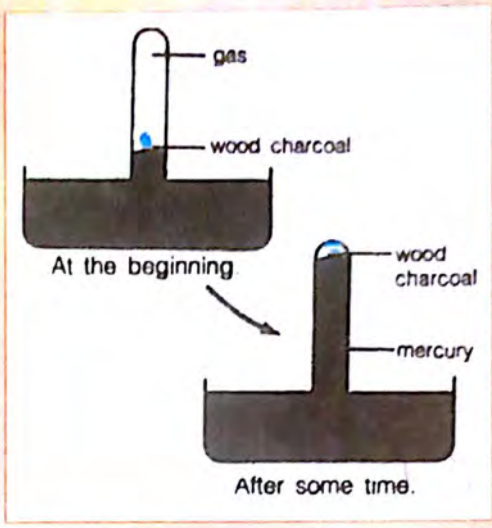
Method Fill a test-tube with ammonia gas. Invert it into a trough of mercury. Insert a piece of wood charcoal into the tube through the mercury. Observe what happens.

CAUTION Do this experiment in a well-ventilated laboratory. Avoid inhaling too much mercury vapour and touching the mercury.

Result The mercury rises to the top of the test-tube when the piece of charcoal is inserted into the tube.

Conclusion Wood charcoal adsorbs gases.

Fig. 7.3 Wood charcoal adsorbs gases.



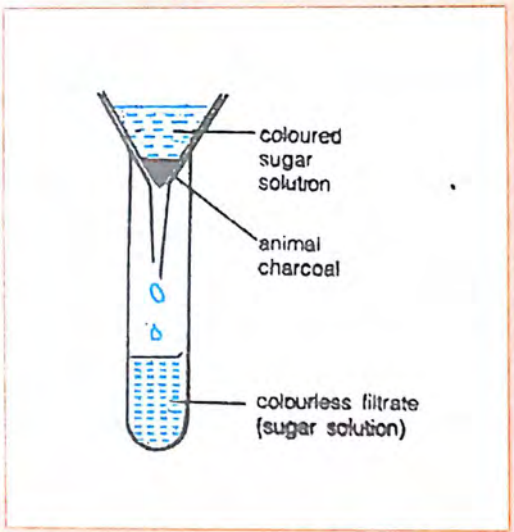
Experiment 7.2 To investigate the ability of bone charcoal to adsorb colouring matter.

Method Place some crushed animal bones in a crucible. Cover the crucible tightly. Heat the bones strongly until a black, porous residue, bone charcoal, is formed. Next, prepare a sugar solution coloured with blue ink. Transfer the bone charcoal into the coloured sugar solution and shake vigorously. Filter the solution and evaporate the filtrate to dryness. Note the colour of the crystals.

Result The filtrate is colourless. Upon evaporation, white crystals of sugar are obtained.

Conclusion Bone charcoal adsorbs colouring matter.

Fig. 7.4 Bone charcoal adsorbs colouring matter.



the sugar in a limited supply of air or by the action of concentrated tetraoxosulphate(VI) acid. It is the purest form of amorphous carbon.

Animal charcoal is produced when bones and animal refuse are heated in a limited supply of air. It contains a high percentage of calcium tetraoxophosphate(V) as impurity.

Charcoal has a very porous structure. It allows small molecules of gases and dyes to adsorb or adhere to its internal surfaces. Thus, it is a good adsorbent, particularly when activated by heating in steam. Wood charcoal is used in gas-masks adsorbing for poisonous gases. It is also used for purification of the noble gases and the recovery of industrial solvents. Similarly, animal charcoal which has the property of adsorbing colouring matter, is used in removing the brown colour from crude sugar, and in decolourizing petroleum jelly. Like coal, wood charcoal is also used mainly as a domestic fuel in Nigeria.

Carbon fibres

Carbon fibres are produced by carefully heating fibres of materials such as poly(propenonitrile) until they char to form carbon. Carbon fibres are incorporated into plastics to produce a very light but stiff and strong material.

General Properties of Carbon

All the carbon allotropes, except diamond, are black or greyish-black solids. They are odourless and tasteless. Their melting points are very high, about 3 500 °C. They are insoluble in common solvents like water, alkalis, acids, petrol and carbon(IV) sulphide. That is why carbon deposits inside motor engines have to be removed mechanically. This is known as the *decarbonization* of motor engines.

Chemically, carbon is not a very reactive element and most carbon compounds are stable. This is because the carbon atom has a valency of four and forms compounds with four covalent bonds. In these compounds, it does not have any lone pair of electrons and so is unreactive since it cannot function as an electron-pair donor. The stability of carbon compounds is also due to the strong carbon–carbon bond.

Carbon can form single or multiple bonds with itself and other elements such as hydrogen, nitrogen, oxygen and sulphur. Owing to the strong carbon–carbon bond, carbon atoms can group together to form long chains or rings. This is known as *catenation*. This unique property of carbon enables it to form numerous compounds in which the molecules range from small to extremely large ones.

All the allotropes of carbon have similar chemical properties since they are all chemically identical. However, diamond and graphite are usually less reactive than amorphous carbon.

Combustion

All forms of carbon burn in excess oxygen to produce carbon(IV) oxide only, although the temperatures required differ.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

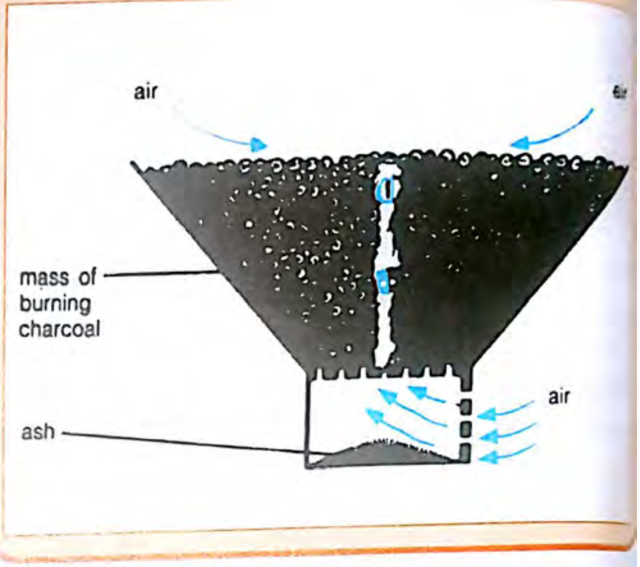
This shows that different allotropes are in fact forms of the same element. When the supply of air is limited, combustion may not be complete. Carbon(II) oxid formed instead of carbon(IV) oxide.

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

Charcoal fire In countries like Nigeria and Gha charcoal is used extensively for making fires. As th charcoal burns, carbon(IV) oxide and carbon(II) oxi are formed at various levels inside the charcoal p

A charcoal pot fire receives its air supply throu an aperture below the fire and also at the free surfa above.

Fig. 7.5 Charcoal fire.



Reactions at

level C $2CO + O_2 \rightarrow 2CO_2$

level B $CO_2 + C \rightarrow 2CO$

level A $C + O_2 \rightarrow CO_2$

At level *A*, air is plentiful and the charcoal burn to produce carbon(IV) oxide only.

At level *B*, the middle of the charcoal heap, the ai supply is very limited. As a result, the ascendin carbon(IV) oxide from level *A* becomes reduced t carbon(II) oxide by the carbon.

At level *C*, the air supply is again plentiful, so tha the carbon(II) oxide formed at level *B* is reoxidize to give carbon(IV) oxide.

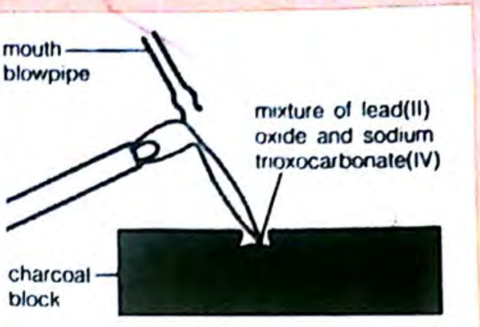
Some carbon(II) oxide, however, escape oxidation and contaminates the atmosphere. This i dangerous if the area around the fire is not wel ventilated because carbon(II) oxide is poisonous.

Experiment 7.3 To study the reducing action of carbon.

Method (a) Dig a small hole in a charcoal block and place a mixture of lead(II) oxide and anhydrous sodium trioxocarbonate(IV) into the hole. The charcoal block is the reducing agent. (Sodium trioxocarbonate(IV) prevents the metal formed from being reoxidized.) Using a mouth blowpipe, direct a jet of the luminous part of the Bunsen flame onto the mixture. Heat it for a few minutes.

(b) Mix an equal amount of powdered carbon with silver oxide and place it in a test-tube. Heat the mixture over a small Bunsen flame. Pass any gas that is evolved through lime water and observe what happens.

Fig. 7.6 Charcoal block test.



Result (a) The lead(II) oxide is reduced to a globule of silvery grey lead.

(b) Silver is obtained from silver oxide.

Conclusion Carbon is a strong reducing agent. It reduces the metallic oxides to their corresponding metals and carbon(II) oxide.

Combination reactions

Carbon combines directly with certain elements such as sulphur, hydrogen, calcium and aluminium at very high temperatures.

$$C(s) + 2S(s) \rightarrow \underset{\text{carbon(IV) sulphide}}{CS_2(l)}$$

$$C(s) + 2H_2(g) \rightarrow \underset{\text{methane}}{CH_4(g)}$$

$$2C(s) + Ca(s) \rightarrow \underset{\text{calcium carbide}}{CaC_2(s)}$$

$$3C(s) + 4Al(s) \rightarrow \underset{\text{aluminium carbide}}{Al_4C_3(s)}$$

As a reducing agent

Carbon is a strong reducing agent. It reduces the oxides of the less active metals to the metals, although very high temperatures may be required in some cases. Carbon itself is oxidized to either carbon(IV) oxide or carbon(II) oxide, depending on the conditions of the reaction. At high temperatures, carbon also reduces steam to hydrogen, and carbon(IV) oxide to carbon(II) oxide.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

$$2CuO(s) + C(s) \rightarrow 2Cu(s) + CO_2(g)$$

$$H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$$

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

Reaction with strong oxidizing agents

When carbon is heated with concentrated trioxonitrate(V) acid or concentrated tetraoxosulphate(VI) acid, it is oxidized to carbon(IV) oxide.

$$C(s) + 4HNO_3(aq) \rightarrow 2H_2O(l) + 4NO_2(g) + CO_2(g)$$

$$C(s) + 2H_2SO_4(aq) \rightarrow 2H_2O(l) + 2SO_2(g) + CO_2(g)$$

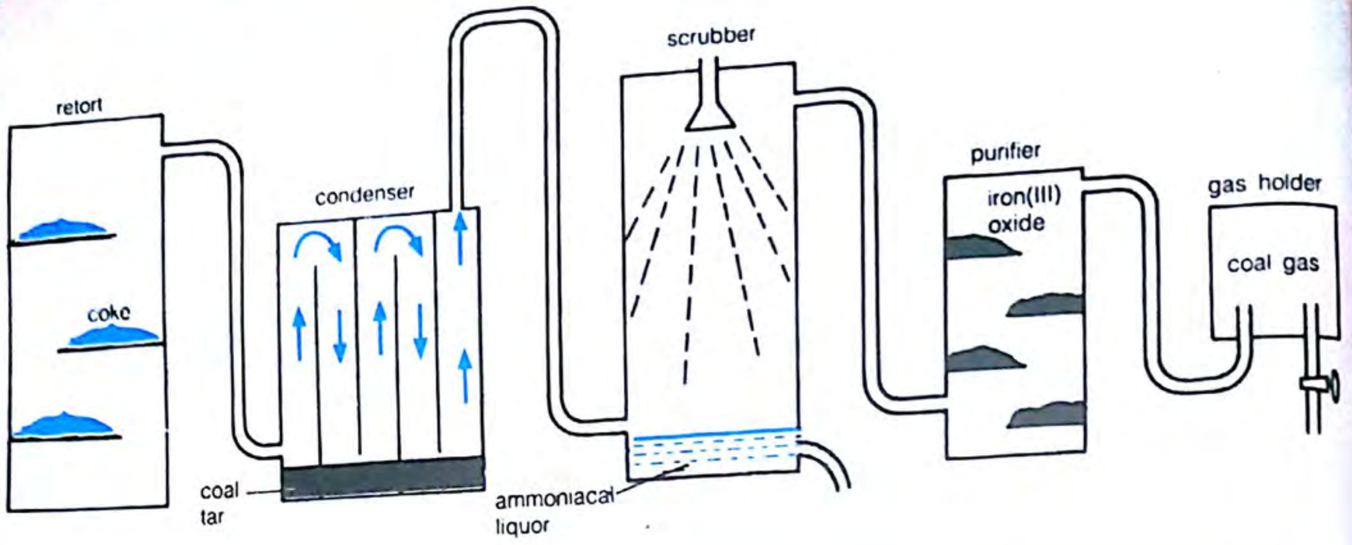
Destructive distillation of coal and wood

Coal is a complex mixture of compounds composed mainly of carbon, hydrogen and oxygen, with small amounts of nitrogen, sulphur and phosphorus as impurities. A wide variety of substances can be obtained from it by a process known as the *destructive distillation* of coal.

coal → coke + ammoniacal liquor + coal tar + coal gas

During this process, coal is heated to a very high temperature in the absence of air so that all the volatile components distil over. Some of these condense on cooling to form an almost black tar, called *coal tar*.

Fig. 7.7 Industrial manufacture of coal gas by the destructive distillation of coal.



and an aqueous liquid known as *ammoniacal liquor*. Coal tar is a mixture of more than 200 different substances which can be separated by fractional distillation. Most of these, e.g. benzene, toluene, phenol and naphthalene, are used in the synthesis of important commercial products like dyes, paints, insecticides, drugs, plastics and explosives. Ammoniacal liquor is a solution of ammonia in water. It is converted into ammonium tetraoxosulphate(VI) for use as a fertilizer.

The volatile components are collected as *coal gas*, which usually contains about 50% hydrogen, 30% methane, 10% carbon(II) oxide and small amounts of other gases, e.g. ethene and hydrogen sulphide. Coal gas is an important gaseous fuel because it is cleaner and more efficient than coal or other solid fuels.

The non-volatile residue which is left behind after destructive distillation is *coke*, which can be used as a fuel or for other purposes. Unlike ordinary distillation, the coal is destroyed by this distillation process.

Wood is a complex substance like coal except that the percentage composition of the elements present in it is different. For example, wood has a higher percentage of hydrogen and oxygen but a lower percentage of carbon than coal. Destructive distillation of wood yields these four fractions:

$$\text{wood} \rightarrow \begin{matrix}\text{wood}\\\text{charcoal}\end{matrix} + \begin{matrix}\text{pyroligneous}\\\text{acid}\end{matrix} + \begin{matrix}\text{wood}\\\text{tar}\end{matrix} + \begin{matrix}\text{wood}\\\text{gas}\end{matrix}$$

Pyroligneous acid, which is the liquid fraction, contains mainly ethanoic acid, propanone, methanol and some other compounds.

CARBON(IV) OXIDE

Carbon forms two important oxides, namely carbon(IV) oxide, CO_2, and carbon(II) oxide, CO. The atmosphere contains about 0.03% by volume of carbon(IV) oxide. A small percentage of carbon(IV) oxide is also found in the dissolved form in water. In the combined form, it is found mainly as metallic trioxocarbonates(IV) and hydrogentrioxocarbonates(IV) in the earth's crust, especially in limestone regions and coral reefs.

Carbon(IV) Oxide is found in the combined form in corals.

Experiment 7.4 To investigate the destructive distillation of wood.

Method Fill a boiling-tube with some dry saw-dust. Set up the apparatus as shown (without the gas jar). Heat the saw dust to drive away the air in the apparatus. Then connect the gas jar and collect the gaseous products formed on further heating.

CAUTION This experiment is dangerous and should be done in a fume cupboard.

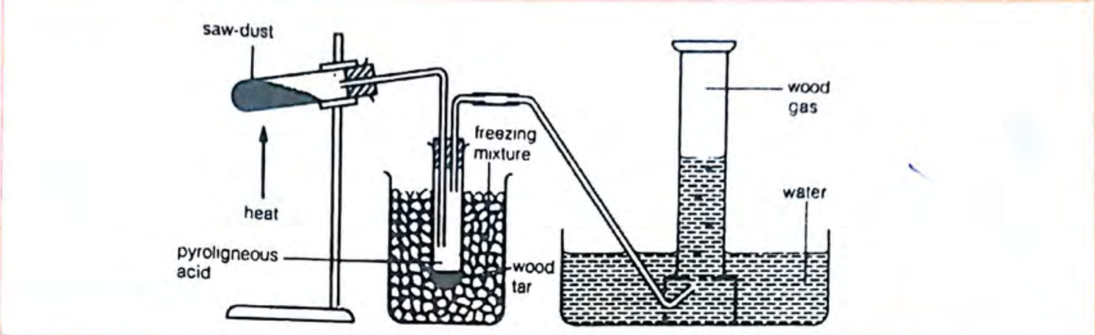


Fig. 7.8 Destructive distillation of wood.

Result Brownish fumes are given off when the saw-dust is heated. Some of these fumes cool and condense in the second boiling-tube to form two liquid layers. The top layer is a brown aqueous liquid (containing ethanoic acid) which turns blue litmus red, while the darker bottom layer contains wood tar. The insoluble gaseous products collected over water are known as wood gas, and they include carbon(IV) oxide, hydrogen and some hydrocarbons. The solid residue left behind in the boiling-tube is wood charcoal.

Conclusion On heating in the absence of air, wood (saw-dust) undergoes destructive distillation to yield four different fractions of simple substances.

Preparation

Carbon(IV) oxide is prepared in the laboratory by the action of dilute acids on a trioxocarbonate(IV), or a hydrogentrioxocarbonate(IV). Usually, calcium trioxocarbonate(IV), in the form of marble chips, shells or "potash", is used with hydrochloric acid or trioxonitrate(V) acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

$$NaHCO_3(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l) + CO_2(g)$$

Carbon(IV) oxide is also obtained by heating metallic trioxocarbonates(IV) (except those of sodium and potassium), or the hydrogentrioxocarbonates(IV) of sodium or potassium.

$$CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$$

$$2KHCO_3(aq) \rightarrow K_2CO_3(aq) + H_2O(l) + CO_2(g)$$

A Kipp's apparatus is used to provide a supply of the gas whenever it is needed in the laboratory.

In the Kipp's apparatus. carbon(IV) oxide i produced by the action of dilute hydrochloric acid or marble chips.

Industrially, carbon(IV) oxide is obtained as a by-product in fermentation processes and when limestone is heated to make quicklime.

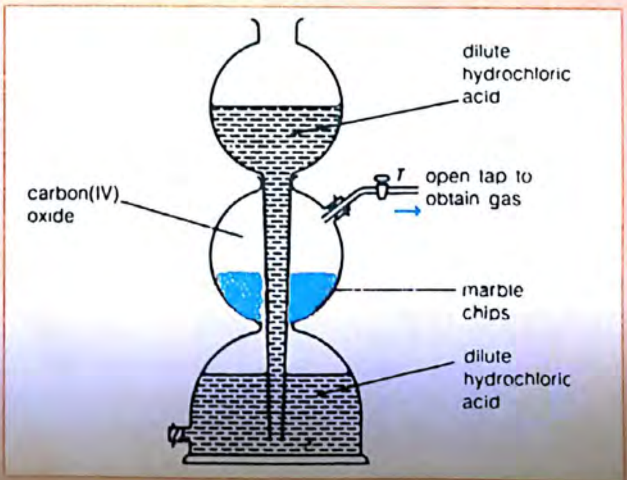
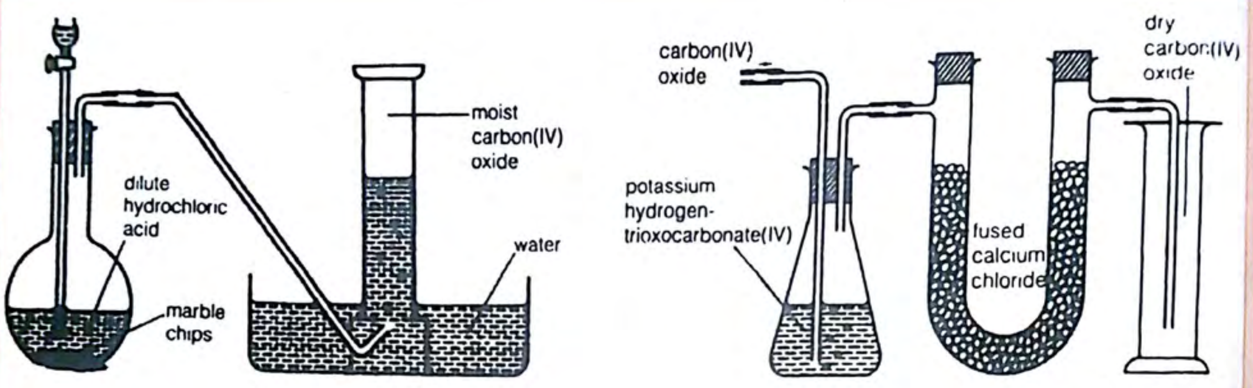


Fig. 7.9 Kipp's apparatus.

Experiment 7.5 To prepare carbon(IV) oxide.

Method Put a few marble chips in a flat-bottomed flask. Add some dilute hydrochloric or trioxonitrate(V) acid to the chips and collect the gas formed over water. (Note that a little of the gas will dissolve in the water.) If the dry gas is required, pass it through a potassium hydrogentrioxocarbonate(IV) solution first to remove any acid fumes, and then through a U-tube containing fused calcium chloride to remove the water vapour. The dry gas is then collected by downward delivery as carbon(IV) oxide is heavier than air.

Fig. 7.10 Preparation of carbon(IV) oxide.



Result As soon as the acid reaches the marble chips, effervescence occurs as carbon(IV) oxide is evolved. The gas, which is colourless, is then collected in a gas jar.

Conclusion Carbon(IV) oxide is produced by the reaction between a dilute acid and calcium trioxocarbonate(IV).

Physical Properties

1 Carbon(IV) oxide is a colourless, odourless gas with a sharp, refreshing taste.
2 It is about 1.5 times denser than air.
3 It is soluble in water. At room temperature and standard pressure, water dissolves its own volume of the gas.
4 It changes damp blue litmus paper pink because carbon(IV) oxide dissolves in water to yield trioxocarbonate(IV) acid.
5 On cooling, it readily liquefies and solidifies (−78 °C) to form a white solid known as *dry ice*.

Chemical Properties

Reaction with water

Carbon(IV) oxide is not very active chemically. It dissolves in water to form trioxocarbonate(IV) acid (soda water). This is a weak, dibasic acid which ionizes slightly.

(a) $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

(b) $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$

(c) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

On heating, trioxocarbonate(IV) acid decomposes to form water and carbon(IV) oxide.

Reaction with alkalis

It reacts directly with alkalis to yield trioxocarbonates(IV).

$$CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$$

Ionically,

$$CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}\ (s\ or\ aq) + H_2O(l)$$

In the presence of excess carbon(IV) oxide, the trioxocarbonates(IV) formed react with the carbon(IV) oxide to produce hydrogentrioxocarbonates(IV).

$$Na_2CO_3(aq) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(aq)$$

Ionically,

$$CO_3^{2-}(s\ or\ aq) + H_2O(l) + CO_2(g) \rightarrow 2HCO_3^-(aq)$$

Solutions of alkalis absorb carbon(IV) oxide readily and are frequently used to remove it from a mixture of gases.

Reaction with burning magnesium

Carbon(IV) oxide does not burn, nor does it support the combustion of most substances. The intense heat produced by burning magnesium, however, decomposes carbon(IV) oxide to release oxygen for the further oxidation of magnesium. The products of the combustion are carbon deposits and white magnesium oxide ash.

$$CO_2(g) + 2Mg(s) \rightarrow 2MgO(s) + C(s)$$

Reaction with red-hot carbon

If the gas is passed over red-hot carbon, it is reduced to carbon(II) oxide. This reaction is reversible and is of great commercial importance.

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Test for carbon(IV) oxide

Bubble the unknown gas through lime water (calcium hydroxide). If the gas is carbon(IV) oxide, the lime water turns milky due to the precipitation of insoluble calcium trioxocarbonate(IV).

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

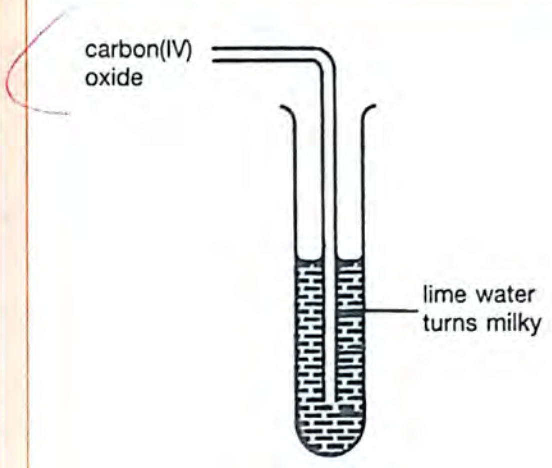
Continue bubbling more of the gas through the solution. The milkiness should disappear leaving a clear solution. This is because carbon(IV) oxide reacts with insoluble calcium trioxocarbonate(IV) to form soluble calcium hydrogentrioxocarbonate(IV).

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

Finally, heat the clear solution. It should become milky again due to the decomposition of soluble calcium hydrogentrioxocarbonate(IV) to form insoluble calcium trioxocarbonate(IV).

$$Ca(HCO_3)_2(aq) \xrightarrow{heat} CaCO_3(s) + H_2O(l) + CO_2(g)$$

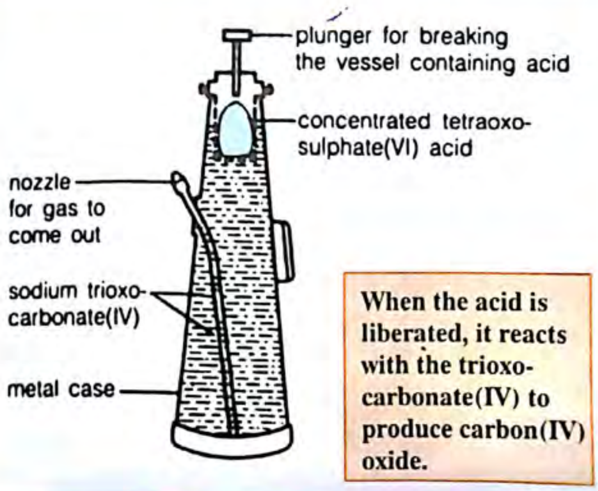
Fig. 7.11 Test for carbon(IV) oxide.



Uses

Many fire extinguishers use carbon(IV) oxide to put out fires as the gas does not support combustion. Being heavier than air, it envelopes the burning material and cuts off the oxygen supply. Carbon(IV) oxide is more effective than water in putting out petrol or oil fires because these materials float on water. Some fire

Fig. 7.12 An acid-soda fire extinguisher.



When the acid is liberated, it reacts with the trioxo-carbonate(IV) to produce carbon(IV) oxide.

extinguishers produce carbon(IV) oxide by chemical reaction, others contain the gas under high pressure.

Carbon(IV) oxide gives carbonated (aerated) drinks their refreshing taste. The gas is dissolved in these drinks under high pressure. Beer, cider and champagne also contain carbon(IV) oxide.

Many health salts contain a solid mixture of sodium hydrogentrioxocarbonate(IV) and citric or tartaric acid. When they are dissolved in water, the acid reacts with the trioxocarbonate(IV), producing an effervescence of carbon(IV) oxide.

Carbon(IV) oxide is used in the manufacture of

- sodium trioxocarbonate(IV) (washing soda) by the Solvay process,
- sodium hydrogentrioxocarbonate(IV),
- lead(II) trioxocarbonate(IV),
- urea and ammonium tetraoxosulphate(VI).

The last two substances are important fertilizers.

Yeast and baking powder are used in baking to produce carbon(IV) oxide which causes the dough to rise, making the dough 'light'.

Solid carbon(IV) oxide (i.e. dry ice) is used as a refrigerant for perishable goods, e.g. ice-cream. It sublimes on warming and provides a lower temperature. Gaseous carbon(IV) oxide is used to preserve fruits. Carbon(IV) oxide is also used as a coolant in nuclear reactors.

CARBON(II) OXIDE

Carbon(II) oxide, CO, is produced by the incomplete combustion of carbon compounds, such as the octane, C_8H_{18}, found in petrol.

$$2C_8H_{18}(l) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(l)$$

Carbon(II) oxide occurs in traces as an impurity in the atmosphere. The percentage present may be higher in cities where the gas is released in the exhaust fumes of motor cars, and in industrial areas due to the combustion of fuels.

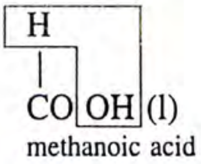
Carbon(II) oxide is a poisonous gas. As little as 0.5% of it in the air may cause a person to die. Since the gas has no colour or odour, its presence is difficult to detect, so it is very dangerous.

Preparation

Carbon(II) oxide is prepared from carbon(IV) oxide by passing the latter through red-hot carbon as shown in fig. 7.13. Most of the carbon(IV) oxide gets reduced to carbon(II) oxide. Unchanged carbon(IV) oxide is removed when the mixture of gases passes through concentrated sodium hydroxide. The pure carbon(II) oxide is collected over water.

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

Carbon(II) oxide can also be prepared by dehydrating methanoic (formic) acid or ethanedioic (oxalic) acid using concentrated tetraoxosulphate(VI) acid. The latter serves as a dehydrating agent.



$$\boxed{H}\!\!-\!CO\boxed{OH}(l) \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} CO(g)$$

methanoic acid

Fig. 7.13 Preparation of carbon(II) oxide from carbon(IV) oxide.

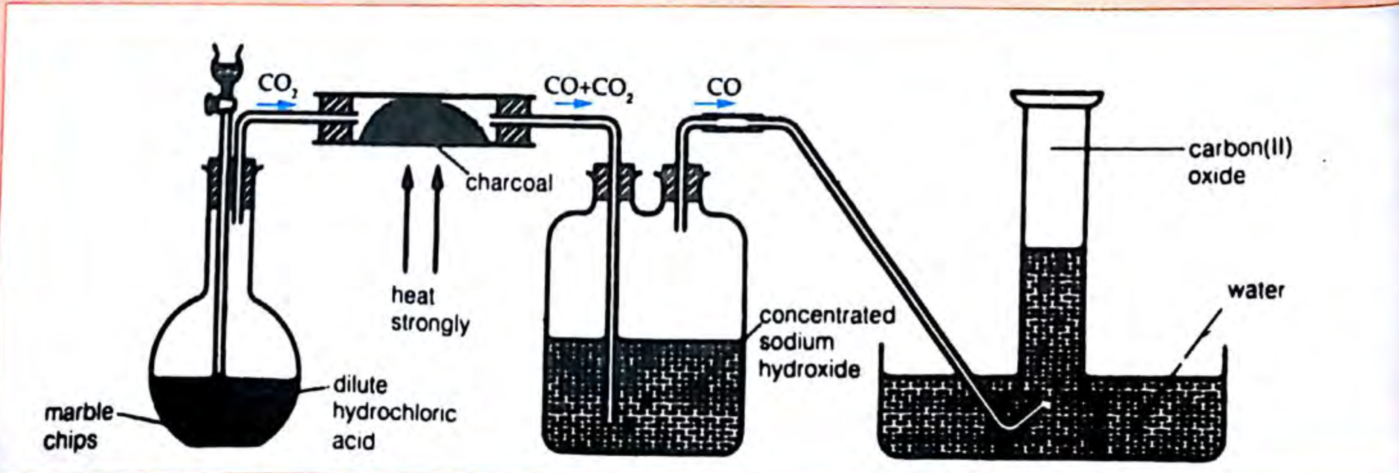
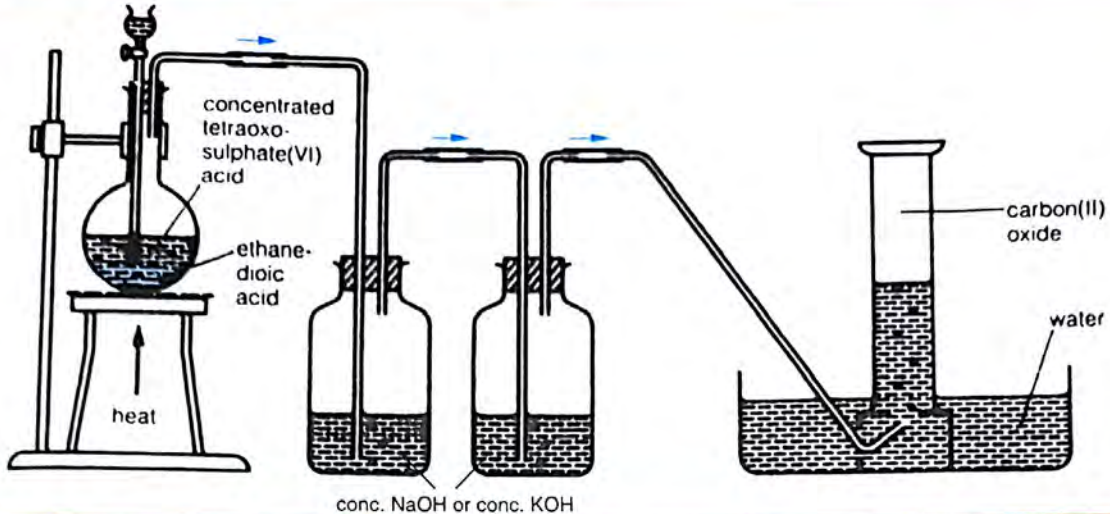
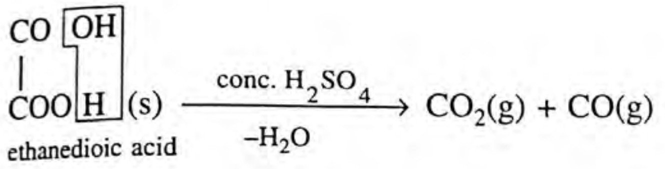


Fig. 7.14 Preparation of carbon(II) oxide from ethanedioic acid.





$$\underset{\text{ethanedioic acid}}{\begin{matrix}\text{CO}\boxed{\text{OH}}\\ |\\ \text{COO}\boxed{\text{H}}\end{matrix}}(s) \xrightarrow[-H_2O]{\text{conc. }H_2SO_4} CO_2(g) + CO(g)$$

Fig. 7.14 shows how carbon(II) oxide is prepared from ethanedioic acid. The reactants in the flask are warmed gently. Effervescence occurs and equal volumes of carbon(II) oxide and carbon(IV) oxide are evolved. The gaseous mixture is passed through concentrated sodium hydroxide to remove the carbon(IV) oxide.

CAUTION The preparation of carbon(II) oxide must be done in a fume cupboard as the gas is poisonous.

Physical properties

1 Carbon(II) oxide is a colourless, tasteless and odourless gas.
2 It is insoluble in water, but dissolves in a solution of ammoniacal copper(I) chloride.
3 It is slightly less dense than air.
4 It is neutral to litmus.

Chemical properties

As a reducing agent

Carbon(II) oxide is a strong reducing agent. It reduces some metallic oxides to metals and is itself oxidized to carbon(IV) oxide.

$$PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$$

Carbon(II) oxide also reduces iodine(V) oxide to iodine, and steam to hydrogen.

$$I_2O_5(s) + 5CO(g) \rightarrow I_2(s) + 5CO_2(g)$$
$$H_2O(g) + CO(g) \rightarrow H_2(g) + CO_2(g)$$

Combination reactions

With oxygen Carbon(II) oxide burns in air with a faint blue flame forming carbon(IV) oxide.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

With haemoglobin Carbon(II) oxide is a poisonous gas since it combines with the haemoglobin in the red blood cells to form a stable compound. This stable compound prevents the haemoglobin from transporting oxygen in our body. A person will die from lack of oxygen when one-third of the haemoglobin in the body is combined with carbon(II) oxide.

Test for carbon(II) oxide

Bubble some of the unknown gas through a test-tube containing lime water. Next, apply a lighted splint to a test-tube containing the unknown gas. Note what happens. Then add some lime water to the test-tube and shake.

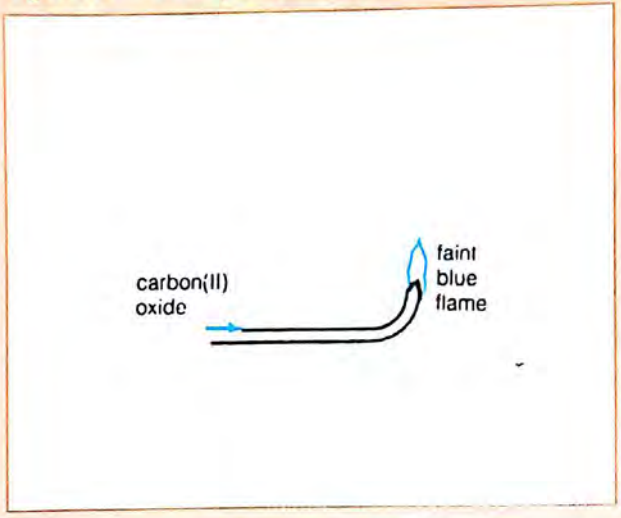


Fig. 7.15 Burning of carbon(II) oxide.

If the gas is carbon(II) oxide, it will burn with a blue flame and turn lime water milky after burning, but not before burning.

Uses

Carbon(II) oxide is used in the extraction of metals from their ores. It is also an important constituent of gaseous fuels like producer gas and water gas.

Fuel Gases

Producer gas

Producer gas is a mixture of nitrogen and carbon(II) oxide, prepared by passing a stream of air through red-hot coke. The oxygen in the air oxidizes the coke to carbon(II) oxide, with the liberation of a lot of heat, while the nitrogen is unchanged. Some carbon(IV) oxide may be formed but this is usually reduced by the hot coke to carbon(II) oxide.

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

Producer gas has a low heating power because it contains about 67% non-combustible nitrogen and 33% carbon(II) oxide. However, it is inexpensive and is widely used to heat furnaces, retorts (in the manufacture of zinc and coal gas) and limekilns. It is also a source of nitrogen for the manufacture of ammonia (Haber process).

Water gas

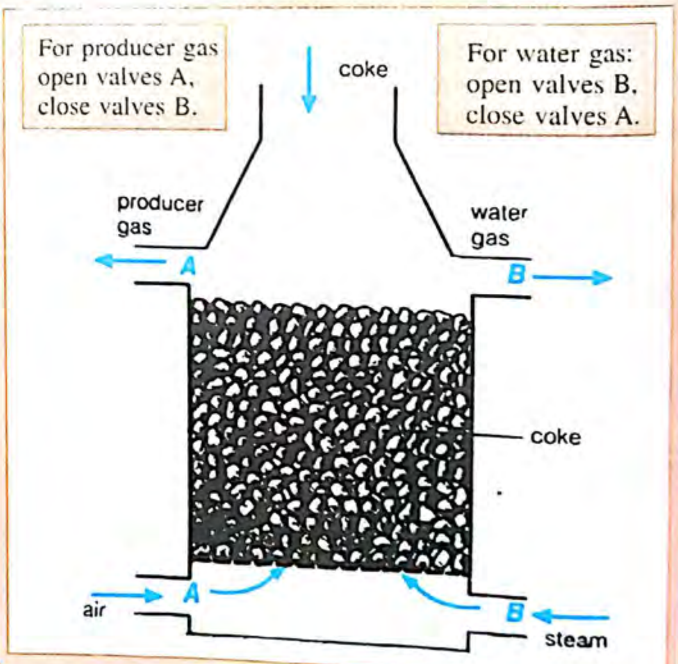
Water gas is a mixture containing equal volumes of hydrogen and carbon(II) oxide, prepared by passing steam over white-hot coke at 1 000 °C.

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

During the process, the coke quickly cools to a temperature too low for reaction if heat is not supplied externally. Industrially, producer gas and water gas are made in the same plant, known as the *producer*, by passing air and steam alternately through the heated coke. The heat produced when producer gas is formed is sufficient for water gas formation.

Both the hydrogen and the carbon(II) oxide in water gas burn in air releasing a lot of heat. This makes water gas an important industrial fuel. However, it has too high a carbon(II) oxide content for domestic use. Water gas is also an industrial source of hydrogen and other organic compounds, e.g. methanol and butanol.

Fig. 7.16 Production of producer and water gases.



TRIOXOCARBONATES(IV)

Trioxocarbonate(IV) acid is a dibasic acid. It forms two series of salts:

- the normal trioxocarbonates(IV), and
- the acidic hydrogentrioxocarbonates(IV).

Trioxocarbonates(IV) are formed naturally when trioxocarbonate(IV) acid, formed when carbon(IV) oxide dissolves in water, reacts with free metals, metallic oxides or other dissolved salts. Metallic trioxocarbonates(IV) are usually found as natural ores or deposits.

Preparation

Preparation of soluble trioxocarbonates(IV)

Of the common trioxocarbonates(IV), only sodium, potassium and ammonium trioxocarbonates(IV) are soluble in water. They are prepared in the laboratory by bubbling carbon(IV) oxide through a solution of the corresponding alkali.

$$2KOH(aq) + CO_2(g) \rightarrow K_2CO_3(aq) + H_2O(l)$$

Since sodium and potassium trioxocarbonates(IV) are not decomposed by heating, they can also be prepared by heating the corresponding hydrogentrioxocarbonates(IV).

$$2KHCO_3(s) \xrightarrow{\text{heat}} K_2CO_3(s) + H_2O(l) + CO_2(g)$$

Preparation of insoluble trioxocarbonates(IV)

The insoluble metallic trioxocarbonates(IV) can be prepared as precipitates by adding a solution of sodium trioxocarbonate(IV) or sodium hydrogentrioxocarbonate(IV) to a solution of the corresponding metal salt.

$$CaCl_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaCl(aq)$$

$$CaCl_2(aq) + 2NaHCO_3(aq) \rightarrow CaCO_3(s) + 2NaCl(aq) + H_2O(l) + CO_2(g)$$

$$2AgNO_3(aq) + Na_2CO_3(aq) \rightarrow Ag_2CO_3(s) + 2NaNO_3(aq)$$

$$2AgNO_3(aq) + 2NaHCO_3(aq) \rightarrow Ag_2CO_3(s) + 2NaNO_3(aq) + H_2O(l) + CO_2(g)$$

Ionically, the formation of calcium trioxocarbonate(IV) can be represented as follows:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$
$$Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$$

When preparing the trioxocarbonates(IV) of the less electropositive metals like copper, sodium hydrogentrioxocarbonate(IV) is used instead of sodium trioxocarbonate(IV). This is because with the latter, the basic trioxocarbonates(IV), e.g.

- $CuCO_3.Cu(OH)_2$ and
- $MgCO_3.Mg(OH)_2.4H_2O$,

are precipitated.

Aluminium trioxocarbonate(IV) does not exist. If an aluminium salt is added to sodium trioxocarbonate(IV) or hydrogentrioxocarbonate(IV) aluminium hydroxide is formed.

Properties

Solubility

Most metallic trioxocarbonates(IV) are insoluble in water. The trioxocarbonates(IV) of the alkali metals and ammonium trioxocarbonates(IV), however, are insoluble.

When the soluble trioxocarbonates(IV) dissolve in water, they become hydrolyzed and form the corresponding hydroxides, e.g.

(a) $Na_2CO_3(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2CO_3(aq)$

The hydroxide produced ionizes completely in solution while the trioxocarbonate(IV) acid is only partially ionized. The resulting solution is alkaline to litmus because the number of hydroxide ions exceed that of the hydrogen ions.

(b) $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

(c) $H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$

Action of heat

With the exception of sodium, potassium and barium trioxocarbonates(IV), all the other trioxocarbonates(IV) decompose on heating to liberate carbon(IV) oxide.

$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$
$$2Ag_2CO_3(s) \rightarrow 4Ag(s) + 2CO_2(g) + O_2(g)$$
$$(NH_4)_2CO_3(s) \rightarrow 2NH_3(g) + CO_2(g) + H_2O(l)$$

Reaction with dilute acids

All trioxocarbonates(IV) react with dilute acids to form carbon(IV) oxide, water and a salt.

$$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$$ZnCO_3(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l) + CO_2(g)$$

Ionically,

$$CO_3^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l) + CO_2(g)$$

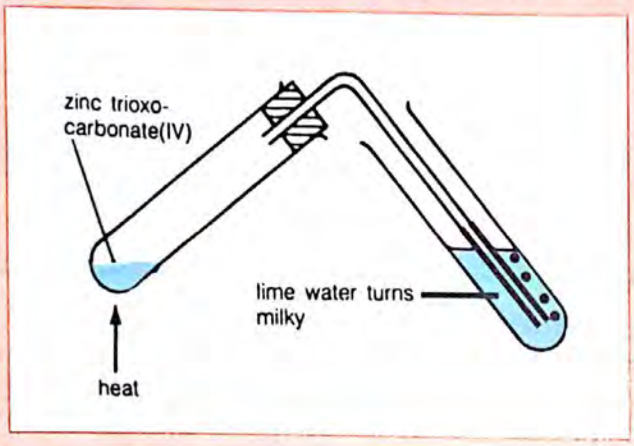


Fig. 7.17 Decomposition of zinc trioxocarbonate(IV).

HYDROGEN TRIOXOCARBONATES(IV)

Hydrogentrioxocarbonates(IV) are the acid salts of trioxocarbonate(IV) acid. They are formed when a metal or ammonium radical replaces one of the two hydrogen atoms in the trioxocarbonate(IV) acid molecule. They are soluble in water. Only the hydrogentrioxocarbonates(IV) of ammonium, potassium and sodium can be isolated as solids. Calcium hydrogentrioxocarbonate(IV) is responsible for hardness in water.

Hydrogentrioxocarbonates(IV) may be prepared by passing carbon(IV) oxide through a cold solution of the corresponding hydroxides or trioxocarbonates(IV).

(a) $2OH^-(aq) + CO_2(g) \rightarrow CO_3^{2-}(aq) + H_2O(l)$
(b) $CO_3^{2-}(aq) + CO_2(g) + H_2O(l)\ 2HCO_3^-(aq)$

All hydrogentrioxocarbonates(IV) decompose readily on heating or when their solutions are boiled to yield carbon(IV) oxide, water and the corresponding trioxocarbonates(IV).

$$2HCO_3^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l) + CO_2(g)$$

Like trioxocarbonates(IV), hydrogentrioxocarbonates(IV) too react with acids to produce carbon(IV) oxide. This reaction is used to test for hydrogentrioxocarbonates(IV).

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$$

CARBON CYCLE

Carbon is being continuously circulated in nature by a series of changes known as the Carbon Cycle. Atmospheric carbon(IV) oxide forms the vital link between the various carbon compounds in the cycle. The level of carbon(IV) oxide in the air is always kept at a constant value of 0.03% by volume. This is achieved through a natural balance between its rate of formation and its rate of removal from the atmosphere.

Processes which liberate carbon(IV) oxide into the atomosphere

There are several processes which liberate carbon(IV) oxide. One of the most important of these is the respiration of living organisms. During this process, sugar undergoes complete oxidation to produce carbon(IV) oxide as one of the products.

$$\underset{\text{sugar}}{C_6H_{12}O_6(aq)} + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) + \text{energy}$$

Thus, exhaled air contains 3% carbon(IV) oxide, which is 100 times greater than the amount found in inhaled air. Carbon(IV) oxide is also released during the combustion of all substances containing carbon (e.g. wood, coal, petrol and methane), the decay of all organic material, the heating of trioxocarbonates(IV) and hydrogentrioxocarbonates(IV) (e.g. the heating of limestone and chalk in limekilns), the eruption of volcanoes, and the fermentation of sugars and other carbohydrates.

Processes which remove carbon(IV) oxide from the atomosphere

Photosynthesis is the most important process which removes carbon(IV) oxide from the atmosphere. During this process, plants use carbon(IV) oxide, water and solar energy to synthesize carbohydrate.

$$6CO_2(g) + 6H_2O(l) + \text{energy} \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

Carbon(IV) oxide is also removed from the atmosphere when it dissolves in rain water and natural water bodies. Some of the dissolved gas is used by marine organisms for building up their bones and shells. When the organisms die, the sedimentation of these shells leads to the formation of chalk, limestone and other trioxocarbonate(IV) minerals. The dissolved carbon(IV) oxide may also combine with calcium and magnesium trioxocarbonates(IV), particularly in the sea, to form hydrogentrioxocarbonates(IV). This reaction and the solution of carbon(IV) oxide in water are easily reversible. This enables the sea and other water bodies to act as reservoirs for atmospheric carbon(IV) oxide,

- releasing the gas when its level is low in the atmosphere; and
- removing the gas when its level is high in the atmosphere.

Carbon(IV) oxide is also absorbed by chemicals like alkalis. During the hardening of mortar and whitewash, the slaked lime in them reacts slowly with the gas to form calcium trioxocarbonate(IV).

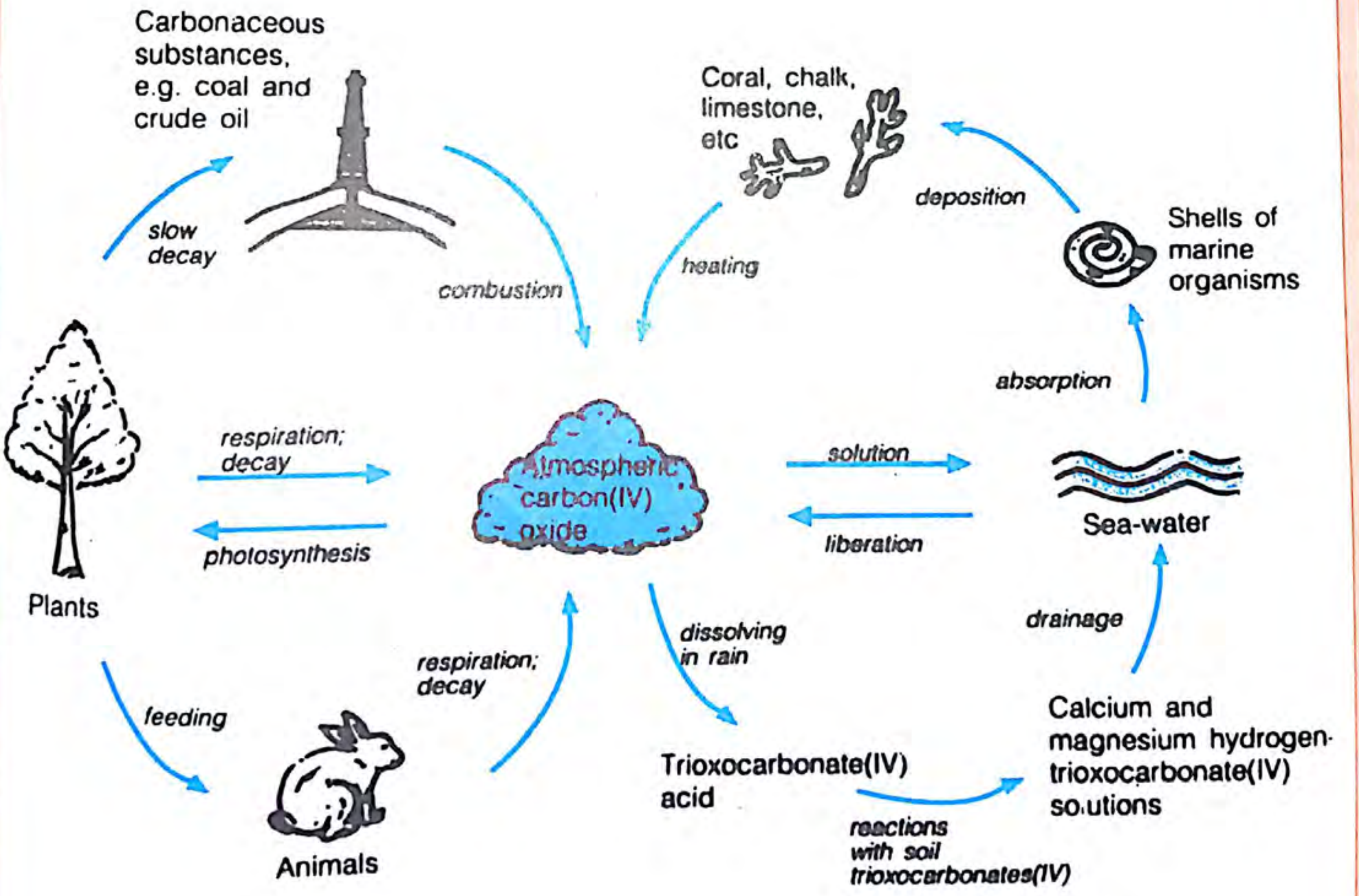
$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

Human activities and the carbon cycle

Human activities are upsetting the natural balance which keeps the carbon(IV) oxide level constant in the atmosphere. These activities are

- an increase in the combustion of fossil fuels in industries, homes and vehicles; and
- deforestation so that the forests which release carbon(IV) oxide into the atmosphere are much reduced in size.

Fig. 7.18 Carbon cycle.



SUMMARY

Carbon

- Carbon occurs freely in the earth's crust and in the combined state as trioxocarbonates(IV), carbon(I oxide and in organic matter.
- Carbon exists in two allotropic forms, namely diamond and graphite. The two forms are in the sa physical state but they have different properties because of their different bonding structures: diamond basically a three-dimensional molecule and graphite a two-dimensional molecule arranged in layers.
- Amorphous carbons are not crystalline. They include coal, coke and charcoal which are important fue Charcoal, owing to its porous nature, is also a good adsorbent.
- Carbon is not very reactive chemically. It forms stable compounds with other elements by single multiple bonds. It has a maximum covalency of four and has no lone pair of electrons.
- The ability of carbon atoms to form long chains or rings is known as catenation.
- Carbon undergoes combustion; combines directly with certain elements at high temperatures; reduc metallic oxides to metals (it is a strong reducing agent); reacts with strong oxidizing agents; undergo destructive distillation to give four different fractions; and is widely used as fuel.
- Carbon forms two oxides, namely carbon(IV) oxide and carbon(II) oxide.
- Carbon is used for the production of fuel gases like producer gas and water gas.

Carbon(IV) oxide

- Carbon(IV) oxide is prepared by the action of dilute acids on the trioxocarbonates(IV) hydrogentrioxocarbonates(IV).
- Carbon(IV) oxide is moderately soluble in water, forming a weak dibasic acid; neutralizes alkalis to for trioxocarbonates(IV) and in excess, forms the hydrogentrioxocarbonates(IV); does not support combustio (except strongly burning magnesium); reduces to carbon(II) oxide by red-hot carbon; and turns lime wat milky.
- ***Test for carbon(IV) oxide*** It turns lime water (calcium hydroxide solution) milky and when bubbled excess, the lime water becomes clear again.

Carbon(II) oxide

- Carbon(II) oxide is prepared by reducing carbon(IV) oxide with red-hot carbon or by the dehydration methanoic or ethanedioic acid by concentrated tetraoxosulphate(VI) acid.
- Carbon(II) oxide is a very poisonous gas; dissolves in ammoniacal copper(I) chloride; is a strong reducin agent used in the extraction of metals from their oxides; and undergoes combination reaction wi haemoglobin of the blood.

Trioxocarbonates(IV)

- Soluble trioxocarbonates(IV) are prepared by bubbling carbon(IV) oxide in alkalis while insoluble trioxocarbonates(IV) are prepared by double decomposition.
- Summary of properties of the common metallic trioxocarbonates(IV).

Metal	**Properties of the corresponding trioxocarbonates(IV)**		
	Solubility	**Effect of heating**	**Reaction with acids**
K Na	These trioxocarbonates(IV) are soluble in water. They form alkalis.	These trioxocarbonates(IV) do not decompose on heating.	These trioxocarbonates(IV) react with dilute acids to give a salt, water and carbon(IV) oxide.
Ca Mg Zn Fe	These trioxocarbonates(IV) are insoluble in water.	All trioxocarbonates(IV) decompose on heating to yield carbon(IV) oxide and the corresponding oxides.	
Pb Cu			
Ag		Ag_2CO_3 decomposes to give metallic silver, oxygen and carbon(IV) oxide.	

- *Test for trioxocarbonates(IV)* When warmed with dilute acids, they liberate carbon(IV) oxide.

Hydrogentrioxocarbonates(IV)

- Hydrogentrioxocarbonates(IV) are prepared by dissolving excess carbon(IV) oxide in alkalis.
- All hydrogentrioxocarbonates(IV) decompose on heating to form the corresponding trioxocarbonates(IV), water and carbon(IV) oxide; and with acids, they release carbon(IV) oxide.

Carbon cycle

- The *carbon cycle* shows that carbon is being continuously circulated in nature as carbon(IV) oxide. The quantity of carbon(IV) oxide remains constant due to a balance of processes which use up carbon(IV) oxide and those which liberate it.

EXERCISES

1. Which is the odd-man-out?
A Diamond
B Graphite
[✓ C] Bronze
D Coal

2. Ability of an element existing in two or more physical states but maintaining the same chemical characteristics is called
A isotopy.
B isomerism.
[✓ C] allotropy.
D defraction grating.

3. When graphite is subjected to a very high temperature and pressure for several hours in the presence of catalyst nickel, the product is
A soot.
B quartz.
C aritificial diamond.
D graphite flakes.

4. Acheson process is a process of producing
A graphite from coke at high temperature.
B producing coke using graphite at high temperature.
C anthracite from carbon.
D wood–charcoal from coal.

5. One of these is not a reaction of charcoal
A $C + O_2 \rightarrow CO_2$
B $CO_2 + C \rightarrow CO$
C $2CO + O_2 \rightarrow 2CO_2$
D $CO_2 + 2CO \rightarrow 2CO$

6. The equation $Fe_2O_3\,(s) + 3Cs \rightarrow 2Fe\,(s) + 3CO\,(g)$
A is oxidation reaction of carbon.
B reduction reaction of carbon.
C carbonization of Fe_2O_3.
D destructive distillation of Fe_2O_3.

7. The liquid product of the destructive distillation of coal is
[✓ A] ammonical liquor.
B coal fume.
C dyestuff.
D coal plasma.

8. Where else is CO_2 found in free state apart
the atmosphere?
A In carbonated trees.
B Dissolved form in water.
C In corals.
D In limestone region.

9. Kipp's apparatus is an instrument for prepa
intermitent supply of gases by reacting
A liquid with gas.
B liquid with solid.
C solid with gas.
D liquid with liquid.

10. Gas prepared by the reaction between metha
acid and conc. tetraoxosulphate(VI) acid is
A SO_2
B CO
C CO_2
D H_2S

11. Gas which dissolves in ammonical copp
chloride but insoluble in water is
A NH_3
B CO
C N_2O
D CO_2

12. Producer gas is a gas with a low heating po
because it contains more
A CO_2 than O_2.
[✓ B] nitrogen than carbon II oxide.
C CO_2 than nitrogen.
D nitrogen than CO_2.

13. All are decomposed by heat except
A $BaCO_3$
B $CuCO_3$
C $ZnCO_3$
D Ag_2CO_3

14. Temporary hardness of water is removed
heating because
A it is easy to remove.
B the causes of temporary hardness are mai
soluble salts.
C calcium hydrogen trioxocarbonate IV
water is decomposed by heat.
D Calcium trioxocarbonate IV is produce

15. It is dangerous to stay in a badly ventilated room which has a charcoal fire because of the presence of

A carbon(II) oxide.
B carbon(IV) oxide.
C hydrogen sulphide.
D methane.
E producer gas.

16. The property of graphite that makes it a good lubricant is its

A low melting point.
B low density.
C electrical conductivity.
D softness.
E planar molecular structure.

17. Which of the following trioxocarbonates(IV) are not decomposed by heat?

A Calcium and sodium trioxocarbonates(IV)
B Potassium and zinc trioxocarbonates(IV)
C Magnesium and potassium trioxocarbonates(IV)
D Sodium and potassium trioxocarbonates(IV)
E Zinc and potassium trioxocarbonates(IV)

18. (a) Explain why graphite is a good conductor of electricity while diamond is not, although both are true allotropes of carbon. Compare the other properties of graphite and diamond.

(b) Write short notes on the preparations and uses of

(i) charcoal. (iii) lamp-black.
(ii) coke. (iv) animal charcoal.

19. (a) Draw a charcoal pot fire and explain, using equations, the reactions taking place at the lower, middle and upper parts of the fire.

(b) Why is carbon(II) oxide poisonous?

(c) Give two uses of
(i) diamond, (ii) graphite.
Give the properties responsible for these uses.

20. (a) Using a diagram, describe how you would collect the products formed during the destructive distillation of wood.

(b) Give the uses of two of the products.

(c) How would you prove that beer contains dissolved carbon(IV) oxide?

(d) Name four products obtained in the destructive distillation of coal.

21. (a) Describe and explain what happens when magnesium burns in a jar of carbon(IV) oxide. Give the equation of the reaction.

(b) Describe and explain what happens when carbon(IV) oxide is passed into lime water for a long time. What happens when the final product is heated? Give the equations of the reactions taking place.

(c) Which properties of carbon(IV) oxide account for its use in
(i) fire extinguisher?
(ii) refrigeration of fruits?

(d) Describe the composition of baking powder and explain the part it plays in the baking industry.

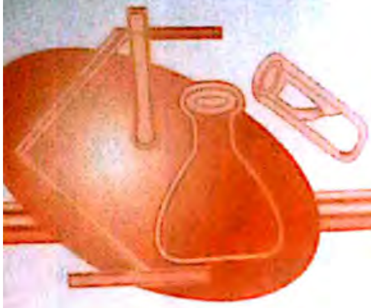
22. (a) Using diagrams and equations describe how you would prepare samples of carbon(II) oxide from
(i) carbon(IV) oxide and other reagents.
(ii) ethanedioic acid and other reagents.

(b) Write short notes on the preparation and uses of
(i) producer gas. (ii) water gas.

23. (a) Describe the various processes by uhich carbon(IV) oxide is added to and removed from the atmosphere.

(b) How does carbon(II) oxide react with iron(III) oxide? Give the reaction equation.

24. The amount of carbon(IV) oxide in the atmosphere is maintained at a fairly constant level. How is this achieved? How do human activities threaten to upset this balance?



8

PERIODIC TABLE • FAMILIES OF ELEMENTS

PERIODIC TABLE

The most important classification in chemistry is the arrangement of the elements in the Periodic Table. In 1869, Mendeléev, a Russian scientist, was the first to construct a Periodic Table. He arranged the elements in order of increasing relative atomic mass. He pointed out that elements with similar properties kept recurring at regular intervals or periods.

Mendeléev's Periodic Table had many gaps. He predicted that there were undiscovered elements which could fill these gaps. He even predicted the possible properties of these elements.

Later, elements such as scandium, gallium, germanium, etc, were discovered, which not only fitted exactly into Mendeléev's Table, but also had the properties he predicted. This clearly showed the great usefulness of the Periodic Table as it helps us to correlate the properties of the elements and thus remember their chemistry.

With the discovery of the electronic structure of the atoms, it became clear that elements do vary regularly, not with their relative atomic mass, but with their atomic number. The basic assumption behind the modern Periodic Table, known as the *Periodic Law*, is as follows:

> *The modern Periodic Law states that the properties of the elements are a periodic function of their atomic numbers.*

Electronic configuration of atoms as the basis of the Periodic Table

The atomic number is the number of protons in an atom. As an atom is neutral, the number of protons is equal to the number of electrons. The electrons and their arrangement in the atom of an element are responsible for many of the properties of the element. The key to the periodicity of elements lies in th electronic configurations of their atoms.

We know that an atom consists of a centr positively charged nucleus with electrons revolvin around it at great speed. The electrons are negativel charged and revolve around the nucleus in spheric regions called *shells* or *energy levels*, situated a various distances from the nucleus. The radius of eac shell from the nucleus is specific. Electrons in shells nearer the nucleus possess less energy than thos farther away.

Starting from the shell nearest the nucleus, the shells are named as *K*, *L*, *M*, *N*, *O*, ... These correspond to the energy levels numbered *1*, *2*, *3*, *4*, *5*, ... An atom may have several electron shells but all the electrons in a given shell possess approximately equal energy. The maximum possible number of electrons in a shell is given by the formula $2n^2$, where n is the energy level number of the shell.

Table 8.1 Maximum number of electrons for the K, L, M and N shells

Shell	Energy level (n)	Maximum number of electrons($2n^2$)
K	*1*	$2(1)^2 = 2$
L	*2*	$2(2)^2 = 8$
M	*3*	$2(3)^2 = 18$
N	*4*	$2(4)^2 = 32$

The simplest atom, the hydrogen atom, has on proton in its nucleus and one electron in the *K* shel Atoms of other elements show a progressive increas in the number of protons and electrons. The electroni configurations of the atoms of the first 20 elemen (see page 48) show that electrons are added to a shel until a stable duplet (for the *K* shell) or an oct configuration is reached. Further increase in th number of electrons results in the electrons occupyi the shell with the next highest energy level.

This pattern of electron arrangement in the shells of the atoms of elements can also be seen in the arrangement of elements in the Periodic Table.

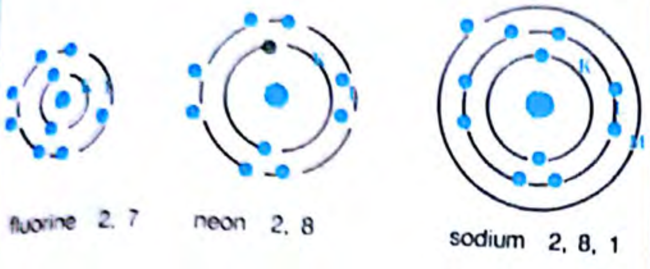


Fig. 8.1 Electronic configurations of fluorine, neon and sodium.

Groups and periods

he modern form of the Periodic Table is divided into ight vertical columns known as *groups* and seven orizontal rows known as *periods*.

roups The vertical columns of elements, or groups, e numbered from 0 to 7. Elements in the same group ve the same number of electrons in the outermost ell of their atoms, i.e. they have the same number *valence electrons*.

Hydrogen does not fit into any group. But for convenience, it is placed in Group 1 because of the single electron. In Group 0, helium has two electrons, while the other elements have eight valence electrons.

Besides the eight main groups, there are also the transition groups of elements. These lie between Groups 2 and 3 in the Periodic Table.

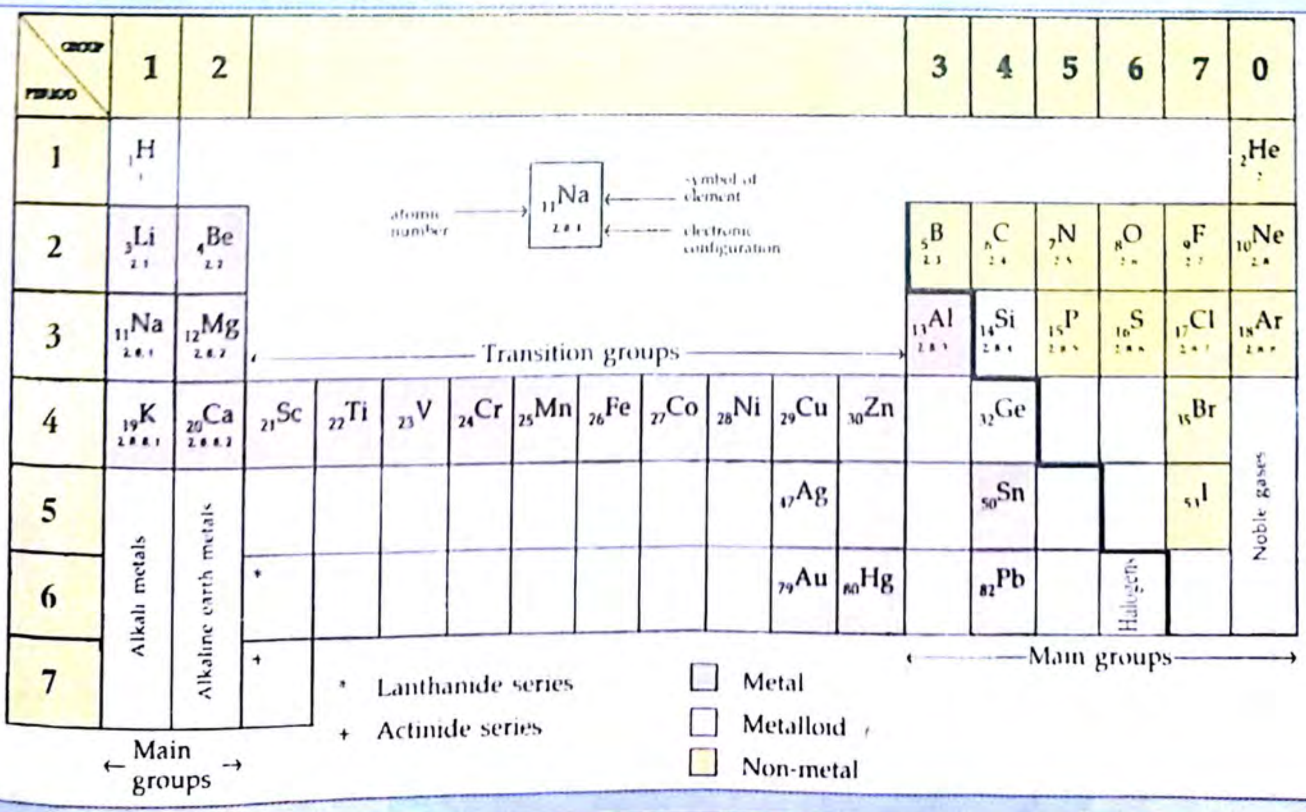
Periods The horizontal rows of elements, or periods, are numbered from 1 to 7. Elements in the same period have the same number of electron shells, i.e. elements of Period 2 have two electron shells (*K*, *L*), those of Period 3 have three (*K*, *L*, *M*), and so on. The number of valence electrons of the elements in the same period increases progressively by one across the period from left to right.

Among the elements in Periods 6 and 7 are the elements of the *lanthanide* and *actinide* series respectively. They are also known as the *inner transition elements*.

Metals, metalloids and non-metals

The Periodic Table shows a diagonal division of the elements into metals and non-metals, as indicated by the black boundary line in fig. 8.2. The metals are found on the left side of this line and the non-metals on the right. The metalloids occur along the boundary line.

Fig. 8.2 Features of the Periodic Table.



Electronic Configuration and Periodic Table

In the modern form of the Periodic Table, the atoms of the elements in Groups 1 to 7 and 0 have the following electronic configurations in their outermost energy levels.

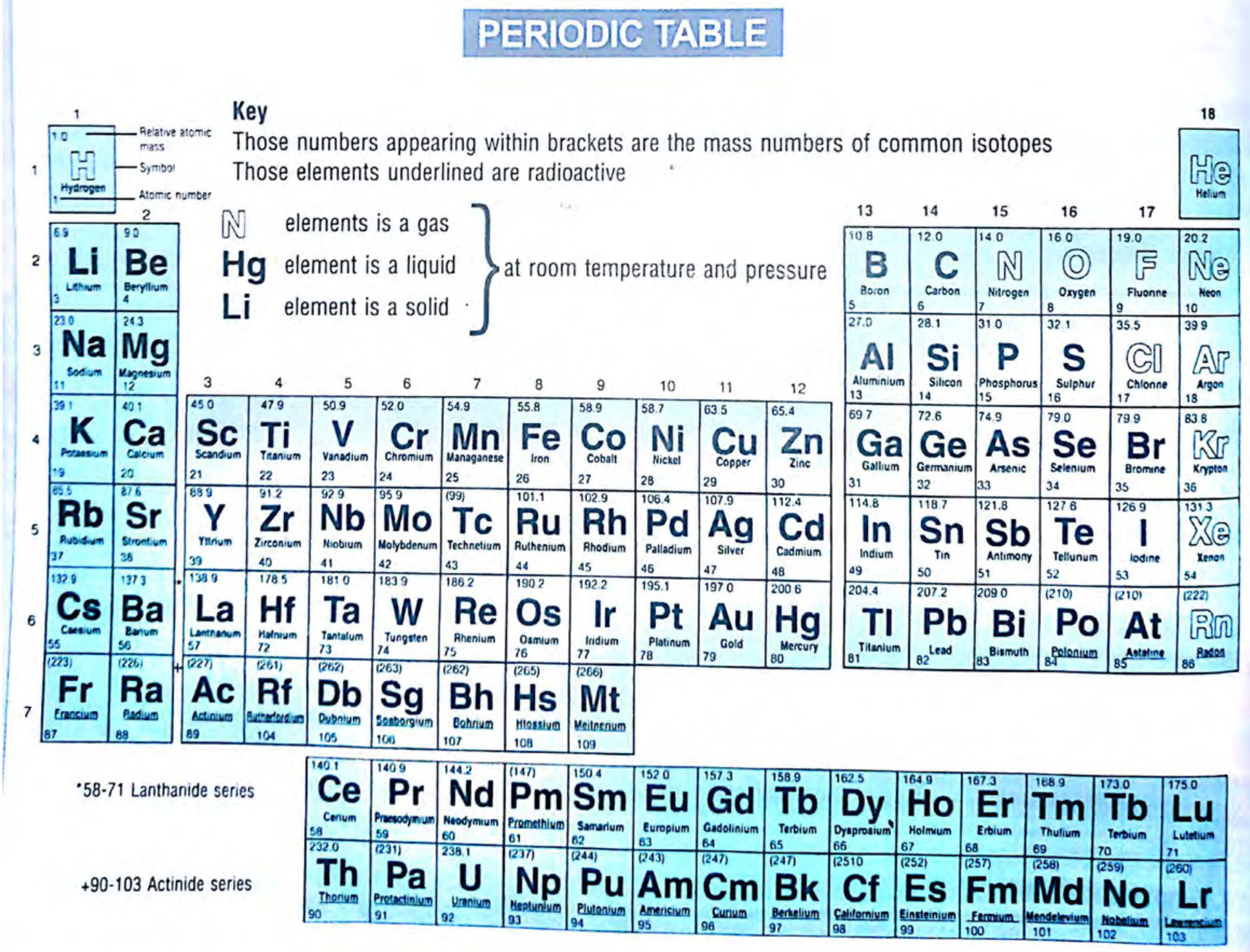
Group 1 one *s* electrons }
Group 2 two *s* electrons } *s*-block

Group 3 two *s* electrons + one *p* electron }
Group 4 two *s* electrons + two *p* electrons }
Group 5 two *s* electrons + three *p* electrons }
Group 6 two *s* electrons + four *p* electrons } *p*-block
Group 7 two *s* electrons + five *p* electrons }
Group 0 two *s* electrons + six *p* electrons }

Groups 1 and 2 make up the *s*-block. The elements in this block are the reactive alkali and alkali-earth metals. Groups 3 to 7 and 0 form the *p*-block. Electron are added progressively to the *p* orbitals as we mov across the table from Groups 3 to 7 and 0. The elemen in the *p*-block change from moderately active metal in Group 3 to the very active non-metals in Group 7 and finally the unreactive noble gases in Group (which appropriately mark the end of each period. Thu we see that the positions of the *s-block* and *p*-bloc elements in the Periodic Table are related to the *s* and *p* electrons occupying the outermost energy levels o the atoms.

The transition elements occur between Groups 2 and 3 in the Periodic Table. They form the *d*-block because they contain d electrons in addition to the s and p electrons. As we progress across the transition series from left to right, the electrons that are added fill up the incomplete inner *d* orbitals of the atoms of

Fig. 8.3 Periodic Table in block form according to the types of electrons most related to the positions of the elements.



PERIODIC TABLE

Key
Those numbers appearing within brackets are the mass numbers of common isotopes
Those elements underlined are radioactive

1.0 — Relative atomic mass
H — Symbol
Hydrogen
1 — Atomic number

N elements is a gas }
Hg element is a liquid } at room temperature and pressure
Li element is a solid }

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1.0 H Hydrogen 1																	He Helium
2	6.9 Li Lithium 3	9.0 Be Beryllium 4											10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12											27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulphur 16	35.5 Cl Chlorine 17	39.9 Ar Argon 18
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Managanese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	(99) Tc Technetium 43	101.1 Ru Ruthenium 44	102.9 Rh Rhodium 45	106.4 Pd Palladium 46	107.9 Ag Silver 47	112.4 Cd Cadmium 48	114.8 In Indium 49	118.7 Sn Tin 50	121.8 Sb Antimony 51	127.6 Te Tellurium 52	126.9 I Iodine 53	131.3 Xe Xenon 54
6	132.9 Cs Caesium 55	137.3 Ba Barium 56	* 138.9 La Lanthanum 57	178.5 Hf Hafnium 72	181.0 Ta Tantalum 73	183.9 W Tungsten 74	186.2 Re Rhenium 75	190.2 Os Osmium 76	192.2 Ir Iridium 77	195.1 Pt Platinum 78	197.0 Au Gold 79	200.6 Hg Mercury 80	204.4 Tl Titanium 81	207.2 Pb Lead 82	209.0 Bi Bismuth 83	(210) Po Polonium 84	(210) At Astatine 85	(222) Rn Radon 86
7	(223) Fr Francium 87	(226) Ra Radium 88	+ (227) Ac Actinium 89	(261) Rf Rutherfordium 104	(262) Db Dubnium 105	(263) Sg Seaborgium 106	(262) Bh Bohrium 107	(265) Hs Hassium 108	(266) Mt Meitnerium 109									

*58-71 Lanthanide series	140.1 Ce Cerium 58	140.9 Pr Praesodymium 59	144.2 Nd Neodymium 60	(147) Pm Promethium 61	150.4 Sm Samarium 62	152.0 Eu Europium 63	157.3 Gd Gadolinium 64	158.9 Tb Terbium 65	162.5 Dy Dysprosium 66	164.9 Ho Holmium 67	167.3 Er Erbium 68	168.9 Tm Thulium 69	173.0 Tb Terbium 70	175.0 Lu Lutetium 71
+90-103 Actinide series	232.0 Th Thorium 90	(231) Pa Protactinium 91	238.1 U Uranium 92	(237) Np Neptunium 93	(244) Pu Plutonium 94	(243) Am Americium 95	(247) Cm Curium 96	(247) Bk Berkelium 97	(251) Cf Californium 98	(252) Es Einsteinium 99	(257) Fm Fermium 100	(258) Md Mendelevium 101	(259) No Nobelium 102	(260) Lr Lawrencium 103

the elements. The electronic configuration of the outermost energy level remains fixed at one or two *s* electrons. Here, we see that the positions of the transition elements in the Periodic Table are related to the presence of the *d* electrons, occupying the inner orbitals of the atoms. The partially filled *d* orbitals confer special properties on the transition elements. The transition elements which are all metals, are similar among themselves and different from the *s*-block metals.

The lanthanides and the actinides also occur between Groups 2 and 3 in Periods 6 and 7 respectively. They form the *f*-block because they contain *f* electrons in addition to the *s, p* and *d* electrons. The *f* electrons are added to the inner orbitals of the atoms. The lanthanides and the actinides exhibit very similar properties which are due to the presence of the *f* electrons.

Fig. 8.3 shows how the Periodic Table can be divided into the different blocks as discussed above, clearly showing the relationship between electronic configuration and the position of the elements in the Periodic Table.

PERIODIC TABLE AND ATOMIC PROPERTIES

In this chapter, we have learnt that some physical and chemical properties of the elements vary periodically with the atomic number. This led to the postulation of the Periodic Table which provides an organized structure to our knowledge and understanding of inorganic chemistry.

The early chemists used bulk properties of the elements such as density, melting and boiling points and molar volumes to show periodicity. However, we now know that there is also a periodic variation in the atomic properties of the elements. The atomic properties that we shall discuss will include *atomic size, ionization energy, electron affinity* and *electronegativity.*

Atomic and Ionic Sizes

In an atom, the orbiting electrons may be best represented by an electron cloud. Since the electron cloud of an atom has no definite limit, the size of an atom cannot be defined easily. However, using X-ray and electron diffraction techniques, it is possible to determine the distance between covalently bonded atoms. For example, the distance between the nuclei of iodine atoms in an iodine molecule is 0.266 nm; so the *atomic radius* of an iodine atom can be taken to be 0.133 nm. Generally, the atomic radius is taken to be one-half the distance of closest approach between the nuclei of atoms in the elemental substance.

Ions of elements are formed by electron loss or gain. Their sizes are different from the atomic sizes of elements. Ionic sizes are given by *ionic radii.* They can be measured in a similar way as the atomic radii. The ionic radius of a given compound is obtained by measuring the distance between the centre of one ion and the centre of its nearest neighbour of opposite charge.

Fig. 8.4 Atomic radius of iodine.

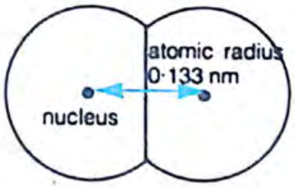


Table 8.2 Values of the atomic radii of the first twenty elements in the Periodic Table.

Element	Hydrogen							Helium
atomic radius/nm	0.037							0.049
Element	Litium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
atomic radius/nm	0.152	0.111	0.088	0.077	0.070	0.066	0.064	0.070
Element	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine	Argon
atomic radius/nm	0.186	0.160	0.143	0.117	0.110	0.104	0.099	0.094
Element	Potassium	Calcium						
atomic radius/nm	0.231	0.197						

Atomic size across a period From table 8.2, we see that the size of the atoms of elements in the same period decreases steadily as the atomic number increases. When we move from one element to the next across a period, electrons are being added to the same shell at about the same distance from the nucleus; simultaneously, protons are also being added to the nucleus. Two forces are acting on these electrons. In heavier atoms, the larger nuclear charge would exert a progressively stronger attraction upon the electrons around it and would tend to pull them towards the nuclei. There will also be forces of mutual repulsion amongst the electrons as more electrons are added. Evidence shows that the nuclear attraction increases more rapidly across a period than the repulsive forces between the electrons. As a result, the atomic radius decreases with increasing atomic number, while the attractive force exerted by the nucleus on the outermost electrons of the atom increases across a period. Thus, the elements become progressively more electronegative from left to right.

Atomic size down a group There is an increase in atomic radius as the atomic number increases down a given group. In this case, the increase in the attractive force exerted by the nucleus as its positive charge gets greater is more than counterbalanced by the additional space taken up by the extra shell of electrons added in each period. Thus, the elements of any one group become decreasingly electronegative with increasing atomic number, i.e. as we go down the group.

Ionic size We shall deal with ionic sizes in electrovalent compounds. A study of the variation of ionic radii with atomic numbers shows that

- the ionic radii of positive ions are smaller than the corresponding atomic radii (a positive ion is formed by removing electrons from the outermost shell, making it smaller);
- the ionic radii of negative ions are greater than the corresponding atomic radii (a negative ion is formed by adding electrons to the outermost shell, making it bigger);
- in a group of ions having the same number of lectrons, the ionic radius decreases as the atomic umber increases (as the nuclear charge increases, e electron cloud contracts as it is pulled more fectively towards the nucleus by an increasing sitive charge).

PERIODICITY OF SOME PROPERTIE

Periodicity is the recurrence of similar phenomena regular intervals. With respect to the Periodic Tab periodicity is the variation of the properties of elemen in a regular pattern both down the groups and acro the periods.

We shall now look at how some properties elements vary, using the first twenty elements and th elements of Period 3 as examples. Important properti of elements which show periodicity are

- melting and boiling points;
- electrical and thermal conductivities;
- ionization energies and electron affinities;
- electronegativities;

Variations in physical properties

Melting and boiling points Fig. 8.5 shows the periodicity of the melting and boiling points of the first twenty elements.

The two curves have roughly the same shape; the elements appear at somewhat similar positions along the curves. As the atomic number increases from 1 to 10, the two curves reach maximum values which correspond to the carbon element. The curves for the next ten elements roughly show the same trend although they are of lesser magnitude. How do we explain these curves?

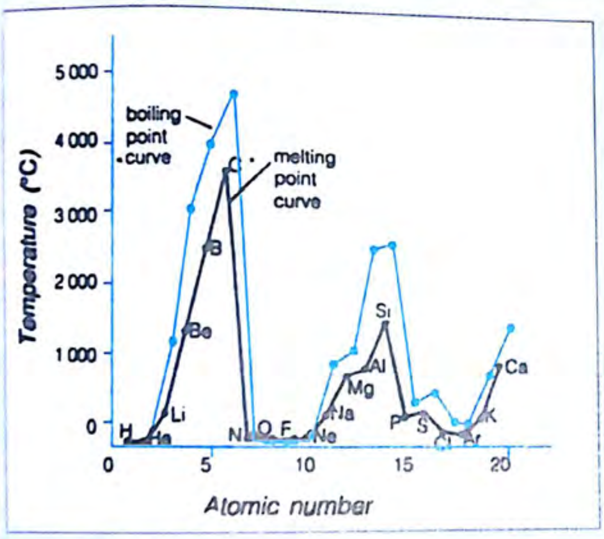
Elements in Groups 1, 2 and 3 have strong metallic bonds which increase in strength from Group 1 to Group 3 across any particular period. Their melting and boiling points also increase correspondingly since a lot of energy is needed to break these bonds. In Group 4, the elements show very high melting and boiling points. These elements have covalent bonds that interlink the atoms together, forming giant three-dimensional crystalline lattices like that of diamond. Very high temperatures are needed to overcome these bondings. Beyond Group 4, the curves plunge steeply. This is because elements in Groups 5, 6, 7 and 0, such as nitrogen, oxygen, fluorine and neon, exist as simple covalent molecules that are held together by weak intermolecular forces. Relatively less energy is required to break these weak bonds. This accounts for the low melting and boiling points of these elements which exist mainly as gases at room temperature.

Generally, within a period, the melting and boiling points of metallic elements increase from left to right, those of non-metallic elements decrease. Within a group, the melting and boiling points of metallic elements decrease down the group, and those of non-metallic elements increase.

Electrical and thermal conductivities These properties of elements decrease across the period and increase down the group. Thus, metals are good electrical and thermal conductors, and non-metals are poor electrical and thermal conductors.

Ionization energy This is the energy required to remove a valence electron from an atom of the element to form an ion. Generally, there is a tendency for ionization energies to increase across a period and decrease down a group.

Fig. 8.5 Periodicity of the melting points and boiling points.



Ionization Energy

The first ionization energy of an element is the amount of energy required to remove one electron from each atom in a mole of gaseous atoms, producing one mole of gaseous ions with a positive charge

Within a period, the first ionization energy tends to increase as atomic number increases. The ionization energy of an atom is affected by

- the distance of the outermost electron from the nucleus;
- the size of the positive nuclear charge; and
- the screening effect of the inner electrons.

Distance of the outermost electron from the nucleus Across the period, as the atomic number increases, the atomic radius decreases. As the distance decreases, the attraction of the positive nucleus for the electron will increase. More energy is needed to remove the outermost electron, thus the ionization energy increases.

Size of the positive nuclear charge As the nuclear charge increases, its attraction for the outermost electron increases, and so more energy is required to remove the outermost electron. Hence, the ionization energy increases.

Fig. 8.6 Variation in atomic radius with atomic number for the first twenty elements.

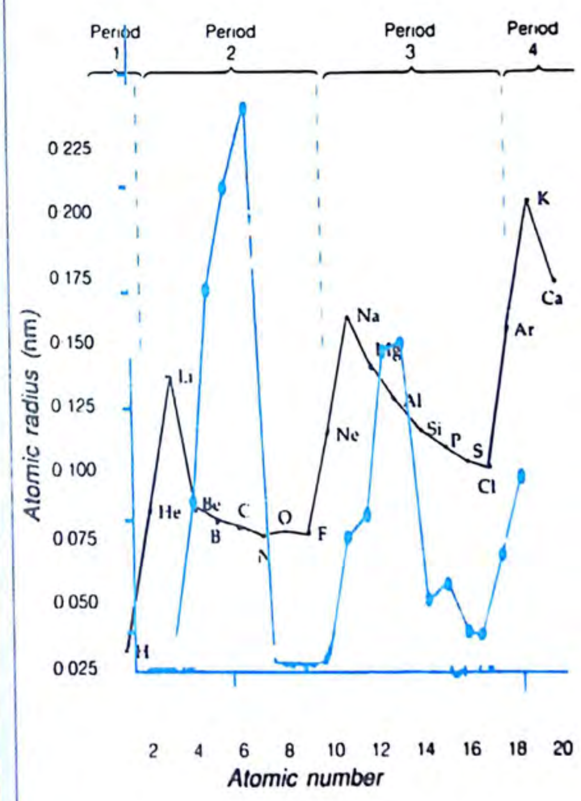
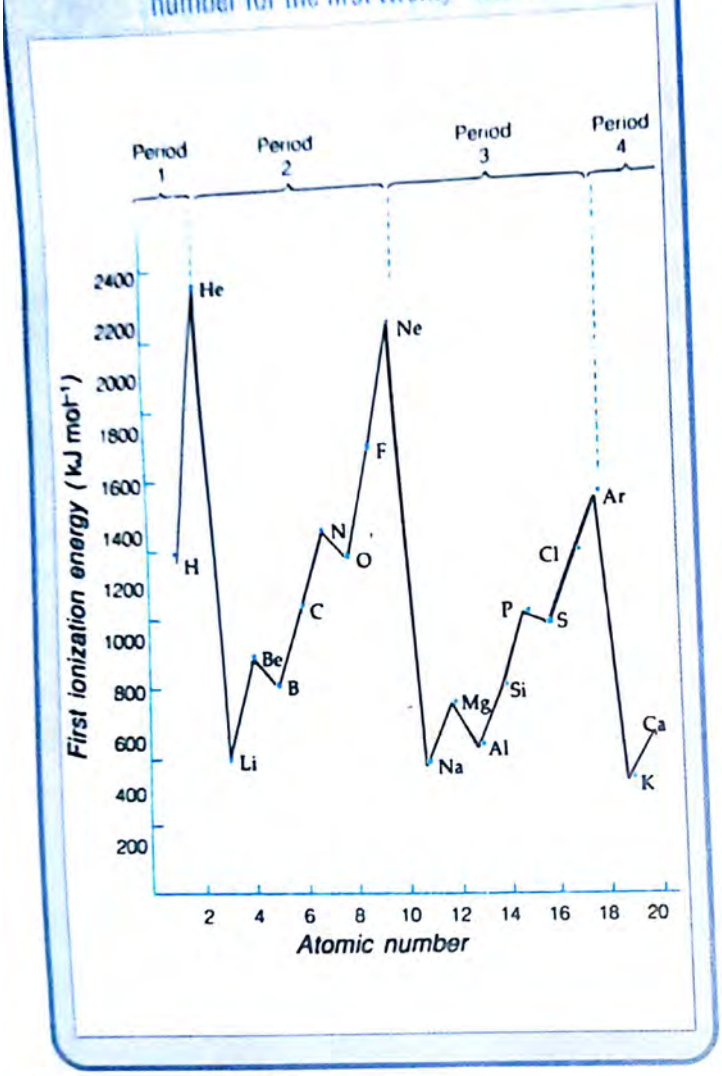


Fig. 8.7 Variation in ionization energy with atomic number for the first twenty elements.



Screening effect of the inner electrons The outermost electrons are repelled by all the other electrons in the atom, besides being attracted by the positively charged nucleus. Chemists say that the outermost electrons are screened (or shielded) from the nucleus by the repelling effect of the inner electrons. In general, however, the screening effect by the inner electrons is more effective, the closer these electrons are to the nucleus. The electrons in the same shell also exert a screening effect on one another but the effect is very small.

Moving from left to right across a period, there is a general rise in the first ionization energy. This is due to the fact that the nuclear charge is increasing across the period. This in turn causes a decrease in the atomic radius, i.e. a decrease in the distance of the outermost electron from the nucleus. The screening effect remains almost the same across a period since electrons are added to the same shell. This accounts for the increase in ionization energy across the period.

If we look more closely at fig. 8.7, we notice t there is a decrease in the first ionization energy as w move from beryllium to boron. Beryllium has a electronic configuration of $1s^2\ 2s^2$, while boron h an electronic configuration of $1s^2\ 2s^2 2p^1$. All t subshells in beryllium are filled, but the $2p$ subsh of boron contains only one electron. Just as fill electron shells are associated with extra stability (seen by the drop in the ionization energy from heli to lithium or from neon to sodium), there is also so extra energetic stability associated with complete filled subshells. This .means that the electron configuration of beryllium is more stable than that boron and hence has a higher ionization energy.

A similar situation also occurs as we move fro nitrogen to oxygen. The electronic configuration o nitrogen is $1s^2\ 2s^2\ 2p^1$, while that of oxygen is $1s^2\ 2$ $2p^4$. The half-filled $2p$ subshell in nitrogen with i evenly distributed charge (there is one electron in ea of the p orbitals) is more stable than the $2p$ subshe in oxygen which contains four electrons. Thu nitrogen has a higher first ionization energy.

These patterns are also repeated as we move fro magnesium to aluminium and from phosphorus t sulphur. The same explanations hold good in these cases too.

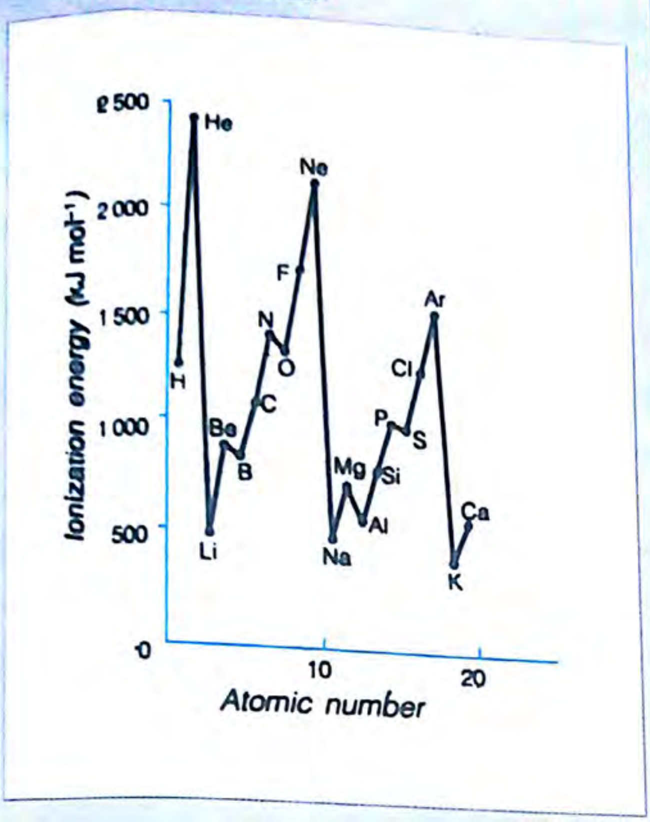
Electron Affinity

Ionization energy deals with the loss of electrons while *electron affinity* deals with the gain of electrons. Electron affinity(first) is the energy change that occurs when a gaseous atom acquires an electron to form a univalent negative ion. When the negative ion forms readily, a lot of energy is given off, i.e. electron affinity has a large negative value. Generally, electron affinities decrease (i.e. increase in negative value) from left to right across a period (except for the noble gases which have positive values), and increase (i.e. decrease in negative value) from top to bottom within a group. This is because atoms with smaller atomic radii tend to have a stronger attraction for electrons and so form negative ions more readily.

Electronegativity

The electronegativity of an atom is the power of that atom in a molecule to attract electrons. Th electronegativity values (based on Pauling's scale

Fig. 8.8 Variation of ionization energy with atomic number.



are plotted against atomic numbers in fig. 8.14.

Electronegativities of elements increase across a period but decrease down a group. The most electronegative elements are the reactive nonmetals (such as fluorine) in the top right hand corner of the Periodic Table, while the least electronegative elements are the reactive metals (such as caesium) in the bottom left-hand corner of the Periodic Table.

As we move from one element to the next across a period, the nuclear charge increases and the atomic radius decreases. These two factors combine to increase the electron-attracting power of the atom. This leads to an increase in the electronegativity of the element.

Variations in chemical properties

The chemical properties of the elements also exhibit a periodic variation, shown particularly by the properties of the compounds of the elements.

Groups Elements in the same group tend to resemble one another in their chemical behaviour because they have the same number of valence electrons. The four groups of elements which show great similarity in their chemical properties are

- Group 1 elements or the alkali metals;
- Group 2 elements or the alkaline earth metals;
- Group 7 elements or the halogens; and
- Group 0 elements or the noble gases.

The Group 1 elements have atoms with one valence electron each. They include metallic elements like lithium, sodium and potassium. They are characterized by their great reactivity and form very stable compounds in which an atom of the alkali metal loses one electron to form a positively charged univalent ion.

The Group 2 elements have atoms with two valence electrons each. They include metallic elements like beryllium, magnesium and calcium. They are less reactive than the Group 1 elements and each of their atoms forms a positively charged divalent ion by losing two electrons.

The halogens have atoms with seven valence electrons each. Each of their atoms only has to gain an electron to attain an octet structure. Hence, the halogens are very reactive and form negatively charged univalent ions readily. Their compounds, the halides, are very stable and unreactive.

The noble gases are colourless, monoatomic molecules. They are especially distinctive because of their unreactive nature. This property is due to their stable duplet or octet structures.

Periods There is a progressive change in the chemical properties of the elements across a period from left to right. The number of valence electrons in the atoms of the elements in the same period increases progressively by one from left to right. The metallic properties tend to decrease across each period, while the non-metallic properties tend to increase. Thus, the first three elements of each period, i.e. those of Groups 1 to 3, are metallic while those of Groups 4 to 7 are more non-metallic in character.

Period 3 elements and their compounds

Period 3 elements clearly show a progressive change in properties from left to right. On the left, we have sodium, magnesium and aluminium — typical metals that form mainly ionic compounds and basic oxides. On the right, we have the non-metals, phosphorus, sulphur and chlorine, which form covalent compounds and acidic oxides.

SUMMARY OF PROPERTIES OF ELEMENTS IN PERIOD3

Group	1	2	3	4	5	6	7	0
Element	Na	Mg	Al	Si	P (white)	S (rhombic)	Cl	Ar
Electronic configuration	2.8.1	2.8.2	2.8.3	2.8.4	2.8.5	2.8.6	2.8.7	2.8.8
Colour and state at 25°C	Silvery, soft solid	Silvery solid	Silvery solid	Black solid	Yellow solid	Yellow solid	Greenish-yellow gas	Colourle gas
Type of element	Metal	Metal	Metal	Metalloid	Non-metal	Non-metal	Non-metal	Non-met

Metallic (electropositive) character increasing

←

Non-metallic (electronegative) character increasing

→

Structure at 25 °C	Giant metallic lattice	Giant metallic lattice	Giant metallic lattice	Giant covalent lattice	Simple covalent molecules	Simple covalent molecules	Simple covalent molecules	Free atoms
M.p./ °C	98	650	660	1 410	44	119	−102	−189
Principal valency	+1	+2	+3	+4	+5	−2	−1	0
Density/g cm^{-3}	0.97	1.7	2.7	2.4	1.8	2.1	1.6	1.4

SUMMARY OF PROPERTIES OF CHLORIDES IN PERIOD 3

Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	(i) PCl_3 (ii) PCl_5	S_2Cl_2	Cl_2
Colour and state at 25 °C	White crystalline solid	White crystalline solid	White solid	Colourless fuming liquid	(i) Colourless liquid (ii) Pale yellow solid	Red liquid	Greenish-yellow gas
Structure at 25 °C	Giant ionic lattice	Giant ionic lattice	Giant ionic-covalent lattice	Covalent molecules	Covalent molecules	Covalent molecules	Covalent molecules
Bonding	Ionic	Mainly ionic	Mainly covalent	Covalent	(i) Covalent (ii) Solid ionic; vapour covalent	Covalent	Covalent
M.p./ °C	801	715	Sublimes at 183	—	(i) −90 (ii) Sublimes at 160	—	−101
B.p./ °C	1 420	1 400	—	59	(i) 76 (ii) Sublimes at 160	137	−34
Reaction with water	Dissolves to form neutral solution	Dissolves to form slightly acidic solution	Hydrolyzed to form $Al(OH)_3$ and HCl	Hydrolyzed completely to form SiO_2 and HCl	Hydrolyzed completely to form (i) H_3PO_3 and HCl (ii) H_3PO_4 and HCl	Decomposes to form S, SO_2 and HCl	Reacts with water to form HOC and HCl

← Acidic solutions →

SUMMARY OF PROPERTIES OF OXIDES IN PERIOD 3

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	(i) P_4O_6 (ii) P_4O_{10}	(i) SO_2 (ii) SO_3	(i) Cl_2O_7 (ii) Cl_2O
Colour and state at 25 °C	White solid	White solid	White solid	White solid	White solid	(i) Colourless liquid (ii) Colourless gas	(i) Colourless liquid (ii) Orange coloured gas
Structure at 25 °C	Giant ionic lattice	Giant ionic lattice	Giant covalent lattice	Giant covalent lattice	Covalent molecules	Simple covalent molecules	Simple diatomic covalent molecules
Bonding	Ionic	Mainly ionic	Partly ionic, partly covalent	Covalent	Covalent	Covalent	Covalent
M.p./°C	Sublimes at 1 275	2 645	2 050	1 710	(i) 25 (ii) 570	(i) −73 (ii) 17	(i) −91 (ii) −20
B.p./°C	—	3 550	3 000	2 250	(i) 172 (ii) 591	(i) −10 (ii) 45	(i) 82 (ii) 2
Acid-base property	Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Strongly acidic
Reaction with water	Forms strong alkali, NaOH	Forms weak alkali, $Mg(OH)_2$	None (insoluble)	None (insoluble)	Forms weak acids (i) H_3PO_3 (cold); H_3PO_4 (hot) (ii) $H_3PO_3 + H_3PO_4$	Forms weak acids (i) H_2SO_3 and (ii) H_2SO_4	Cl_2O_7 forms strong acid, $HClO_4$

FAMILIES OF ELEMENTS

Changes in the properties of elements down a group are gradual and less marked than those across a period. In fact, a marked similarity in chemical behaviour characterizes the elements in a group. Thus, elements in the same group may be said to belong to one *family*.

Elements in the same group show similar properties because their atoms have the same number of valence electrons. At the same time, certain properties of the elements in the same group show a gradual change with increasing atomic numbers. Such properties include physical properties like melting point and density which are affected by an increase in the mass of the atom. In the case of chemical properties, the reactivity may increase or decrease with increasing atomic number. For example, the oxidizing power of halogens decreases with increasing atomic number. Such a gradual change of property within a group is known as *group trend*. We shall discuss the main groups of elements, with reference to group trends in Groups 1, 4, 7 and 0.

Group 1

The familiar elements in Group 1 are sodium and potassium. They are univalent, since each of their atoms has only one valence electron. They ionize very readily to form positive ions by donating electrons and form electrovalent compounds. The ease with which they donate their outermost electrons also makes them good reducing agents. The reducing property increases down the group. They are very good conductors of electricity and are very electropositive, i.e. they have a marked tendency to donate electrons.

$$Na \rightarrow Na^+ + e^-$$

$$K \rightarrow K^+ + e^-$$

They react with cold water vigorously to liberate hydrogen gas and form alkalis; so they are known as the *alkali metals*. This reaction becomes increasingly vigorous on going down the group, i.e. as the atomic number increases. The oxides of alkali metals also dissolve in water to form very strong alkalis. On heating, their trioxonitrate(V) salts decompose with

Table 8.4 Some similarities and trends of the alkali metals.

Element	Symbol	Appearance at room temperature	Metal/ non-metal	Melting point/°C	Boiling point/°C	Reducing agent	Reacti with wa
Lithium	Li	Silvery solid	Metal	181	1 331	Increasing in strength ↓	Increasingly vigorous ↓
Sodium	Na	Silvery solid	Metal	98	890		
Potassium	K	Silvery solid	Metal	64	774		
Rubidium	Rb	Silvery solid	Metal	39	688		

difficulty to give oxygen and dioxonitrate(III) salts.

$$2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$$
$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$
$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$
$$2KNO_3(s) \xrightarrow{\text{heat}} 2KNO_2(s) + O_2(g)$$
$$2NaNO_3(s) \xrightarrow{\text{heat}} 2NaNO_2(s) + O_2(g)$$

Group 2

Calcium and magnesium belong to Group 2. They are divalent elements since each of their atoms has two valence electrons. They are electron donors, form electrovalent compounds and are reducing in nature.

$$Ca \rightarrow Ca^{2+} + 2e^-$$
$$Mg \rightarrow Mg^{2+} + 2e^-$$

Calcium reacts very slowly with cold water. This is hastened if the water is heated. Magnesium reacts with steam only. They both liberate hydrogen from water but while calcium forms a hydroxide, magnesium forms an oxide. Calcium oxide dissolves sparingly in water to form calcium hydroxide solution, which is a very weak alkali, while magnesium oxide is practically insoluble in water.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$
$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$
$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

Their trioxonitrate(V) salts decompose readily o heating to give the oxides, oxygen and the brown ga nitrogen(IV) oxide. Their trioxocarbonates(IV) a insoluble in water. They decompose on heating t give the oxides and carbon(IV) oxide.

$$2Ca(NO_3)_2(s) \xrightarrow{\text{heat}} 2CaO(s) + O_2(g) + 4NO_2(g$$
$$2Mg(NO_3)_2(s) \xrightarrow{\text{heat}} 2MgO(s) + O_2(g) + 4NO_2(g$$
$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$
$$MgCO_3(s) \xrightarrow{\text{heat}} MgO(s) + CO_2(g)$$

Group 3

The only familiar element in Group 3 is aluminiu It is trivalent since each of its atoms has three valenc electrons. Being a potential donor of three electron it is reducing in nature and forms electrovale compounds.

Table 8.5 Group trends exhibited by the elements in Group 4

Element	Symbol	Metal	Melting point/°C	Boiling point/°C	Electrical conductivity	Electro- negativi
Carbon	C (diamond) C (graphite)	Non-metal Non-metal	3 550 3 730	4 830 4 830	Non-conductor Good conductor	Decreases ↓
Silicon	Si	Metalloid	1 410	2 630	Semi-conductor	
Germanium	Ge	Metalloid	937	2 830	Semi-conductor	
Tin	Sn	Metal	232	2 270	Good conductor	
Lead	Pb	Metal	327	1 730	Good conductor	

$$Al \rightarrow Al^{3+} + 3e^-$$

Aluminium reacts with steam above 600 °C to liberate hydrogen. Aluminium oxide is insoluble in water. Aluminium hydroxide is prepared by precipitation. Both the oxide and the hydroxide are amphoteric in nature, i.e. they have both acidic and basic properties. They can form normal and complex salts with acids and alkalis respectively.

$$\underset{}{Al_2O_3(s)} + \underset{\text{acid}}{3H_2SO_4(aq)} \rightarrow \underset{\text{normal salt}}{Al_2(SO_4)_3(aq)} + 3H_2O(l)$$

$$Al_2O_3(s) + \underset{\text{alkali}}{2NaOH(aq)} + 3H_2O(l) \rightarrow \underset{\text{complex salt}}{2NaAl(OH)_4(aq)}$$

$$2Al(OH)_3(s) + \underset{\text{acid}}{3H_2SO_4(aq)} \rightarrow \underset{\text{normal salt}}{Al_2(SO_4)_3(aq)} + 6H_2O(l)$$

$$Al(OH)_3(s) + \underset{\text{alkali}}{NaOH(aq)} \rightarrow \underset{\text{complex salt}}{NaAl(OH)_4(aq)}$$

Aluminium trioxonitrate(V) decomposes to give the oxide, oxygen and nitrogen(IV) oxide gas. Aluminium trioxocarbonate(IV) does not exist.

$$4Al(NO_3)_3(s) \rightarrow 2Al_2O_3(s) + 3O_2(g) + 12NO_2(g)$$

Group 4

Group 4 elements include carbon, silicon, germanium, tin and lead. They are tetravalent, i.e. each of their atoms has four valence electrons. They tend to form covalent compounds.

The most important group trend is the change in the property of the elements from non-metallic to metallic on going down the group. There is also a corresponding decrease in electronegativity, i.e. the tendency to accept electrons.

The compounds of Group 4 elements exhibit two oxidation states, +2 and +4. The stability of the +2 state compounds increases and that of the +4 state compounds decreases on going down the group. Carbon and silicon form more stable +4 state compounds, while tin and lead form more stable +2 state compounds. This is illustrated by the various oxides of the Group 4 elements.

Oxidation +2	CO SiO GeO SnO PbO Stability increase →
	← Stability increases
Oxidation state +4	CO_2 SiO_2 GeO_2 SnO_2 PbO_2

Carbon and silicon form covalent compounds with hydrogen. The hydrides of carbon are very numerous and are known as *hydrocarbons*. Examples are methane, CH_4, ethane, C_2H_6, ethyne, C_2H_2, and benzene, C_6H_6. Examples of silicon hydrides are monosilane, SiH_4, disilane, Si_2H_6, and trisilane, Si_3H_8. Tin forms a tin(IV) hydride which is less stable than those of carbon and silicon.

Carbon does not react with water in any form, but silicon and tin react with steam at red heat to form the +4 state oxides and hydrogen.

$$Si(s) + 2H_2O(g) \rightarrow SiO_2(s) + 2H_2(g)$$

Lead forms lead(II) hydroxide with aerated water. Carbon, silicon and tin form +4 state oxides when heated strongly in air or oxygen. Lead forms lead(II) oxide on heating in air.

Group 5

Nitrogen and phosphorus belong to Group 5 and exhibit very similar properties. They are non-metals and show two common valencies of 3 and 5. They are electron acceptors and both form several oxides which have parallel characteristics. Examples are

- nitrogen(III) oxide, N_2O_3,
- phosphorus(III) oxide, P_4O_6,
- nitrogen(V) oxide, N_2O_5, and
- phosphorus(V) oxide, P_4O_{10}.

All these oxides are acidic and will combine with water to form acids. Nitrogen and phosphorus also form similar hydrides, NH_3 and PH_3, and chlorides, NCl_3 and PCl_3.

Group 6

Elements in Group 6 include oxygen and sulphur which are non-metals. They are electron acceptors and are oxidizing in nature. For example,

$$2Mg(s) + O_2(g) \rightarrow 2Mg^{2+}O^{2-}(s)$$
$$Fe(s) + S(s) \rightarrow Fe^{2+}S^{2-}(s)$$

Oxygen is slightly soluble in water while sulphur is insoluble. Both elements do not attack water in any form. Both oxygen and sulphur combine directly with hydrogen to yield water and hydrogen sulphide respectively.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

$$H_2(g) + S(s) \rightarrow H_2S(g)$$

Group 7

The elements in Group 7 are known as the *halogens*; the word halogen means *salt former*. They are the most reactive non-metals known and are so reactive with the other elements in the environment that, in nature, they exist mainly as salts rather than as free elements.

Halogens show great similarity in their properties because each of their atoms has the same number of valence electrons, i.e. seven. Some of these similarities are as follows.

1 They are all non-metals.

2 They exist as diatomic molecules.

3 They are coloured.

4 They ionize to form univalent negative ions which react with metallic ions to form electrovalent compounds.

5 Their hydrides are covalent gases at room temperature and dissolve readily in water to form acids.

The halogens also show a gradation in their properties from fluorine to iodine due to a progressive increase in

- their atomic numbers, and
- the complexity of their atomic structures.

Table 8.6 Structural properties of the halogens.

Halogen	F_2	Cl_2	Br_2	I_2
Atomic number	9	17	35	53
Electron shells	*K,L*	*K,L,M*	*K,L,M,N*	*K,L,M,N,O*
Electrons in outermost shell	7	7	7	7

The following trends are exhibited by the halogens as we go down the group from fluorine to iodine.

1 A change in state (at 25 °C) — fluorine and chlorine are gases; bromine is a liquid; and iodine is a solid.

2 Their colours become darker — fluorin yellow; chlorine is greenish yellow; bromine is red brown; and iodine is black.

3 Their melting and boiling points incre progressively.

4 The ease with which they ionize to form negat ions decreases, i.e. their electronegativity decrea This is reflected by a decrease in their chemi reactivity. For example,

- in their reactions with hydrogen to form hydrid — fluorine reacts explosively even in the da chlorine, slowly in diffuse light but explosively bright light; bromine, slowly in bright light; and iod slowly and incompletely even in bright light.
- in their displacement reactions, where ea halogen displaces the one following it from a soluti of the latter's salt as shown below:

$$F_2(g) + 2NaCl(aq) \rightarrow 2NaF(aq) + Cl_2(g)$$

$$Cl_2(g) + 2NaBr(aq) \rightarrow 2NaCl(aq) + Br_2(g)$$

$$Br_2(g) + 2NaI(aq) \rightarrow 2NaBr(aq) + I_2(g)$$

Group 0

The elements in Group 0 are known as *rare gases* *noble gases*. They have no bonding electrons in th outermost shell, hence the group is named zero. Th elements include helium, neon, argon, krypton, xeno and radon (which is radioactive). Because of the unreactivity, they form few compounds and exist freel (i.e. uncombined) as monoatomic molecules in th atmosphere. They constitute about 1% of th composition of air. Their unreactive nature can readil be understood from their electronic configuratio which satisfies the octet rule for stability.

The noble gases show very similar properti among themselves. They bear no resemblance to th halogens that come before them and the alkali metal that come after them and so mark the end of eac period very appropriately.

The noble gases exhibit a gradation in thei physical properties which is related to the progressiv increase in their atomic numbers. Thus, their meltin and boiling points increase while their ionizatio energies decrease down the group from helium t radon.

Table 6 … by the noble gases.

Elements	Symbol	Melting point/°C	Boiling point/°C	Ionization energy/kJ mol^{-1}
Helium	He	−270	−269	2 378
Neon	Ne	−249	−246	2 087
Argon	Ar	−189	−186	1 526
Krypton	Kr	−157	−152	1 357
Xenon	Xe	−112	−108	1 176
Radon	Rn	−71	−62	1 044

Transition Elements

Between Groups 2 and 3 is a collection of elements which show similar behaviour. These are the transition elements. Transition elements are all metals with typical metallic properties such as high tensile strength and high melting points. They have variable valencies; their ions are coloured and they have an ability to form complex ions.

Many transition metals like iron, copper, silver and gold are of commercial importance. Some like manganese and nickel are industrial catalysts.

Lanthanides (Rare-Earth Elements)

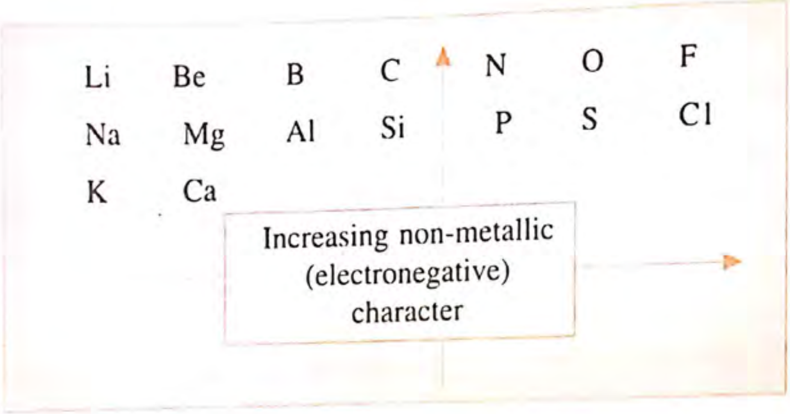
In the sixth period, there is a set of fifteen rare elements, beginning with lanthanum (La), and ending with lutetium (Lu). They show a great resemblance to one another and are classed together as the *lanthanides* or *rare-earth elements*.

Actinides and the Artificial Elements

The *actinides* are similar in many ways to the lanthanides. This set of elements is placed in the seventh period. It starts with actinium (Ac) and includes the well-known element uranium (U) which is used in nuclear reactions. The elements which have atomic numbers from 93 to 103 (i.e. the elements which come after uranium in the Periodic Table) are known as the *artificial elements*. They do not occur naturally but were discovered as products formed during nuclear reactions. They are unstable and disintegrate in a short time. Examples include plutonium (Pu), and curium (Cm).

SUMMARY

- The Periodic Law states that the properties of elements are a periodic function of the atomic number.
- The electronic configuration of an atom is the arrangement of electrons in successive electron shells. It is the basis for the arrangement of the elements in the Periodic Table.
- In the Periodic Table, elements with the same number of valence electrons are arranged in groups. Elements with the same number of electron shells are arranged in periods.
- Generally, the elements on the left of the Periodic Table are metals, i.e. they tend to lose electrons and form positive ions (electropositive). Elements on the right are non-metals, i.e. they tend to gain electrons and form negative ions (electronegative). Elements in the centre vary from metals to metalloids to non-metals. These elements tend to share electrons and form covalent compounds.



- The elements in the Periodic Table may be divided into blocks according to the orbital electrons that are responsible for the positions of the elements. The s block has s electrons in the outermost energy level, while the *p* block has both s and p electrons. The transition elements contain *d* electrons in addition to its *s* and *p* electrons, while the lanthanides and actinides contain *f* electrons in addition to the *s*, *p* and *d* electrons.
- Periodicity of the elements is the variation of their properties in a regular pattern down a group and across a period from left to right. Such patterns are shown by physical properties such as melting point, boiling point, ionization energy and electronegativty. Chemical properties, especially of the compounds of the elements, also show periodicity.
- Elements in the same group show very similar chemical properties since their atoms have the same number of valence electrons. These elements are regarded as members of a family.
- Gradual change in a certain property within a group, known as group trend, is due to the increase in the atomic numbers of elements down a group. Down a group,

  (a) electropositive character increases (electronegativity decreases);
  (b) reactivity of the elements in the metallic groups increases;
  (c) reactivity of the elements in the non-metallic groups decreases (elements in Group 0 are exceptions)

- Changes in properties across a period from left to right are more marked than those down a group. This is because the number of valence electrons in the atoms of elements increases progressively by one across the period from left to right.
- Atomic properties vary across and down the Periodic Table.

Atomic property	Across the Periodic Table	Down the Periodic Table
Atomic radius/nm	Decreases	Increases
Ionic radius/nm	Decreases till Group 3, peaks at Group 4, and then decreases again	Increases
First ionization energy/$kJ\,mol^{-1}$	Increases	Decreases
Electron affinity	Decreases	Increases
Electronegativity	Increases	Decreases

EXERCISES

1. Mendelév periodic table was arranged in order of their
A atomic numbers.
B molecular shapes and orbitals.
C increasing relative atomic mass.
D orbital configuration.

2. Elements in the same group of the periodic table have
A similar electronic configuration.
B similar orbital configuration.
C the same number of valence electrons.
D the same number of electrons.

3. *S*-block elements of the periodic table are made up of
A groups 1, 2, 3.
B groups 1 and 2.
C group 3.
D groups 3 to 7.

4. Special properties of the transition elements are as a result of
A ability to produce coloured ions.
B ability to have variable valencies.
C ability to posses partially filled *d*-orbitals.
D inert octect electrons.

5. Which of the following decrease across the period?
A Atomic size B Electron affinity
C Electronegativity D Inert tendencies

6. Important properties of elements which show periodicity are
A melting and boiling points.
B electrical conductivities.
C ionization energies and atomic size.
D electronegativities.

7. Ionization energy of an atom is affected by
A distance of the outermost electron from the nucleus.
B the size of the positive nuclear charge.
C the screening effect of the inner electrons.
D solvent medium.

8. The following groups of elements show great similarity in their chemical properties except
A group 1.
B group 7.
C group 0.
D group 5.

9. Which of the following is insoluble in water?
A MgO B P_4O_{10}
C K_2O D N_2O_3

10. All these properties belong to the halogens except
A they are all non-metals.
B they exist as diatomic molecules.
C they are coloured.
D they do not ionize to form univalent negative ions.

11. Which of the noble gases has the greatest ionization energy?

A He B Ar
C Xe D Kr

12. Which of these characters does not belong to the first transition elements?

A Ability to form coloured ions.
B Ability to show variable valencies.
C Inability to form complex ions.
D Ability to be used as catalysts.

13. Which of the actinides is commonly used as a nuclear fuel?

A Uranium B Actinium
C Thorium D Palladium

14. What is the chemical formula for Tungsten?

A Ti B W
C Ir D Y

15. In the Periodic Table, elements are arranged according to their

A atomic masses.
B mass numbers.
C atomic numbers.
D electronegativities.
E valence electrons.

16. Energy required to remove the most loosely bound electron from a gaseous atom to form the gaseous ion is

A gaseous energy.
B ionization energy.
C dissociation energy.
D atomization energy.
E electrical energy.

17. Elements in the same group in the Periodic Table have the same

A number of valence electrons.
B number of shells.
C atomic mass.
D atomic number.
E electronic configuration.

18. (a) What is the atomic number of an element?
(b) Define the Periodic Law of elements.
(c) The atomic number of an element X is 14, and its relative atomic mass is 28. How many neutrons does an atom of X contain? Wh the electronic distribution in an atom of Will X react in an electrovalent or coval manner?
Give reasons for your answer.

19. Write briefly the characteristics of:
(a) transition elements;
(b) halogens;
(c) actinides and artificial elements.
Give 4 examples of each group.

20. (a) From the elements carbon, oxygen, neo sodium, magnesium, aluminium, sulph chlorine and argon, name two which are
(i) in the same group of the Periodic Tab
(ii) in the same period of the Periodi Table,
(iii) metals,
(iv) able to form acidic oxides,
(v) not able to form compounds readil
(b) Give the names and formulae of any tw compounds each containing three of th elements in the list given in (a).
(c) Give the formulae of three ions which hav the same electronic configuration as neon.

21. The table below represents part of the Periodic Table with only the atomic numbers of the elements listed. The letters given are not the symbols of the elements. Use these letters to answer the following questions.

$_1$A							$_2$B
$_3$C	$_4$D	$_5$E	$_6$F	$_7$G	$_8$H	$_9$I	$_{10}$J
$_{11}$K	$_{12}$L	$_{13}$M	$_{14}$N	$_{15}$O	$_{16}$P	$_{17}$Q	$_{18}$R

(a) Which are the alkali metals, alkaline earth metals, halogens and noble gases?
(b) Give the electronic configurations of all the elements in Period 2. State how the configurations affect the chemical properties of the elements across the period.
(c) Which are the most reactive metallic and non-metallic elements? Which group will react with oxygen to give
(i) covalent compounds with formula XO_2?

(ii) electrovalent compounds with formula X_2O?

(d) The element *Q* reacts with *C* and *F* to form an ionic solid and a covalent liquid respectively. Suggest the formulae for these products and compare

(i) their solubilities in water,

(ii) their electrical conductivities when molten or fused,

(iii) the types of bonding involved.

(e) Which chlorides in Period 3 react with water? What are the products formed for each case?

22. Without referring to the Periodic Table, name the elements, give their electronic structures and name the groups in the Periodic Table to which elements with the following atomic numbers belong: 3, 9, 12, 17 and 20.

23. Explain briefly, in terms of electronic configurations, the occurrence of periods, groups and transition series in the Periodic Table.

24. (a) Define atomic radius, first ionization energy and electronegativity.

(b) Discuss their trends across the periods and down the groups in the Periodic Table.

25. Using fluorine as an example, explain what is meant by

(a) the four quantum numbers.

(b) the Pauli Exclusion Principle.

(c) Hund's rule.

9 MASS AND VOLUME RELATIONSHIPS IN REACTIO

STOICHIOMETRY OF REACTIONS

IUPAC CONVENTIONS AND S.I. UNITS

Quantity	*Symbol*	*Units*
Mass	m	g or kg
Molar Mass	M	g mol^{-1}
Volume	V	cm^3, dm^3
Molar Volume	Vm	dm^3 mol^{-1}
Amount	n	mol
Molar Concentration	c	mol dm^{-3}
Mass Concentration	p	g mol^{-1}
Avogadro's Constant	L	mol^{-1}
Number	N	—
NB Molar Mass	M	g mol^{-1}

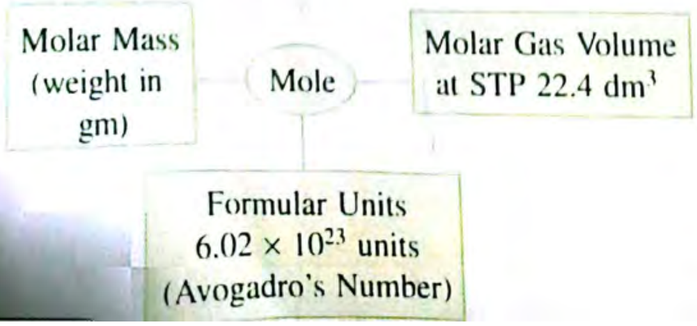
Relationships between Quantities

$$M = \frac{m}{n} \qquad \text{Molar Mass} = \frac{\text{Mass}}{\text{Amount}}$$

b) $$\text{Molar Volume} = \frac{\text{Volume}}{\text{Amount}} = \frac{V}{N}$$

c) $$\text{Avogadro's Constant} = L = \frac{N}{n} = \frac{\text{Number}}{\text{Amount}}$$

A mole is the amount of substance containing Avogadro's number of formular units.



The formula of a compound tells us the elemen present in it. It also tells us the amounts of the differe elements present in it. These amounts are usual expressed as a mole ratio of the different elements i the compound.

Formula		Na_2SO_4			
Elements present	Sodium		Sulphur		Oxyg
Number of moles	2		1		4
Mole ratio	2	:	1	:	4

A balanced equation of a chemical reaction te us the relationship of the amounts of the reactants one another and to the products. This relations between the amounts of reactants and products known as the *stoichiometry of the reaction*.

Mole ratios and mass relationship

A mole is the amount of substance which contain many elementry particles as there are carbon ator 0.012 kg of carbon-12.

A mole is the amount of substance which cont as many formular units as their atoms in 12 gra carbon-12.

The numerical coefficients of a balanced equa represent the numbers of moles of reactants products. From these coefficients, we get the ratio of the reactants and products in a reactior

Equation 1

$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2}$$

	$H_2SO_4(aq)$		$2H^+(aq)$		SO_4^{2}
Number of moles	1		2		1
Mole ratio	1	:	2	:	1

In the ionization reaction in equation 1, one of tetraoxosulphate(VI) acid produces two mo hydrogen ions and one mole of tetraoxosulphat ions in solution

The mole ratio in which reactants combine and products are formed gives the stoichiometry of the reaction

The reactants and products in a chemical reaction may be ions, atoms and/or molecules. The mole quantities involved in the reaction are not affected by the kind of particles present.

Since a mole represents the molar mass of a substance in grams, we can also evaluate the reacting mass relationships between the reactants and products from a balanced equation.

Equation 2

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

	$Mg(s)$	$2HCl(aq)$	$MgCl_2(aq)$	$H_2(g)$
Number of moles	1	2	1	1
Mole ratio	1 :	2 :	1 :	1
Molar mass	24 g	36.5 g	95 g	2 g
Reacting mass	24 g	(2 × 36.5) g	95 g	2 g

From equation 2, we see that

Amount × Molar mass = Reacting mass

$$\text{Amount} = \frac{\text{Reacting mass}}{\text{Molar mass}} = \frac{n}{M}$$

If the reacting mass or the number of moles of any one of the substances in a reaction is given, we can calculate the reacting masses or the numbers of moles of the others from a balanced equation of the reaction.

EXAMPLES

1 *Calculate the number of moles of calcium chloride, $CaCl_2$, that can be obtained from 25 g of limestone, $CaCO_3$, in the presence of excess hydrogen chloride, HCl.* (Ca = *40*, C = *12*, O = *16*, H = 1, Cl = *35.5*)

quation of reaction

$$CO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

From the equation,

1 mole of $CaCO_3$ yields 1 mole of $CaCl_2$.

Number of moles of $CaCO_3$ reacted

$$= \frac{\text{Reacting mass}}{\text{Molar mass}} = \frac{25\text{ g}}{100\text{ g mol}^{-1}} = 0.25\text{ mol}$$

$\therefore$ 0.25 mole of $CaCO_3$ yields 0.25 mole of $CaCl_2$.

2 *What mass of lead(II) trioxonitrate(V),* $Pb(NO_3)_2$, *would be required to yield 9 g of lead(II) chloride,* $PbCl_2$, *on the addition of excess sodium chloride solution,* NaCl? (Pb = *207*, N = *14*, O = *16*, Na = *23*, Cl = *35.5*)

Equation of reaction

A balance equation tells us the relationship of the amounts of reactants to one another and to the products.

$$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$$

	$Pb(NO_3)_2(aq)$	$2NaCl(aq)$	$PbCl_2(s)$	$2NaNO_3(aq)$
	1 mole	2 mole	1 mole	2 mole
Molar mass	331 g		278 g	

278 g of $PbCl_2$ are obtained from 331 g of $Pb(NO_3)_2$.

$$\therefore 9\text{ g of } PbCl_2 \text{ are obtained from } \frac{9 \times 331}{278}$$

$$= 10.7\text{ g of } Pb(NO_3)_2.$$

3 *Determine the mass of carbon(IV) oxide,* CO_2, *produced on burning 104 g of ethyne,* C_2H_2. (C = *12*, O = *16*, H = *1*)

Equation of reaction

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$$

	$2C_2H_2(g)$		$4CO_2(g)$
Molar mass	26 g		44 g
	2 mol	:	4 mol

$$\text{Amount of } C_2H_2 \text{ reacted} = n = \frac{m}{M}$$

$$= \frac{104\text{ g}}{26\text{ g mol}^{-1}} = 4\text{ mol}$$

From the equation,

2 moles of C_2H_2 produce 4 moles of CO_2.

$$\therefore 4 \text{ moles of } C_2H_2 \text{ produce } \frac{4}{2} \times 4 = 8 \text{ moles of } CO_2$$

$$= 8 \times 44 = 352\text{ g of } CO_2$$

$\therefore$ 352 g CO_2 are produced by burning 104 g of C_2H_2.

Reactions involving gas volumes

Equal volumes of gases at a given temperature and pressure contain the same number of molecules. We can calculate the volumes of gases from a balanced chemical equation, provided that the gases are under the same conditions of temperature and pressure. The coefficients of gaseous reactants and products in a balanced equation give the mole relations as well as the volume relations among the gases. In the following equation,

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

$$4 \text{ vol} : 5 \text{ vol} : 4 \text{ vol} : 6 \text{ vol}$$
$$4 \text{ mol} : 5 \text{ mol} : 4 \text{ mol} : 6 \text{ mol}$$

4 volumes of ammonia react with 5 volumes of oxygen to yield 4 volumes of nitrogen(II) oxide and 6 volumes of water vapour.

One mole of any gas at s.t.p. molar volume occupies 22.4 dm^3. Thus, we can calculate the volumes, masses, moles and number of molecules of gaseous reactants and products from a balanced chemical equation.

EXAMPLES

1 *In the industrial preparation of hydrogen trioxonitrate(V) acid, ammonia gas,* NH_3, *is burned in oxygen,* O_2, *in the presence of a catalyst according to the following equation:*

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

If 260 cm^3 *of* NH_3 *are burned completely, what volume of (a)* O_2 *is used up? (b)* NO *is produced?*

Equation of reaction

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$
$$4 \text{ mol} : 5 \text{ mol} : 4 \text{ mol} : 6 \text{ mol}$$
$$1 \text{ mol} : \frac{5}{4} \text{ mol} : \frac{4}{4} \text{ mol} : \frac{6}{4} \text{ mol}$$

260 cm^3 of NH_3 will use up $\frac{5}{4} \times 260 = 325 \text{ cm}^3 \; O_2$.

260 cm^3 of NH_3 will produce $\frac{4}{4} \times 260 = 260 \text{ cm}^3$ NO.

2 *20 cm^3 of CO are mixed and sparked with 200 cm^3 of air containing 21% of* O_2*. If all the wlumes are measured at s.t.p., calculate the total volume of the resulting gases.*

In 200 cm^3 of air,

volume of $O_2 = \frac{21}{100} \times 200 = 42 \text{ cm}^3$,

volume of N_2 and rare gases = 200 − 42 = 158

Equation of reaction

	2CO(g)	+	O_2(g)	→ 2CO
Volume ratio	2	:	1	: 2
Before sparking	20 cm^3		42 cm^3	0
Reacting volume	20 cm^3		10 cm^3	20
After sparking	0 cm^3		32 cm^3	20

∴ volume of resulting gases = (32 + 20 + 158)
= 210 cm^3.

3 *Calculate the wlume of carbon(IV) oxide,* *27 °C and* 750 mm Hg *pressure which could* *obtained by heating 10 g of limestone,* (CaCO$_3$ = 100, CO$_2$ = 44, molar volume of a at s.t.p. = 22.4 dm^3)

Equation of reaction

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

From the equation,
1 mole of $CaCO_3$ yields 1 mole of CO_2.

$$\text{Amount of } CaCO_3 \text{ reacted} = \frac{10 \text{ g}}{100 \text{ g mol}^{-1}}$$

$$= n = \frac{m}{M} = 0.1$$

∴ 0.1 mole of $CaCO_3$ yields 0.1 mole of
At s.t.p., 1 mole of CO_2 occupies 22.4 dm^3.
0.1 mole of CO_2 occupies 22.4 dm^3.

Using the gas equation, $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$, whe

p_1 = s.p. = 760 mm Hg p_2 = 750 mm Hg
T_1 = s.t. = 273 K $T_2 = (27 + 273) \text{ K} = 30$
V_1 = 22.4 dm^3 or 2 240 cm^3

$$V_2 = \frac{p_1V_1T_2}{p_2T_1}$$
$$= \frac{760 \times 2\,240 \times 300}{750 \times 273} = 2\,494 \text{ cm}^3$$

∴ volume of CO_2 liberated = 2 494 cm^3

STUDY OF STOICHIOMETRY

Stoichiometry is the art of measuring chemical elements in quantitative relationship in chemical reactions. It is ordinary chemical arithmetic.

Experiments can be designed to study the stoichiometry of reactions. The types of reaction that are commonly studied include

- precipitation reactions;
- displacement of hydrogen from acids;
- displacement of metallic ions;
- synthesis of metallic oxides; and
- reduction of metallic oxides.

Titration experiments to study stoichiometry of reactions will be done later in this chapter.

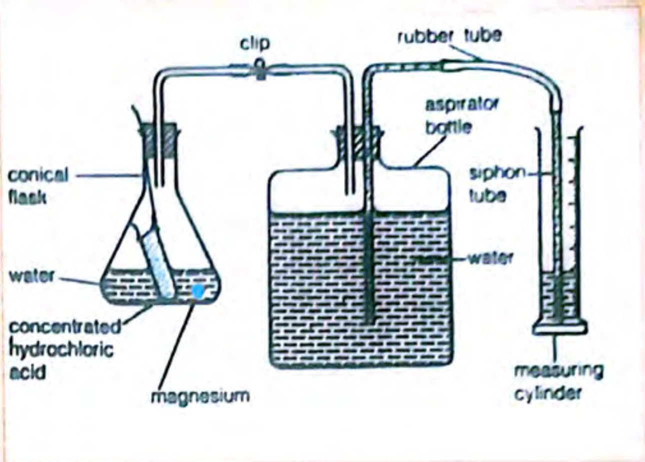
Stoichiometry of a precipitation reaction

Experiment 9.1 is designed to study the stoichiometry of a precipitation reaction. When solutions of barium chloride and potassium tetraoxochromate(VI) are mixed, a precipitate of barium tetraoxochromate(VI) forms instantly. By using molar solutions of the reactants, it is possible to find the ratio in which they combine.

Stoichiometry of the displacement of hydrogen from an acid

Magnesium readily displaces gaseous hydrogen from dilute hydrochloric acid. To study the stoichiometry of this reaction, we react a known mass of magnesium with an excess of the acid, and measure the volume of hydrogen liberated.

Fig. 9.1 Determining the stoichiometry of the displacement of hydrogen from hydrochloric acid.



Set up the apparatus as shown in fig. 9.1. Equalize the water levels in the aspirator bottle and the cylinder by raising or lowering the cylinder. Record the volume of water in the cylinder. Tilt the conical flask and let the acid react with the magnesium. The hydrogen gas given off will displace its own volume of water from the bottle into the cylinder. Allow the apparatus to cool and equalize the water levels in the cylinder and bottle. Record the volume of water in the cylinder. The difference in the two volumes gives the volume of the hydrogen gas evolved. Note the atmospheric pressure and room temperature.

Specimen readings

Mass of magnesium = 0.36 g

Volume of hydrogen displaced = 378 cm^3

Room temperature = 25 °C

Atmospheric pressure = 755 mm Hg

Molar mass of Mg = 24 g

$$\text{Amount of Mg} = n = \frac{m}{M} = \frac{0.36\ \text{g}}{24\ \text{g mol}^{-1}} = 0.016\ \text{mol}$$

From the readings given, we can calculate the mole ratio of the magnesium and hydrogen in this reaction in the following way:

Let V_2 be the volume of hydrogen obtained experimentally at s.t.p.

$T_1 = (25 + 273)\ \text{K} = 298\ \text{K}$ $\quad T_2 = \text{s.t.} = 273\ \text{K}$

$p_1 = 755\ \text{mm Hg}$ $\quad p_2 = \text{s.p.} = 760\ \text{mm Hg}$

$V_1 = 378\ \text{cm}^3$

$$\therefore\ V_2 = \frac{p_1V_1T_2}{p_2T_1} = \frac{755 \times 378 \times 273}{760 \times 298} = 344\ \text{cm}^3$$

Experiment 9.1 To determine the mole ratio in the reaction between barium chloride solution and potassium tetraoxochromate(VI) solution.

Method Prepare 1 molar solutions of barium chloride and potassium tetraoxochromate(VI). To 7 different test-tubes of the same size, add 5 cm^3 of barium chloride solution. Then add varying amounts of the potassium tetraoxochromate(VI) solution as shown in fig. 9.2. Shake the test-tubes to mix the reactants. Allow the precipitate to settle and measure the height of the precipitate in each test-tube.

Record your results and plot a graph of height of precipitate against volume of potassium tetraoxochromate(VI).

Result The amount of precipitate formed increases with increasing volumes of potassium tetraoxochromate(VI), from test-tubes A to E, i.e. up to a volume of 5 cm^3. Further increase in volume of potassium tetraoxochromate(VI) does not result in an increase in the amount of precipitate, as can be seen from the graph.

The point at which barium chloride and potassium tetraoxochromate(VI) are reacting in their stoichiometric amounts is given by test-tube E, the test-tube in which the height of the precipitate reaches its maximum value first.

In test-tubes A to D, the barium chloride is in excess. In test-tubes F and G, the potassium tetraoxochromate(VI) is in excess. This can be seen by the yellow colour of the solution in these two test-tubes.

In test-tube E, 5 cm^3 of 1 mol$BaCl_2$ react with 5 cm^3 of 1 mol K_2CrO_4.

Reacting compound	$BaCl_2$	K_2CrO_4
Reacting number of moles	$\frac{5}{1\,000}$ mole	$\frac{5}{1\,000}$ mole
Mole ratio	1	1

Conclusion One mole of barium chloride reacts with one mole of potassium tetraoxochromate(VI) to form barium tetraoxochromate(VI). Thus, the equation of the reaction can be written as follows:

$$BaCl_2(aq) + K_2CrO_4(aq) \rightarrow BaCrO_4(s) + 2KCl(aq)$$

Fig. 9.2 Determining the stoichiometry of the reaction between barium chloride and potassium tetraoxochromate(VI)

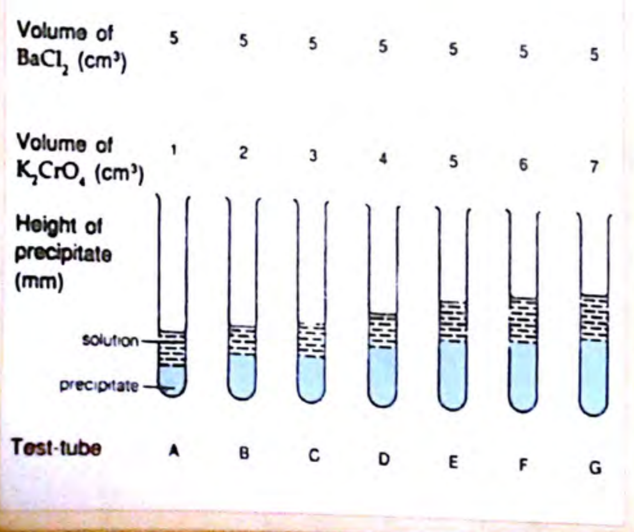
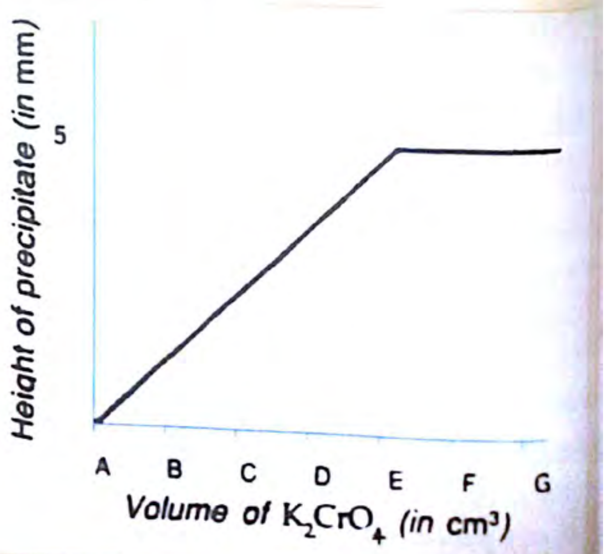


Fig. 9.3 [illegible] of precipitate formed against volume of potassium tetraoxochromate(VI).



Molar volume of any gas = 22.40 dm^3
i.e., 22 400 cm^3 = 1 mole H_2
∴ The amount of H_2 gas in 1 mole of H_2

$$n = \frac{V}{m} = \frac{344}{22\,400} \times 1$$

$$n = 0.015 \text{ mole of } H_2$$

∴ 0.015 mole of Mg displaces 0.015 mole of H_2 from the acid.

Reacting substance	Hydrogen		Magnesium
Amount of moles	0.015 mol		0.015 mol
Mole ratio	1	:	1

One mole of magnesium atoms liberates one mole of hydrogen molecules from dilute hydro chloric acid (i.e. it displaces two moles of hydrogen atoms from the acid). The equation of the reaction can now be written.

Equation

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Mole ratio 1 : 2 : 1 : 1

Stoichiometry of the displacement of copper ions by zinc metal

Zinc displaces copper(II) ions from a solution of copper(II) tetraoxosulphate(VI). To study the stoichiometry of this reaction, we find the mass of metallic copper displaced by a known mass of zinc dust.

Place a known amount of zinc dust in a test-tube. Pour concentrated copper(II) tetraoxosulphate(VI) solution, a little at a time, onto the zinc dust (with intermittent shaking of the tube) until the latter is completely replaced by a reddish-brown deposit of copper. Add an excess of the copper(II) tetraoxosulphate(VI) solution to ensure that all the zinc dust has reacted. Filter the mixture in the test-tube. Dry the copper residue on the filter paper and find its mass.

Specimen readings and calculation

Mass of zinc dust	= 3.93 g
Mass of copper deposits	= 3.84 g

Reacting element	Zinc		Copper
Reacting mass	3.93 g		3.84 g
Molar mass	65 g		63.5 g
Number of moles	$\frac{3.93}{65}$ = 0.06	:	$\frac{3.84}{63.5}$ = 0.06
Mole ratio	1		1

One mole of zinc atoms displaces one mole of copper(II) ions from a solution of copper(II) salt in the following way:

Equation

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Mole ratio 1 : 1 : 1 : 1

Stoichiometry of the synthesis and the reduction of metallic oxides

We can carry out experiments 3.2 and 3.4 to study the stoichiometry of the synthesis and the reduction of a metallic oxide respectively.

Results obtained from experiment 3.2 show that 1 mole of magnesium atoms combines with 1 mole of oxygen atoms to give 1 mole of magnesium oxide molecules. From this result we get,

$$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$$

i.e. $$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

Results obtained from experiment 3.4 show that (for example *A*),

3.55 g of copper(II) oxide is reduced to 2.81 g of copper. Since

3.55 g copper(II) oxide $= \frac{3.55}{79.5} = 0.045$ mole

2.81 g copper $= \frac{2.81}{63.5} = 0.045$ mole

1 mole of copper(II) oxide is reduced to 1 mole of copper. From this, we get

$$CuO(s) \rightarrow Cu(s) + \frac{1}{2}O_2(g)$$

i.e. $$2CuO(s) \rightarrow 2Cu(s) + O_2(g)$$

VOLUMETRIC ANALYSIS

One important area of chemistry is the analysis of substances to determine their composition, either qualitatively or quantitatively.

In qualitative analysis, we identify the elements and compounds that are present in a sample of a given substance. In quantitative analysis, we calculate the amount or quantity of an element or compound present in a given sample.

There are two approaches to quantitative analysis, namely *volumetric analysis* and *gravimetric analysis*. Volumetric analysis is based on volume measurements of solutions while gravimetric analysis is based on direct mass measurements of the substances. Volumetric analysis is commonly used as it is faster and more convenient, although less accurate, than the gravimetric method.

Titration

Titration is the method employed in volumetric analysis. In this method, a solution from a graduated vessel is added to a known volume of a second solution until the chemical reaction between the two is just completed. This is shown by a colour change in the resulting solution or in an added indicator.

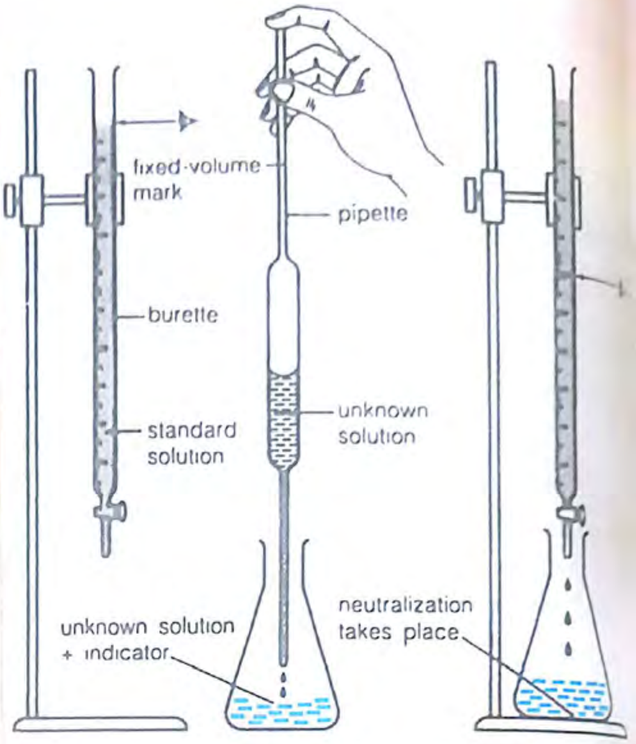
In any titration, a *standard solution*, i.e. one with a concentration which is accurately known, must be used to react with a solution of unknown concentration. The reacting volumes of the solutions are then used to calculate the unknown concentration of the solution.

The concentration of a solution is the amount of solute in 1 dm^3 or 1000 cm^3 of the solution. It can be expressed as mol dm^{-3} or g dm^{-3}.

Table 9.1 Indicators for acid-base titrations

Acid and base	Indicator
Strong acid and strong base	Any indicator
Strong acid and weak bases or trioxocarbonate(IV)	Methyl orange
Weak acid and strong base	Phenolphthalein
Weak acid and weak base	No suitable indicator

Fig. 9.4 Acid-base titration



At this level, volumetric analysis usually includ titrations of

acid against base or trioxocarbonate(IV);
oxidizing agent against reducing agent;
one substance against another substance, givi a precipitate.

Acid-base or acid-trioxocarbonate(IV) titratio are actually neutralization reactions. We use indicato to determine the end-point of this type of titratio

The concentration of a solution in mol dm^{-3} the molar concentration.

In titrations, the concentrations of the reacti solutions give an accurate picture of the quantitati behaviour of the reacting particles.

The following equations are useful in calculatio involving concentration.

$$\text{Amount of a substance} = \frac{\text{Number of particles}}{6.02 \times 10^{23}} = \frac{N}{L} = \text{mo}$$

$$\text{Amount of a substance} = \frac{\text{Mass of substance}}{\text{Molar mass}} = \frac{N}{M} = \text{mo}$$

$$= \frac{\text{Mass of substance}}{\text{Mass of 1 mole of substance}} \frac{m}{M} = \text{g mol}^{-1}$$

e 9.2 The relationship between the molar concentration and mass concentration of some common substances.

stance	Molar mass in g	Molar concentration in mol dm^{-3}	Mass concentration in g dm^{-3}	Number of specified entities
HCl	36.5	1	36.5	6.02×10^{23}
HCl	36.5	0.1	36.5	$0.1 \times 6.02 \times 10^{23}$
NO_3^-	62	1	62	6.02×10^{23}
O_3^-	62	0.25	15.5	$0.25 \times 6.02 \times 10^{23}$
H_2SO_4	98	1	98	6.02×10^{23}
SO_4	98	0.5	49	$0.5 \times 6.02 \times 10^{23}$
Na_2CO_3	106	1	106	6.02×10^{23}
Na_2CO_3	106	2	212	$2 \times 6.02 \times 10^{23}$

olar olution

ution of a compound is one which
e mole or the molar mass of the
in one dm^3 of the solution.

The molar masses of sodium and potassium hydroxides are 40 g and 56 g respectively. Therefore, a molar solution of sodium hydroxide contains 1 mole or 40 g of the hydroxide in 1 dm^3 of the solution, while a molar solution of potassium hydroxide contains 1 mole or 56 g of the hydroxide in 1 dm^3 of the solution.

From table 9.2, we get the following relationships which are helpful in calculations involving molarity.

1 By definition, molar concentration C = mol dm^{-3}
2 By definition, number of specified entities per dm^3
= mol dm^{-3} × $6.02 \times 10^{23} \times 6.02 \times 10^{23}$
3 Concentration (g dm^{-3})
= mol dm^{-3} × molar mass
= molarity (M) × molar mass

EXAMPLES

1 *Calculate (a) the mass of anhydrous sodium trioxocarbonate(IV),* Na_2CO_3, *present in 300* cm^3 *of 0.1 mol dm*$^{-3}$; *(b) the number of* Na_2CO_3 *particles present in the solution.* (Na = *23*, C = *12*, O = *16*)

(a) Molar concentration of the Na_2CO_3 solution
= 0.1 mol dm^{-3}
Molar mass of Na_2CO_3 = 106 g mol^{-1}
Mass concentration (g dm^{-3})
= molar concentration × molar mass
0.1 mol dm^{-3} × 106 g mol^{-1} × m
0.1 mol dm^{-3} × 106 g mol^{-1} = 10.6 g dm^{-3}
This means 1 000 cm^3 of 0.1 M solution contain 10.6 g of Na_2CO_3.
∴ 300 cm^3 of 0.1 M solution contain

$$\frac{300 \times 10.6}{1\,000} = 3.18 \text{ g of } Na_2CO_3.$$

(b) Number of Na_2CO_3 particles N= nL
= Amount × 6.02×10^{23}
= $0.1 \times 6.02 \times 10^{23}$
N = 0.602×10^{23}
This means 1 000 cm^3 of 0.1 M solution contain 0.602×10^{23} Na_2CO_3 particles.
∴ 300 cm^3 of 0.1 mol dm^{-3} solution contain

$$\frac{300 \times 0.602 \times 10^{23}}{1\,000} = 0.181 \times 10^{23} \text{ particles of } Na_2CO_3.$$

2 *Calculate the volume of 0.25 mol dm*$^{-3}$ *solution of tetraoxosulphate(VI) acid,* H_2SO_4, *that will contain a mass of 4.5* g *of the raw acid.* (H = *1*, S = *32*, O = *16*)
Molarity of the given H_2SO_4 = 0.25 M
Molar mass of H_2SO_4 = 98 g mol^{-1}
Mass concentration (g dm^{-3})
= molar concentration × molar mass
$e = C \times M = 0.25 \times 98 = 24.5$ g dm^{-3}
This means 24.5 g H_2SO_4 are combined in 1 000 cm^3.

$$4.5 \text{ g } H_2SO_4 \text{ are contained in } \frac{4.5 \times 1\,000}{24.5} = 184 \text{ cm}^3.$$

i.e. 184 cm^3 of 0.25 mol dm^{-3} solution of H_2SO_4 contain 4.5 g of the raw acid.

3 *Calculate the volume of hydrogen chloride gas at s.t.p. that would yield 1.2 dm³ of 0.15 mol dm⁻³ aqueous hydrogen chloride solution. (Molar volume of all gases at s.t.p. = 22.4 dm³)*

Concentration of the HCl solution
$$= 0.15 \text{ mol dm}^{-3}$$

1 dm³ of the HCl solution contains 0.15 mol of HCl.

$$\therefore 1.2 \text{ dm}^3 \text{ of the solution contain } \frac{1.2\times0.15}{1}$$
$$= 0.18 \text{ mol of HCl.}$$

1 mole of HCl gas at s.t.p. occupies 22.4 dm³.
∴ 0.18 mole at s.t.p. occupies 0.18 × 22.4
$$= 4.03 \text{ dm}^3.$$

∴ 4.03 dm³ of HCl gas at s.t.p. would be required to yield 1.2 dm³ of 0.15 *mol dm⁻³* aqueous solution.

Statements of equivalence in concentration

Let us look again at the reaction between tetraoxosulphate(VI) acid and sodium hydroxide.

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

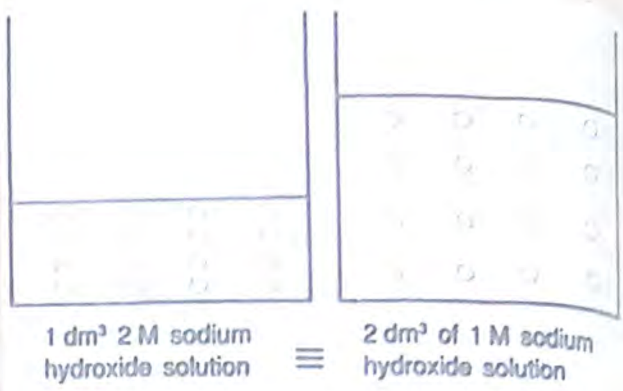
Mole ratio	1	:	2
Reacting mass	98 g		2 × 40 g
Amount	1 mol	:	2 mol
Mole ratio	1 mole	:	2 moles

(*Only if the reacting mass is dissolved in 1 dm³ of water.)

From the above chemical equation, we can make the following statements about the chemical equivalence between the two reactants. Such statements are very helpful in calculations involving molarity.

(a) 1 mole H_2SO_4 ≡ 2 moles NaOH
(b) 98 g H_2SO_4 ≡ 80 g NaOH
(c) 1 dm³ 1 mole H_2SO_4 ≡ 1 dm³ 2 moles NaOH
(d) 98 g H_2SO_4 ≡ 1 dm³ 2 M NaOH
(e) 1 dm³ 0.1 mole H_2SO_4 ≡ 1 dm³ 0.2 moles NaOH
(f) 1 dm³ 0.1 mole H_2SO_4 ≡ 2 dm³ 0.1 mole NaOH
(g) 33 cm³ x mole H_2SO_4 ≡ (2×33) cm³ x moles NaOH

Fig. 9.5 Equivalence between two solutions at th
[illegible] concentration but different quantities



NOTE The ≡ sign is used in chemistry to show th equivalence of solutions or reacting substances.

If 1 mole and 2 moles solutions of sodiu hydroxide are prepared separately, 1 dm³ of the moles sodium hydroxide solution will contain the sam number of particles as 2 dm³ of the 1 mole sodiu hydroxide solution, i.e. 2 moles or 2 × (6.02 × 10 particles. The two solutions are then said to b equivalent. They can serve as conversion factors calculations involving molarity. From this, we ca also make the following statements of equivalen about the two solutions in fig. 9.5.

(a) 1 dm³ 2 moles NaOH ≡ 2 dm³ 1 M NaOH
(b) 20 cm³ 2 moles NaOH ≡ 40 cm³ 1 moles NaO
(c) 10 cm³ 1 mole NaOH ≡ 20 cm³ 0.5 moles NaO
(d) 75 cm³ 0.1 mole NaOH ≡ 150 cm³ 0.05 mol NaOH

Thus, if 50 cm³ 0.1 mole NaOH ≡ 33 cm³ x mol NaOH, we would expect x moles to be greater th 0.1 moles because 50 cm³ is more than 33 cm³.

$$x = \frac{50}{33}\times0.1 = 0.1515 \text{ mole}$$

∴ 50 cm³ 0.1 moles NaOH ≡ 33 cm³ 0.1515 mo NaOH.

Calculations in Volumetric Analysis

Volumetric analysis is used to standardize unknow solutions, determine the purity of substances ar

xperiment 9.2 To determine the concentration of hydrochloric acid using standard sodium hydroxide solution.

Requirement Hydrochloric acid, standard sodium hydroxide solution, 50 cm^3 burette, 25 cm^3 pipette, methyl orange indicator.

Method Fill the burette with hydrochloric acid and adjust its level to the zero mark. Pipette 25 cm^3 of the sodium hydroxide solution into a conical flask and add two drops of methyl orange.

Titrate the acid against the alkali, swirling the flask all the time to mix the two solutions. Keep titrating till the end-point is reached (i.e. when the indicator turns orange). Note the volume of acid used to neutralize the alkali. This first titration reading is only an approximate value. Carry out two more accurate titrations. When approaching the end-point, add in the acid drop by drop until one drop of the acid changes the colour of the indicator permanently. Then record the burette readings.

Result Record your result in the way shown for the following specimen readings.

Burette reading/Titrations	**First**	**Second**	**Third**
Final	21.8 cm^3	21.5 cm^3	22.0 cm^3
Initial	0.0 cm^3	0.5 cm^3	1.0 cm^3
Volume of acid added	21.8 cm^3	21.0 cm^3	21.0 cm^3

Average volume of acid used = 21.0 cm^3. (Take the average of the two concordant titrations.)

Calculation The titration results show that 25.0 cm^3 of 0.1 M sodium hydroxide, NaOH, is needed to neutralize 21.0 cm^3 of hydrochloric acid, HCl, whose concentration has to be determined. (HCl = 36.5; NaOH = 40)

Equation of reaction $\mathrm{NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)}$

Mole ratio 1 : 1 : 1 : 1

Note that molarity is the number of moles per unit volume, therefore, molarity × volume = number of moles.

$$\frac{\text{Concentration of acids } (C_A) \times \text{Volume of acid } (V_A)}{\text{Concentration of base } (C_B) \times \text{Volume of base } (V_B)} = \frac{\text{Number of moles of acid}}{\text{Number of moles of base}}$$

$$i.e. \quad \frac{C_A V_A}{C_B V_B} = \text{Mole ratio of } \frac{\text{acid}}{\text{base}}$$

$$\therefore \quad \frac{C_A \times 21.0}{0.1 \times 25} = \frac{1}{1}$$

$$\therefore \quad C_A = \frac{0.1 \times 25}{21} = 0.119 \text{ mol dm}^{-3}$$

Mass concentration (g dm^{-3}) = molar concentration × molar mass

$$= 0.119 \times 36.5 = 4.344 \text{ g dm}^{-3}$$

Thus, the mass concentration of HCl is 4.344 g dm^{-3}.

Conclusion The mass concentration of hydrochloric acid is 4.344 g dm^{-3}.

calculate molar mass, molar concentration, mass concentration. Number of ions/particles water of crystallization and solubility product. The experimental procedures used in these determinations are similar to that given in experiment 9.2. The calculations in each of these analyses involve

balanced equation of the reaction;
volumes of solutions used; and
concentration of the standard solution.

Through worked examples, we shall see how the calculations, in the various practical applications of volumetric analysis, are done.

The numerical coefficients of a balanced equation represents the number of moles of reactants and products. Assume a reaction between an acid A and a base B. Using the equation A + B = Products. A certain amounts (a) of A reacts with an amount (b) of B to give the products = aA + bB = Products where a and b are the coefficients of the reactants. It is possible to derive an expression in terms of the concentrations of A and B, their volumes and mole ratio are:-

$$\frac{\text{Amount of A}}{\text{Amount of B}} = \frac{a}{b} = \text{mole ratio}$$

$$\text{Concentration} = \frac{\text{Amount}}{\text{Volume}} = \frac{n}{v}$$

$$\therefore \text{Amount} = \text{Concentration} \times \text{Volume}$$

$$n = c \times v.$$

$$\therefore \frac{C_A V_A}{C_B V_B} = \frac{na}{nb} = \text{mole ratio}$$

Standardization

The unknown concentration of a given solution can be determined by titrating it with another solution of known molarity (experiment 9.2).

EXAMPLE

Y cm^3 *of hydrogen chloride gas,* HCl, *at s.t.p. were passed into 60* cm^3 *of 0.1 mol* dm^{-1} *sodium trioxocarbonate(IV),* Na_2CO_3, *solution. The excess trioxocarbonate(IV) was neutralized by 20* cm^3 *of 0.05 mol* dm^{-1} *tetraoxosulphate(VI) acid,* H_2SO_4. *Calculate (a) the mass of excess sodium trioxocarbonate(IV) in* g dm^{-3}, *(b) the value of Y. (Molar volume of a gas at s.t.p. = 22.4* dm^{-3}, Na_2CO_3 *= 106)*

(a) ***Equation of reaction***

$$H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2$$

1 dm^3 1 M   106 g

1 dm^3 1 mole $H_2SO_4 \equiv 106$ g dm^{-3} Na_2CO_3

From the equation,

1 000 cm^3 1 mole $H_2SO_4 \equiv 106$ g dm^{-3} Na_2CO_3

1 000 cm^3 0.05 mole $H_2SO_4 \equiv 106 \times 0.05$

$= 5.3$ g dm^{-3} Na_2CO_3

$$\therefore 20\ cm^3\ 0.05\ \text{moles}\ H_2SO_4 \equiv \frac{20 \times 5.3}{1\,000}$$

P = 0.106 g dm^{-3} Na_2C

∴ mass of excess Na_2CO_3 (which reacted with H_2SO

$= 0.106$ g dm^{-3}

1 000 cm^3 1 moles Na_2CO_3 contain 106 g Na_2CO

1 000 cm^3 0.1 moles Na_2CO_3 contain 106 g Na_2CO

$$60\ cm^3\ 0.1\ \text{mole}\ Na_2CO_3\ \text{contain}\ \frac{60 \times 10.6}{1\,000}\ \text{g}\ Na_2CO$$

∴ mass of Na_2CO_3 neutralized by Y cm^3 HCl gas

$= 0.636 - 0.106 = 0.530$

(b) ***Equation of reaction***

$$Na_2CO_3(aq) + 2HCl(g) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g$$

106 g   2 × 22.4 dm^3 at s.t.p.

106 g $Na_2CO_3 \equiv 2 \times 22.4$ dm^3 HCl gas at s.t.p.

From the equation,

106 g $Na_2CO_3 \equiv 2 \times 22\,400$ cm^3 HCl gas at s.t.p.

$$0.530\ \text{g}\ Na_2CO_3 \equiv \frac{2 \times 22\,400 \times 0.530}{106}$$

$$= 224\ cm^3\ \text{HCl at s.t.p.}$$

Purity of substances

Volumetric analysis is often used to determine the purity of substances (usually expressed as a percentage). It is especially useful in determining the amount of dissolved impurities in water from various sources.

EXAMPLES

1 *12 g of a mixture of anhydrous sodium trioxocarbonate(IV),* Na_2CO_3, *and sodium chloride, NaCl, were made up to 1* dm^3 *of aqueous*

solution. 25 cm^3 of this mixture were neutralized by 20 cm^3 of 0.2 M hydrochloric acid, HCl. Calculate the mass of the sodium chloride impurity. Find also the percentage purity of the trioxocarbonate(IV) sample.
(Na_2CO_3 = *106*, HCl = *36.5*)

ation of reaction

$Na_2CO_3(aq) + 2HCl(aq)$
$\rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

e ratio 1 : 2

$$\frac{C_AV_A}{C_BV_B} = \frac{N_A}{N_B} \text{ Mole ratio of } \frac{\text{acid}}{\text{base}}$$

$$= \frac{0.2 \text{ mol dm}^{-1} \times 20 \text{ cm}^3}{C_B \times 25 \text{ cm}^3} \qquad C_B = \frac{2}{1}$$

$$C_B = \frac{0.2 \times 20}{25 \times 2} = 0.08 \text{ mol dm}^{-3}$$

e. molar concentration of Na_2CO_3 = 0.08 mol dm^{-3}

ass concentration of Na_2CO_3 = 0.08 × 106
= 8.48 g dm^{-3}

$= C \times M = 0.08 \text{ mol dm}^{-3} \times 106 \text{ g mol}^{-1}$
$= 8.48 \text{ g dm}^{-3}$

. mass of NaCl impurity = 12 − 8.48 = 3.52 g

ercentage purity of the Na_2CO_3 sample

$$= \frac{8.48}{12} \times 100\% = 70.7\%$$

2 *A piece of limestone,* $CaCO_3$*, was added to 1 dm^3 of 0.1 mol dm^{-3} hydrochloric acid,* HCl. *After effervescence had stopped, 31.25 cm^3 of the resulting solution required 25 cm^3 of 0.05 mol dm^{-3} sodium hydroxide,* NaOH, *for complete neutralization. Calculate the mass of limestone added.* ($CaCO_3$ = *100*, HCl = *36.5*, NaOH = *40*)

quation of reaction

(a) $CaCO_3(s) + 2HCl(aq)$
$\rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
100 g 2 × 36.5 g

(b) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
Mole ratio 1 : 1

From equation (b),

$$\frac{CAVA}{CBVB} = \frac{a}{b} \quad \text{Mole ratio of } \frac{\text{acid}}{\text{base}}$$

$$\frac{C_A \times 31.25}{0.05 \text{ mol dm}^{-3} \times 25} = \frac{1}{1}$$

$$C_A = \frac{0.05 \times 25}{31.25} = 0.04 \text{ mol dm}^{-3}$$

Mass concentration of HCl = 0.04 × 36.5 = 1.46 g dm^{-3}

∴ mass of HCl that reacted with NaOH = 1.46 g dm^{-3}

0.1 mol dm^{-3} HCl contains 3.65 g dm^{-3}.

∴ mass of HCl that reacted with $CaCO_3$ = 3.65 − 1.46
= 2.19 g

From equation (a),

73 g HCl ≡ 100 g $CaCO_3$

$$\therefore \ 2.19 \text{ g HCl} \equiv \frac{2.19 \times 100}{73}$$
$$= 3 \text{ g } CaCO_3$$

∴ mass of $CaCO_3$ added = 3 g

NOTE *Example 2 shows how the amount of trioxocarbonate(IV) impurity present in a given sample of water can be calculated by acid-base titration.*

MOLAR MASS, WATER OF CRYSTALLIZATION AND SOLUBILITY OF SUBSTANCES

Volumetric analysis can be used to calculate

- the molar mass of a metal acid, or base;
- the number of molecules of water of crystallization of a hydrate; and
- the solubility of a substance in water.

EXAMPLES

1 28.0 cm^3 *hydrochloric acid,* HCl, *of concentration 4.1 g dm^{-3} neutralized 25.0 cm^3 of an unknown alkali, YOH, whose concentrntion was 7.0 g dm^{-3}. Calculate* **(a)** *the molarity of YOH,* **(b)** *the relative atomic mass of the element Y. Name the element if possible.* (HCl = *36.5*)

Equation $HCl + YOH \rightarrow YCl + H_2O$
Mole ratio 1 : 1

(a) Molar concentration of HCl

$$= \frac{\text{Mass concentration}}{\text{Molar mass}} = C = \frac{P}{M}$$

$$= \frac{4.1}{36.5} = 0.112 \text{ mol dm}^{-3}$$

$$\frac{C_AV_A}{C_BV_B} = \frac{1}{1}$$

$$C_B = \frac{0.112 \times 28}{25} = 0.125 \text{ mol dm}^{-3}$$

∴ molarity of YOH = 0.125 mol dm^{-3}

(**b**) Let y be the relative atomic mass of Y.

$$\text{Molar concentration} = \frac{\text{Mass concentration}}{\text{Molar mass}} = \text{M} = \frac{\text{P}}{\text{C}}$$

$$\therefore 0.125 = \frac{7.0}{y+17}$$

$$y + 17 = \frac{7.0}{0.125}$$

$$y = \frac{7000}{125} - 17 = 39$$

Relative atomic mass of Y = 39

Thus, the element Y is potassium and the alkali is potassium hydroxide, KOH.

2 *Some crystals of washing soda were exposed to the atmosphere for efflorescence to take place. 6.02 g of this partly effloresced washing soda,* $Na_2CO_3.yH_2O$*, were then dissolved in 500* cm^3 *of water. 25* cm^3 *of this trioxocarbonate(IV) solution required 32.10* cm^3 *of 0.097* mol dm^{-3} *hydrochloric acid,* HCl*, for complete neutralization. Calculate y. Hence, write the formula of the effloresced washing soda.* (Na = *23*, H = *1*, C = *12*, Cl = *35.5*, O = *16*)

Equation of reaction

$$Na_2CO_3.yH_2O(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g) + yH_2O(l)$$

Mole ratio 1 : 2

$$\frac{C_AV_A}{C_BV_B} = \frac{2}{1}$$

$$\frac{0.097 \times 32.1}{C_B \times 25} = \frac{2}{1}$$

$$C_B = \frac{0.097 \times 32.1}{2 \times 25} = 0.0623 \text{ mol dm}^{-3}$$

∴ Molar concentration of $Na_2CO_3.yH_2O$
= 0.0623 mol dm^{-3}

Mass Concentration of $Na_2CO_3.yH_2O$

$$= \frac{6.02 \times 1\,000}{500}$$

$$= 12.04 \text{ g dm}^{-3}$$

Molar mass of $Na_2CO_3.yH_2O$ = (106 + 18y) g

$$\text{Molar mass} = \frac{\text{Mass concentration}}{\text{Molar concentration}} = \text{M} = \frac{\text{C}}{\text{C}}$$

$$106 + 18y = \frac{12.04}{0.0623}$$

$$18y = 87.3$$

$$y = 4.9$$

∴ the formula of the effloresced washing sod $Na_2CO_3.5H_2O$.

3 *A saturated solution of lead(II) trioxonitrate* $Pb(NO_3)_2$*, was prepared at 22 °C. 27* cm^3 *of solution required 46* cm^3 *of sodium chloride,* N *solution containing 96* g dm^{-3} *for complete pr pitation. Find the solubility of the lead(II) trio nitrate(V) at 22 °C in* (***a***) mol dm^{-3}, (***b***) g dn (Na = *23*, Cl = *35.5*, Pb = *207*, N = *14*, O =

Equation of reaction

$$2NaCl(aq) + Pb(NO_3)_2(aq) \rightarrow PbCl_2(s) + 2NaNO_3$$

Mole ratio 2 : 1

$$\text{Molarity of the NaCl solution} = \frac{96}{58.5} = 1.641 \text{ M}$$

$$\frac{C_AV_A}{C_BV_B} = \text{Mole ratio of } \frac{a}{b} = \frac{2}{1}$$

[where A represents NaCl and B represents $Pb(NO_3)$

$$= \frac{1.641 \times 46}{2 \times 27} = 1.398 \text{ mol dm}^{-3}$$

∴ molar concentration of the $Pb(NO_3)_2$ solutio
= 1.398 mol dm^{-3}.

Mass concentration = molar concentration × molar ma
= 1.398 × 331 = 462.7 g dm^{-3}

∴ the solubility of $Pb(NO_3)_2$ at 22 °C is
(*a*) 1.398 mol dm^{-3}, (*b*) 462.7 g dm^{-3}.

SUMMARY

The mole is the amount of substance that contains as many formular units as there are atoms in 12 grams of carbon-12.

The mole ratio in which reactants combine and products are formed gives the stoichiometry of the reactions. This is depicted by a balanced chemical equation.

In a reaction involving gases, the coefficients of the gaseous reactants and products in the balanced equation represent both the mole ratio and the volume relations between the gases.

Stoichiometric calculations of the relationships among moles, mass, volume and number of molecules can be done easily if we remember the following:

1 mole = 1 molar mass (M_r in grams) = 22.4 dm^3 of gas at s.t.p. = 6.02×10^{23} particles

Volumetric analysis uses volume measurements of solutions to determine the amount of a substance present in a given sample.

Titration is the method used in volumetric analysis, whereby a solution from a burette is added to a known volume of a second solution until the chemical reaction between the two is just completed.

The concentration of a solution is the amount of solute in a given volume of the solution. It can be expressed as mol dm^{-3} or g dm^{-3}. A standard solution is one whose concentration is known accurately.

Molarity is the concentration of a solution in moles per dm^3.

(a) The molar mass of any substance is the mass of one mole of that substance expressed in grams (g mol^{-1}).

(b) A molar solution is one which contains one mole of the solute in one dm^3 of the solvent (usually water).

(c) The relationship between the molarity (M) and concentration is:

Mass concentration (g dm^{-3}) = molar concentration (mol dm^{-3}) × molar mass (g)

Titrations can be used to determine

(a) the concentration of a solution, ie. molar concentration and mass concentration
(b) the percentage purity of a substance,
(c) the molar mass of a metal, acid or base,
(d) the number of water molecules in a hydrate,
(e) the solubility product of a substance in water.

$$= \frac{n(\text{solute})}{v(\text{solution})} = n = cv. \quad n = \frac{m}{M}; \; V_m = \frac{v}{n}; \; L = \frac{N}{n}.$$

$$C_A V_A = C_B V_B.$$

$$\frac{C_A V_A}{C_B V_B} = \frac{na}{nb}.$$

Mass concentration = molar concentration × molar mass

$$\rho = C \times M$$

$$C = \frac{\rho}{M}$$

$$\rho = \frac{m}{v}; \quad \frac{\rho}{c} = \frac{m\,|\,v}{n\,|\,v} = \frac{m}{n} = M \qquad \frac{\rho}{c} = M.$$

EXERCISES

What is the S. I. unit for molar mass?

A mol dm^{-3}
B mol^{-1}
C g mol^{-1}
D mol

2. From this balanced equation, what is the value of x $Pb(NO_3)_2$ (aq) + XNacl (aq) → $Pbcl_2$(s) + $2NaNO_3$(aq)?

A 1
B 2
C 3
D 4

3. Calculate the number of moles of magnesium chloride produced by reacting 168g of magnesium trioxocarbonate (iv) with excess hydrochloric acid. Mg = 24, C = 12, O = 16, H = 1,Cl = 35.5
A 4 m B 3 m
C 2 m D 1 m

4. What volume of steam is produced when 10 g of propyne is burnt in excess oxygen at s.t.p.?
A 44.8 dm B 11.2 dm^3
C 22.4 dm^3 D 11.2 cm^3

5. If a hydrated salt weighs *x* grams and water recovered after strong heating in *y* grams, the formula for determining the percentage of water of crystallization is

A $\frac{x}{y} \times \frac{100}{1} \%$ B $\frac{y}{x} \times \frac{100}{1} \%$

C $\frac{yx}{y} \times \frac{100}{1} \%$ D $\frac{x}{xy} \times \frac{100}{1} \%$

6. What phenomenon does this expression/ equation show?
$Na_2\ CO_3.\ 10H_2O \rightarrow Na_2\ 10_3.\ H_2O + 9H_2O$
(colourless crystals) (white powder)
A Deliquiscence
B Hygroscopy
C Efflorescence
D Decomposition

7. Number of specified entities in 0.1 m $H_2\ SO_4$ is
A $\frac{6.02 \times 10^{23}}{0.1}$
B $0.1 \times 6.02 \times 10^{23}$
C $10 \times 6.02 \times 10^{23}$
D $0.1 \times 12.04 \times 10^{23}$

8. What mass of anhydrous sodium trioxocarbonate IV, Na_2CO_3, present in 500 cm^3 of 0.1 mol dm^{-3}? (Na = 23, C = 12, O = 16)
A 10.6 g B 212 g
C 5.3 g D 106 g

9. Filling the burette for titration involves these except
A wash with water.
B rinse with acid.
C eject air bubbles.
D read at eye level.

10. In the titration of acid against base solution averaging must involve
A rough reading.
B concordant reading.
C higher reading
D all the titres obtained.

11. Solution produced in the conical flask after eac titration (containing salt and water) is called
A alliquot mixture.
B titration mixture.
C salt mixture.
D effluent mixture.

12. On heating 20g sample of hydrated salt, Na_2 CC XH_2O, strongly, 5.5g of the anhydrous salt wa obtained, what is the value of x in the hydrate salt? Solved from one of the expressions.

A $\frac{5.5}{20} = \frac{106}{106 + 18x}$

B $\frac{20}{5.5} = \frac{106}{106 + 18x}$

C $\frac{106}{20} = \frac{5.5}{106 + 18x}$

D $\frac{106}{18x} = \frac{5.5}{20}$

13. Volumetric anaylsis may be used in th determination of the following except
A molar mass of a metal acid or base.
B percentage purity or impurity of a give salt solution.
C solubility of a substance in aguous medium
D water of crystallization of anhydrous sal solution.

14. These are volumetric analysis tools except
A indicator.
B deflagrating spoon.
C white background for example white tile.
D wash bottle.

15. A blind student may not carry out volumetric analysis adequately because
A he/she is blind.
B he/she may not observe the end-point.
C he/she may not use the funnel adequately.
D he/she may not carry out the calculation adequately.

16. In a certain reaction, 0.20 g of hydrogen gas combines with 3.20 g of oxygen gas. If the relative molecular mass of the compound is 34.0, find its molecular formula. (H = 1, O = 16)

17. Define *mole*. What is a molar solution? Give the mass concentrations of the following solutions.
(a) 1 mol dm^{-3} potassium hydroxide solution
(b) 0.1 mol dm^{-3} trioxonitrate(V) acid
(c) 0.05 mol dm^{-3} solution of sodium trioxocarbonate(IV)-decahydrate (K = 39, H = 1, O = 16, N = 14, Na = 23, C = 12)

18. A metal *X* with relative atomic mass 56 forms an oxide with formula X_2O_3. How many grams of the metal will combine with 10 g of oxygen? (O = 16)

19. Calculate the mass concentrations in g dm^{-3} of the ions in the following solutions:
(a) Cl^- ions in 0.2 mol dm^{-3} sodium chloride solution
(b) NO_3^- ions in 0.75 mol dm^{-3} trioxonitrate(V) acid
(c) SO_4^{2-} ions in 2 mol dm^{-3} potassium tetraoxo-sulphate(VI) solution (Cl = 35.5, N = 14, O = 16, S = 32)

20. Ethane burns completely in oxygen according to the equation below.

$$C_2H_6(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

What is the amount in moles of carbon(IV) oxide will be produced when 6.0 g of ethane are completely burnt in oxygen? (O = 16, C = 12, H = 1)

21. 39.8 g of a mixture of potassium chloride, KCl, and potassium trioxochlorate(V), $KClO_3$, were heated to a constant mass. If the residue weighed 28.9 g, what was the percentage mass of the potassium chloride in the mixture? (K = 39, Cl = 35.5, O = 16)
HINT KCl is not decomposed on heating.

22. 12.5 g of zinc trioxocarbonate(IV), $ZnCO_3$, were heated very strongly to a constant mass and the residue treated with excess hydrochloric acid, HCl. Calculate the mass of zinc chloride, $ZnCl_2$, that would be obtained.
(Zn = 65, C = 12, O = 16, H = 1, Cl = 35.5)

23. An excess of a divalent metal M was dissolved in a limited volume of hydrochloric acid. If 576 cm^3 of hydrogen were liberated at s.t.p. what was the mass of the metal that produce this volume of hydrogen? (M = 24, H = 1, molar volume of a gas at s.t.p. = 22.4 dm^3)

24. 19.04 g of ammonia gas were mixed with 31.10 g of hydrogen chloride gas in a closed container.
(a) Which of the reactants was in excess and by how much?
(b) How much ammonium chloride was formed?
(c) How much more of the insufficient reactant would be needed to completely react with the excess of the other reactant? (N = 14, H = 1, Cl = 35.5)

25. (a) Find the volume of oxygen produced by 1 mole of potassium trioxochlorate(V) at s.t.p. in the following reaction.

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

(b) Find the mass of sodium trioxocarbonate(IV) needed to give 22.4 dm^3 of carbon(IV) oxide at s.t.p. in this reaction.

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

(Na = 23, O = 16, C = 12, molar volume of a gas at s.t.p. = 22.4 dm^3)

26. A solution of trioxonitrate(V) acid contained 0.67 g in 100 cm^3. 31.0 cm^3 of this solution neutralized 25 cm^3 of a sodium trioxocarbonate(IV) solution. Calculate the concentration of the trioxocarbonate(IV) solution. (HNO_3 = 63, Na_2CO_3 = 106)

27. 2 g of a mixture of sodium hydroxide and sodium chloride (as impurity) were dissolved in 500 cm^3 of water. If 25 cm^3 of this solution were neutralized by 21 cm^3 0.1 mol dm^{-3} hydrochloric acid, calculate the percentage of the sodium chloride impurity.
(NaOH = 40, HCl = 36.5, NaCl = 58.5)

28. A piece of zinc was added to 1 000 cm^3 of 0.2 M hydrochloric acid. After effervescence had stopped, 28 cm^3 of the resulting solution required 17 cm^3 of 0.08 M sodium trioxocarbonate(IV) solution for complete neutralization. Calculate the mass of the zinc added. Zn = 65, HCl = 36.5, Na_2CO_3 = 106)

29. Calculate the mass of pure sodium chloride that will yield enough hydrogen chloride gas to neutralize 25 cm^3 of 0.5 M potassium trioxocarbonate(IV) solution.
(NaCl = 58.5, HCl = 36.5, K_2CO_3 = 138)

30. A saturated solution of potassium chloride was prepared at X °C. If 30 cm^3 of this solution required 22.5 cm^3 of silver trioxonitrate(V) solution, containing 34 g in 100 cm^3 solution, for complete precipitation, calculate the solubility of potassium chloride at X °C in (a) mol dm^{-3} (b) g dm^{-3}.

(KCl = 74.5, $AgNO_3$ = 170)

TYPES OF REACTIONS • 10

XIDATION AND REDUCTION

TYPES OF REACTIONS

Chemical reactions are changes in which some new chemical substances are formed. The substances which undergo the chemical change are known as *reactants*, while the new substances formed are called *products*. Chemical reactions can be grouped in the following way:

- Combination
- Decomposition
- Displacement
- Double decomposition
- Catalytic reactions
- Reversible reactions
- Thermal dissociation
- Oxidation and reduction

Combination

When two or more substances combine to form one single compound, a combination reaction is said to have taken place. Combinations can occur in any one of the following ways:

element + **element** → **compound**
e.g. $Fe(s) + S(s) \rightarrow FeS(s)$

compound + **compound** → **bigger compound**
e.g. $PbO_2(s) + SO_2(g) \rightarrow PbSO_4(s)$

Many organic compounds also undergo combination reactions. The polymerization of ethyne, for example, is a special type of combination reaction.

Decomposition

Decomposition reactions are characterized by a single compound splitting up into two or more simpler substances. When heat is needed to bring about decomposition, the reaction is known as *thermal decomposition*.

$$2Pb(NO_3)_2(s) \xrightarrow{heat} 2PbO(s) + 4NO_2(g) + O_2(g)$$

Displacement

In displacement, one element (or radical) replaces another element (or radical) in a compound, i.e.

$$A + BY \rightarrow B + AY$$

The ability of an element (or radical) to displace another is determined by their relative positions in the electrochemical series. Thus, the more electropositive zinc will displace the less electropositive copper from an aqueous solution of a copper(II) salt.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

Chlorine which is a more electronegative non-metal will displace bromine which is less electronegative from a solution of a bromide.

$$Cl_2(g) + 2KBr(aq) \rightarrow 2KCl(aq) + Br_2(l)$$

Double Decomposition

In double decomposition, the reactants decompose to form new substances by an exchange of radicals.

$$AB + CD \rightarrow AD + CB$$

The two reactants are soluble, and one of the products is soluble while the other is insoluble, volatile or gaseous, e.g.

$$AgNO_3(aq) + NaCl(aq) \rightarrow \underset{\text{precipitate}}{AgCl(s)} + NaNO_3(aq)$$

$$KNO_3(aq) + H_2SO_4(aq) \rightarrow \underset{\text{volatile}}{HNO_3(g)} + KHSO_4(aq)$$

$$NaCl(aq) + H_2SO_4(aq) \rightarrow HCl(g) + NaHSO_4(aq)$$

A double decomposition reaction is used in the preparation of an insoluble or volatile compound, since it can be separated from the other substances in the reaction system. The two reactants must be chosen such that each supplies one of the groups or ions of the desired compound. In qualitative analysis, anions like chloride and tetraoxosulphate(VI) are detected by the formation of precipitates by double decomposition.

Catalytic Reaction

Certain substances are used to alter the rates of chemical reactions. These substances, which remain chemically and quantitatively unchanged at the end of the reactions, are known as *catalysts*. The acceleration or retardation of reactions by catalysts is known as *catalysis*.

Any type of chemical reaction which uses a catalyst is a *catalytic reaction*. Thus, we have catalytic combination, catalytic decomposition, catalytic reversible reaction, catalytic redox reaction and so on. There are two types of catalyzed reactions: *homogeneous catalysis* and *heterogeneous catalysis*.

Homogeneous catalysis In this reaction, the catalyst, reactants and products are all in the same phase. For example, the oxidation of sulphur(IV) oxide using nitrogen(II) oxide as catalyst occurs in the gaseous phase.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

Heterogeneous catalysis The reactants, products and catalysts are in different phases in heterogeneous catalysis. Most catalytic reactions are in this category.

$$N_2(g) + 3H_2(g) \xrightleftharpoons{Fe(s)} 2NH_3(g)$$

$$H_2(g) + I_2(g) \xrightarrow{Pt(s)} 2HI(g)$$

The formation of margarine from vegetable oil in the presence of a nickel catalyst is also an example of heterogeneous catalysis.

$$\text{vegetable oil(l)} + H_2(g) \xrightarrow{Ni(s)} \text{margarine(s)}$$

Characteristics of a catalyst

1 A catalyst alters the rate of a chemical reaction.

2 A catalyst remains unchanged in chemical nature and mass at the end of a reaction. Its physical features such as colour and texture, however, m be changed.

3 A catalyst is specific in action, i.e. a given catal will act on only one particular reaction, althou many inorganic catalysts will catalyze more th one reaction.

4 A catalyst cannot start a reaction. It is effecti only in a reaction which is already in progre

5 A catalyst does not affect the types of produc formed in a reaction.

6 A catalyst has no effect on the equilibrium of reversible reaction.

7 A catalyst will affect the rate of a reaction eve though it is present in very small amounts. A increase in the amount of catalyst up to a certai limit, however, would usually increase th reaction rate.

8 The effect of a solid catalyst is improved b increasing its surface area.

NOTE Since a catalyst does not affect the overa reaction, it is written above the arrow in an equatio

A catalyst is a substance which alters the rate of a chemical reaction, but itself remains chemically and quantitatively unchanged at the end of the reaction.

Types of catalysts

Catalysts may be inorganic or organic substances Inorganic catalysts can be grouped into *positive* anc *negative* catalysts. Organic catalysts are known as enzymes and are produced by living cells.

Positive and negative catalysts A catalyst which increases the rate of a reaction is a positive catalyst. An example is manganese(IV) oxide which speeds up the decomposition of potassium trioxochlorate(V). Positive catalysts are important in chemical industry since they can speed up slow reactions sufficiently to make them commercially feasible.

$$2KClO_3(s) \xrightarrow{MnO_2} 2KCl(s) + 3O_2(g)$$

A catalyst which decreases the rate of a reaction is a *negative catalyst*. For example, tetraoxo-phosphate(V) acid decreases the rate of decomposition of hydrogen peroxide, while a 2% ethanol solution suppresses the oxidation of trichloromethane by air.

Experiment 10.1 To verify the definition of a catalyst by studying the decomposition of hydrogen peroxide, using manganese(IV) oxide as the catalyst.

Method Fill two test-tubes with $10\ cm^3$ of hydrogen peroxide each. Add about 2 g of granular manganese(IV) oxide to one test-tube. Place both the tubes in a warm water-bath and insert a glowing splinter into each of the tubes to test for the release of oxygen. Note the time taken for each splinter to rekindle.

When no more oxygen is given off, filter the mixture in the test-tube that contains the catalyst to collect the manganese(IV) oxide. Wash, dry and weigh the residue. Examine its physical appearance.

Result The glowing splinter is rekindled much earlier and more brightly in the tube containing the manganese(IV) oxide than in the one without the catalyst.

The black residue of the filter paper is manganese(IV) oxide. Upon drying, it weighs approximately 2 g, which is the initial mass of the manganese(IV) oxide used. However, the oxide is now powdery, not granular.

Conclusion Manganese(IV) oxide increases the rate of decomposition of hydrogen peroxide by acting as a positive catalyst. Its mass remains unchanged at the end of the chemical reaction, but its physical appearance changes.

Thus, negative catalysts are used to suppress undesirable reactions.

$$2H_2O_2(l) \xrightarrow{\text{hindered by } H_3PO_4} 2H_2O(l) + O_2(g)$$

Enzymes Enzymes are organic catalysts which control the rate of biochemical reactions in living organisms.

Enzymes help to digest the food we eat. They cause blood to clot and fruit juices to ferment. The industrial manufacture of alcohol from sugars and starches uses enzymes.

The unripe fruit and leaves of pawpaw contain papains, an enzyme which breaks down proteins and is used to tenderize meat before cooking.

Promoters and inhibitors These are not the catalysts themselves but they influence the rate of a reaction by affecting the efficiency of the catalysts. For example, the iron catalyst used in the Haber process for the production of ammonia is activated by the addition of trace amounts of aluminium oxide or molybdenum. Such substances which improve the efficiency of a catalyst are known as *promoters*. Some substances inhibit a catalyst, and are known as *inhibitors* or catalyst poisons. Hydrogen sulphide, arsenic(III) oxide, hydrogen cyanide and mercury salts are catalyst poisons which harm us by inhibiting important enzymes in our bodies.

Reversible Reactions

Many reactions can proceed only in one direction, for example, $A + B \rightarrow C + D$, i.e. only the reactants A and B will react together to form the products C and D. There are other reactions, however, in which the direction of chemical change can be reversed. Depending on the reaction conditions, the products formed may react to form the original reactants. Such reactions are known as reversible reactions. To represent the reversibility of a reaction in an equation, the symbol $\rightleftharpoons$ is used. For example,

$$A + B \rightleftharpoons C + D$$

The conditions for the reverse reaction (i.e. the reaction between C and D) may or may not be the same as the conditions for the forward reaction (i.e.

20 °C and 140 °C, dinitrogen(IV) oxide and nitrogen(IV) oxide exist together in an equilibrium mixture.

$$N_2O_4(g) \underset{\text{cool (20 °C)}}{\overset{\text{heat (140 °C)}}{\rightleftharpoons}} 2NO_2(g)$$

OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions involve two opposing yet complementary processes: *oxidation* and *reduction*. Every oxidation must be accompanied by a reduction and vice versa. In fact, the reactions cannot be regarded as separate but rather as different aspects of the same fundamental change, i.e. the transfer of electrons from one atom or ion to another. Oxidation-reduction reactions are abbreviated as *redox reactions*.

Definitions of Oxidation and Reduction

The definitions for the terms *oxidation*, *reduction*, *oxidizing agent* and *reducing agent* passed through several stages before arriving at the present definition, which is in terms of electron transfer.

Addition of oxygen

At first, oxidation was used to describe as a reaction in which oxygen combined with a substance. Reduction, the opposing process, referred to a reaction in which oxygen was removed from a substance. The donor of the oxygen was the oxidizing agent (O.A.) while the acceptor was the reducing agent (R.A.). For example,

oxidation

$$\underset{\text{R.A.}}{C(s)} + \underset{\text{O.A.}}{2ZnO(s)} \rightarrow CO_2(g) + 2Zn(s)$$

reduction

We can say that the oxidizing agent, zinc oxide, donates oxygen to the carbon and oxidizes it to carbon(IV) oxide; or the reducing agent, carbon, removes oxygen from zinc oxide and reduces it to metallic zinc.

Removal of hydrogen

The above narrow definitions of oxidation and reduction gave way to more comprehensive ones including a wider range of reactions. The first type of reactions to be included were those involving the transfer of hydrogen. The definition of oxidation was extended to mean the removal of hydrogen, while that of reduction included the addition of hydrogen.

oxidation

$$\underset{\text{R.A.}}{H_2S(g)} + \underset{\text{O.A.}}{Cl_2(g)} \rightarrow 2HCl(g) + S(s)$$

reduction

Addition of electronegative elements

The definition of oxidation was further extended to include the addition of electronegative elements and the removal of electropositive elements, while that of reduction included the removal of electronegative elements as well as the addition of electropositive elements.

Note Electronegative elements tend to gain electrons, e.g. non-metals like chlorine. Electropositive elements tend to lose electrons and become positive ions, e.g. metals like sodium.

Equation 1

oxidation

$$\underset{\text{R.A.}}{2Na(s)} + \underset{\text{O.A.}}{Cl_2(g)} \rightarrow 2NaCl(s)$$

reduction

Equation 2

oxidation

$$\underset{\text{R.A.}}{H_2S(g)} + \underset{\text{O.A.}}{Br_2(g)} \rightarrow 2HBr(g) + S(s)$$

reduction

In the reaction in equation 2, both sulphur and bromine are electronegative elements. Bromine, the more electronegative of the two, is regarded as the oxidizing agent. To recognize oxidizing and reducing agents in reactions like this, the relative electronegativities of elements must be known.

Elements (non-metals) F, O, Cl, N, Br, C, I, P
$\longrightarrow$
Electronegativity decreases

Elements (metals) K, Na, Ca, Mg, Al, Zn, Fe, Pb, Cu
$\longleftarrow$
Electronegativity increases

Removal of electrons

An important extension of the concept of oxidation was to include reactions where the oxidation state of a metal was increased. For example, iron(II) chloride reacts with chlorine to form iron(III) chloride.

$$\overset{\text{oxidation}}{\overbrace{\underset{\text{R.A.}}{2FeCl_2(s)} + \underset{\text{O.A.}}{Cl_2(g)} \rightarrow 2FeCl_3(s)}}$$

reduction

The fundamental change in this reaction is that from iron(II) ion, Fe^{2+}, to iron(III) ion, Fe^{3+}. Since this change corresponds exactly to the change from iron(II) oxide to iron(III) oxide, it is clearly an example of an oxidation reaction.

$$4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(s)$$

Similarly, changes such as the conversion of copper(I) to copper(II), lead(II) to lead(IV) and so on are all regarded as oxidation reactions. In all these changes, the charge on a positive ion is increased, e.g. $Cu^+ \rightarrow Cu^{2+}$, while the charge on a negative ion is decreased, e.g. $I^{-1} \rightarrow I^0$. This led eventually to an even broader view of oxidation to include any process which involves the loss of electrons. A substance loses electrons when it is oxidized and gains electrons when it is reduced, while a redox reaction is basically a transfer of electrons from the reducing agent (the electron donor) to the oxidizing agent (the electron acceptor).

$$\underset{\text{electron donor}}{\text{reducing agent}} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} \underset{\text{electron acceptor}}{\text{oxidizing agent}} + \text{electrons}$$

This concept of redox reactions in terms of electron

so far. Thus, the most concise definitions for oxida reduction, oxidizing agent and reducing age modern terms, are those relating to electron tra

Oxidation is a process involving a lo electrons, while reduction is a p involving a gain of electrons. An oxid agent is a substance which accepts elec a reducing agent is a substance which do electrons.

Electron Transfer in Redox Reac

Half-equations

When a little potassium iodide solution is a iron(III) tetraoxosulphate(VI), the reaction turns brown. This is due to the liberation o

$$2KI(aq) + Fe_2(SO_4)_3(aq) \rightarrow I_2(s) + K_2SO_4(aq) + 2Fe$$

Ionically,

$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(s) + 2Fe^{2+}(aq)$$

In this reaction, iodide ions are oxidized to iod molecules and iron(III) ions are reduced to iron ions. The ionic equation for this reaction can be s into two *half-equations* as follows:

$$2I^-(aq) \rightarrow I_2(aq) + 2e^- \qquad \textit{(Oxida}$$
$$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq) \qquad \textit{(Reduct}$$

The half-equation for oxidation shows elect loss, while that for reduction shows electron g Each of these reactions is called a *half-reactio* half-reaction cannot occur by itself. It can only o together with another complementary half-reacti This is because a substance cannot donate or l electrons (oxidation) unless another substance present to accept or gain them (reduction).

Evidence for electron transfer

We can sh

tetraoxosulphate(VI) by carrying out an experiment using the apparatus shown in fig. 10.1.

The apparatus consists of two beakers, one filled with potassium iodide solution and the other with iron(III) tetraoxosulphate(VI) solution. Two platinum rods (electrodes), *A* and *B*, are dipped into the solutions. They are connected by a circuit which includes a milliammeter for detecting the presence of an electric current. To start the experiment, the solutions are connected by a narrow strip of filter paper soaked in sodium chloride solution. This acts as a salt bridge.

In this experiment, the half-reactions are separated, one at each electrode, to show the transfer of electrons. When the solutions are connected by the salt bridge, the milliammeter needle moves, indicating the presence of an electric current. An electric current is actually a flow of electrons. Therefore, there is a transfer of electrons in this reaction.

After some time, a brown colour appears around electrode *A*, indicating the presence of iodine. At the same time, iron(II) ions also appear around electrode *B*.

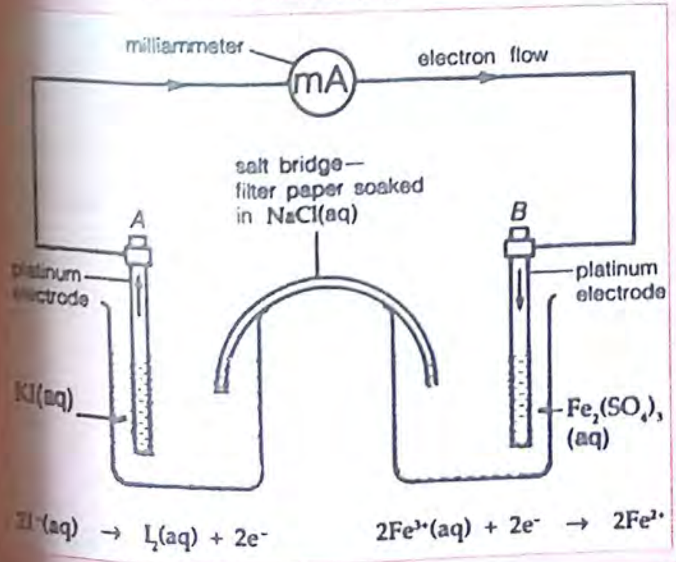
Note Presence of iron(II) ions is detected by adding a few drops of potassium hexacyanoferrate(III) solution.

These observations indicate that the half-reactions at electrodes *A* and *B* are as follows:

$2I^-(aq) \rightarrow I_2(aq) + 2e^-$ (*Oxidation at electrode A*)

$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$ (*Reduction at electrode B*)

10.1 Electron transfer between solutions of an iodide and an iron(III) salt.



The overall reaction is as follows:

$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$$

The electron transfer between the half-reactions is seen as an electric current, i.e. as a flow of electrons from electrodes *A* to *B*.

In this experiment, the chemical energy liberated is converted into electrical energy, i.e. as an electric current. When potassium iodide solution is added directly to iron(III) tetraoxosulphate(VI), the chemical energy is released as heat. The apparatus in fig. 10.1 is a very simple electrochemical cell, made up of two half-cells that are joined by a salt bridge. You will learn more about electrochemical cells in the next chapter.

Oxidation Number

Redox reactions can be recognized with the aid of *oxidation numbers*.

The oxidation number of an element in any particular molecule or ion is defined as the *electrical charge it appears to have as determined by a set of arbitrary rules*. These rules make it possible to calculate the oxidation numbers for the elements in the reactants and products of a chemical change. If an element has gained or lost electrons in a reaction, this would be reflected by a change in its oxidation number, i.e. the oxidation number expresses the oxidation state of an element.

Rules for determining oxidation numbers

The set of rules used for the determination of oxidation numbers are as follows:

1 The oxidation number of all elements in the free state (i.e. uncombined with any other element) is zero. This can be shown as a zero written as a superscript, to the right of its symbol. For example, Na^0, $Cl_2{}^0$, Mg^0, $P_4{}^0$. This zero, however, is often omitted.

2 The oxidation number of a simple ion (i.e. an ion consisting of a single element) has the same size and sign as the charge of the ion. The oxidation number of Na^+, Mg^{2+}, Al^{3+}, Cl^- and S^{2-} are +1, +2, +3, −1 and −2 respectively. Note that the negative or positive sign for an oxidation number always comes before the number.

Where the ion consists of more than one element, its oxidation number is the algebraic sum of the oxidation numbers of all the elements in the ion. This oxidation number must have the same size and sign as the overall charge on the ion. For example in the hydroxide ion, OH^-, the overall charge is −1, so its oxidation number is also −1 and is obtained in the following way:

$$\begin{bmatrix}\text{Oxidation}\\ \text{number of O}\end{bmatrix} + \begin{bmatrix}\text{Oxidation}\\ \text{number of H}\end{bmatrix} = \begin{bmatrix}\text{Oxidation}\\ \text{number of } OH^-\end{bmatrix}$$

$$(-2) \quad + \quad (+1) \quad = \quad -1$$

The oxidation numbers of NH_4^+, NO_3^-, SO_4^{2-}, PO_4^{3-} and MnO_4^- are +1, −1, −2, −3 and −1 respectively.

Using this rule, it is possible to calculate the oxidation number of any element in the ion as long as those of the other elements are known.

3 The algebraic sum of the oxidation numbers of all the elements in a compound is zero. In the compound $MgCl_2$, which may also be written as $(MgCl_2)^0$,

$$\begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of Mg}\end{bmatrix} + 2\begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of Cl}\end{bmatrix} = \begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of } MgCl_2\end{bmatrix} = 0$$

$$(+2) \quad + \quad [2 \times (-1)] \quad = \quad +2 - 2 \quad = 0$$

In a compound, the more electronegative elements will have negative oxidation numbers and the more electropositive ones, positive numbers. This is true not only of ionic compounds, but also of covalent molecules, where each atom present is given an oxidation number equal arbitrarily to the charge it could have if the substance were composed of ions.

Note In most compounds, the oxidation number of oxygen is −2 (except in peroxides where its oxidation number is −1), while that of hydrogen is +1 (except in hydrides where its oxidation number is −1).

EXAMPLES

1 *To find the oxidation number of the manganese atom in potassium tetraoxomanganate(VII),* $KMnO_4$.

$$\begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of K}\end{bmatrix} + \begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of Mn}\end{bmatrix} + 4\begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of O}\end{bmatrix} = 0$$

where the oxidation number of K = +1,
the oxidation number of Mn = x,
and the oxidation number of O = −2.

$$\begin{aligned} \therefore (+1) + x + [4 \times (-2)] &= 0 \\ 1 + x - 8 &= 0 \\ x &= +7 \end{aligned}$$

The oxidation number of the manganese atom potassium tetraoxomanganate(VII) is +7.

2 *To find the oxidation number of the chromiu atom in potassium heptaoxodichromate(V* $K_2Cr_2O_7$.

$$2\begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of K}\end{bmatrix} + 2\begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of Cr}\end{bmatrix} + 7\begin{bmatrix}\text{Oxidation}\\ \text{number}\\ \text{of O}\end{bmatrix} = 0$$

where the oxidation number of K = +1,
the oxidation number of Cr = x,
and the oxidation number of O = −2.

$$\begin{aligned} \therefore 2(+1) + 2(x) + [7 \times (-2)] &= 0 \\ 2 + 2x - 14 &= 0 \\ 2x &= +12 \\ x &= +6 \end{aligned}$$

The oxidation number of the chromium atom in potassium heptaoxodichromate(VI) is +6.

Changes in oxidation numbers during redox reactions

During the process of oxidation, a substance lose electron(s), and its oxidation number increases in th positive direction. For example, when an iron atom i oxidized to iron(III) ion, it passes through thre oxidation states as the atom loses three electron progressively, one at a time. The ionic charge and th oxidation number increase as shown.

$$\xrightarrow{\text{oxidation}}$$

$$Fe^0 \xrightarrow{-e^-} Fe^+ \xrightarrow{-e^-} Fe^{2+} \xrightarrow{-e^-} Fe^{3+}$$

Oxidation state		1st	2nd	3rd
Oxidation number	0	+1	+2	+3

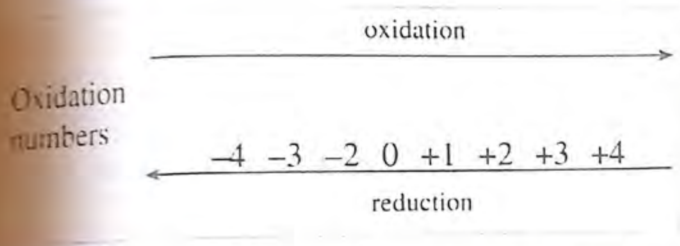
The iron ions at the three oxidation states are known as iron(I), iron(II) and iron(III) ions respectively. The iron(I) ion is unstable and transient, and is not found in natural compounds.

In the oxidation of the iodide ion to iodine, the oxidation number increases from –1 to 0, i.e. it increases in the positive direction.

$$I^- \xrightarrow{-e^-} I^0$$

Conversely, during reduction, a substance gains electrons and its oxidation number decreases in the positive direction, e.g.

when Fe^{3+} is reduced to Fe^0, the oxidation number decreases in the positive direction from +3 to 0; when I^0 is reduced to I^-, the oxidation number decreases from 0 to –1 in the positive direction.



From these examples, we can say that a substance has undergone a redox change if there is a change in its oxidation number. Equations 1 to 5 illustrate how we can identify redox reactions by using oxidation numbers.

Equation 1

$$\underset{\text{R.A.}}{2Mg(s)} + \underset{\text{O.A.}}{O_2(g)} \rightarrow 2MgO(s)$$

When magnesium combines with oxygen, each magnesium atom donates its two valence electrons to oxygen to become oxidized to a magnesium ion, Mg^{2+}, while each oxygen atom accepts two electrons to become reduced to the oxide ion, O^{2-}.

$$Mg - 2e^- \rightarrow Mg^{2+}$$
$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

The oxidation number of magnesium increases in the positive direction from 0 to +2, while that of oxygen decreases in the same direction from 0 to –2. Therefore, this is a redox reaction.

Equation 2

$$\underset{\text{R.A.}}{H_2S(g)} + \underset{\text{O.A.}}{Cl_2(g)} \rightarrow 2HCl(g) + S(s)$$

In this reaction, the sulphide ion, S^{2-}, loses two electrons to be oxidized to sulphur atom, S^0. Its oxidation number increases in the positive direction from –2 to 0. At the same time, these electrons are accepted by the chlorine atoms which become reduced to chloride ions, Cl^-. The oxidation number of chlorine decreases in the positive direction from 0 to –1.

$$S^{2-} - 2e^- \rightarrow S^0$$
$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Equation 3

$$\underset{\text{R.A.}}{2FeCl_2(s)} + \underset{\text{O.A.}}{Cl_2(g)} \rightarrow 2FeCl_3(s)$$

The iron(II) ions, Fe^{2+}, lose an electron each to become oxidized to iron(III) ions, Fe^{3+}. The oxidation number of iron increases from +2 to +3 in the positive direction. The electrons made available by the iron(II) ions are accepted by the chlorine atoms, which become reduced to chloride ions. This is reflected by a change in the oxidation number of chlorine from 0 to –1

$$2Fe^{2+} - 2e^- \rightarrow 2Fe^{3+}$$
$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Equation 4

$$\underset{\text{R.A.}}{Zn(s)} + \underset{\text{O.A}}{CuSO_4(aq)} \rightarrow ZnSO_4(aq) + Cu(s)$$

This is a displacement reaction in which the zinc atom, Zn^0, donates two electrons which are accepted by the copper(II) ion, Cu^{2+}. The zinc atom goes into solution as zinc ion, Zn^{2+}, while the copper(II) ion is deposited as copper atom, Cu^0.

$$Zn^0 - 2e^- \rightarrow Zn^{2+}$$
$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

The oxidation number of zinc increases in the positive direction from 0 to +2, while that of copper decreases in the same direction from +2 to 0.

Equation 5

$$\underset{\text{R.A.}}{3Cu(s)} + \underset{\text{O.A.}}{8HNO_3(aq)}$$
$$\rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

Oxidation number	Sulphur	Nitrogen	Carbon	Iron	Copper	Manganese	Chromi
+7						$KMnO_4$	
+6	H_2SO_4						$K_2Cr_2O_7$
+5		HNO_3					
+4	SO_2	NO_2	$CaCO_3$			MnO_2	
+3		HNO_2		$FeCl_3$			$CrCl_3$
+2		NO	CO	$FeSO_4$	$CuSO_4$	$MnSO_4$	
+1		N_2O			CuCl		
0	S	N_2	C	Fe	Cu	Mn	Cr
−1		NH_2OH	C_2H_2				
−2	H_2S	N_2H_4	C_2H_4				
−3		NH_3	C_2H_6				
−4			CH_4				

Trioxonitrate(V) acid is an oxidizing agent while copper is a reducing agent. The oxidation number of copper increases from 0 to +2 in the positive direction when it donates two electrons per atom to form copper(II) ions. The electrons are accepted by the acid, which becomes partially reduced to nitrogen(II) oxide. The oxidation number of nitrogen decreases in the positive direction from +5 (in HNO_3) to +2 (in NO).

$$3Cu^0 - 6e^- \rightarrow 3Cu^{2+}$$
$$8HNO_3 + 6e^- \rightarrow 6NO_3^- + 4H_2O + 2NO$$

The following are not redox reactions because the oxidation numbers of the elements in the reactants have not undergone any change.

Note The oxidation number of each element in the equations is written below it.

(a) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
(+1) (−1) (+1)(−1)

(b) $2HCl(aq) + CaCO_3(s)$
$\rightarrow CaCl_2\ (aq) + H_2O(l) + CO_2(g)$
(+1)(−1) (+2)(+4)(−2) (+2)(−1) (+1)(−2) (+4)(−2)

Oxidizing and Reducing Agents

In all redox reactions, there are two main reactants – the oxidizing and the reducing agents. In any redox reaction, the oxidizing agent (electron acceptor) will become reduced while the reducing agent (electron donor) becomes oxidized.

Oxidizing agent = electron acceptor
= substance which is reduced
= substance in which oxidation number decreases in the positi
direction

Reducing agent = electron donor
= substance which is oxidized
= substance in which oxidation number increases in the positi
direction

Substances can act as both oxidizing and reduci agents depending on the reaction conditions. F example, water, acting as an oxidizing agent, oxidiz carbon

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$

and as a reducing agent, it reduces fluorine.

$$2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$$

Thus, we must examine a redox reaction carefull before deciding on the behaviour of any substanc that participates in that reaction.

Tests for oxidizing agents

The action of oxidizing agents on iron(II) chlorid and hydrogen sulphide is frequently employed i qualitative analysis as tests for the identification o oxidizing agents.

Action on iron(II) chloride When a green solution of iron(II) chloride, $FeCl_2$, is added to an oxidizing agent, the iron(II) ions donate an electron each to the oxidizing agent. As a result, the iron(II) ions become oxidized to the brown-coloured iron(III) ions.

$$\underset{\text{green}}{Fe^{2+}} \xrightarrow{-e^-} \underset{\text{brown}}{Fe^{3+}}$$

Action on hydrogen sulphide When hydrogen sulphide, H_2S, is passed through a solution of an oxidizing agent, yellow sulphur is deposited, due to the oxidation of the sulphide ions, S^{2-}, by the oxidizing agent. During this process, the sulphide ion donates its two electrons to the oxidizing agent (electron acceptor) to become atomic sulphur, S^0.

$$S^{2-} \xrightarrow{-2e^-} S^0$$

Tests for reducing agents

The action of reducing agents on potassium tetraoxomanganate(VII) and potassium heptaoxochromate(VI), acidified with tetraoxosulphate(VI) acid, is used in qualitative analysis as tests for the identification of reducing agents.

Action on acidified potassium tetraoxomanganate(VII) Reducing agents change a solution of acidified potassium tetraoxomanganate(VII), $KMnO_4$, from purple to colourless. This is because the tetraoxomanganate(VII) ion, MnO_4^-, which is purple in colour, is reduced to the manganese(II) ion, Mn^{2+} which is colourless.

$$\underset{\text{purple}}{MnO_4^-(aq)} + \underset{\text{from acid}}{8H^+(aq)} \xrightarrow{+5e^-} \underset{\text{colourless}}{Mn^{2+}(aq)} + 4H_2O(l)$$

This purple colour can be restored by the addition of an oxidizing agent as the reaction is reversible.

$$\underset{\text{colourless}}{Mn^{2+}(aq)} + 4H_2O(l) \xrightarrow{-5e^-} \underset{\text{purple}}{MnO_4^-(aq)} + 8H^+(aq)$$

Action on acidified potassium heptaoxochromate(VI) Reducing agents change the orange colour of acidified potassium heptaoxo-chromate(VI), $K_2Cr_2O_7$, to green. This is because the heptaoxochromate(VI) ion, $Cr_2O_7^{2-}$, which is orange in colour is reduced to the chromium(III) ion, Cr^{3+}, which is green in colour.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + \underset{\text{from acid}}{14H^+(aq)} \xrightarrow{+6e^-} \underset{\text{green}}{2Cr^{3+}(aq)} + 7H_2O(l)$$

Electrolytic Oxidation and Reduction

In electrolysis (see page 186), metallic ions from the solution are deposited as metal atoms on the cathode (negative pole) by electron gain. At the anode (positive pole), the negative ions from the solution lose electrons and are discharged either as gaseous molecules, or the metallic atoms of the anode are dissolved in solution as positive ions.

Thus, we can say that during electrolysis, oxidation takes place at the anode, and reduction at the cathode.

Balancing Redox Equations

The most common way of balancing redox equations is by considering the two half-equations involved in such reactions.

1 Write down the oxidizing agent and the reducing agent. In each case, deduce what the product should be.
2 Write the half-equations for oxidation and reduction. Balance the atoms and charges for each equation by
   - adding appropriate numerical coefficients;
   - placing the correct number of H_2O, H^+ or OH^- on the appropriate side of the equation if necessary;
   - adding the correct number of electrons
      (i) on the right-hand side for the oxidation half-equation, and
      (ii) on the left-hand side for the reduction half-equation.
3 Make sure that the electron loss in the oxidation half-equation is balanced by the electron gain in the reduction half-equation.
4 Combine the half-equations to eliminate the electrons and get the overall redox equation.

Table 10.2

Oxidizing agent	Effective reduction change
Oxygen	$O_2(g) \rightarrow 2O^{2-}(s)$ or (aq)
Manganese(IV) oxide	$MnO_2(s) \rightarrow Mn^{2+}(aq)$
Hydrogen peroxide	$H_2O_2(aq) \rightarrow 2H_2O(l)$
Acidified potassium tetraoxomanganate(VII)	$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$
Acidified potassium heptaoxochromate(VI)	$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$
Chlorine	$Cl_2(g) \rightarrow 2Cl^-(aq)$
Concentrated trioxonitrate(V) acid	$NO_3^-(aq) \rightarrow NO_2(g)$
Hot concentrated tetraoxosulphate(VI) acid	$SO_4^{2-}(aq) \rightarrow SO_2(g)$
Silver salt (and any metal ion low in the reactivity series)	$Ag^+(aq) \rightarrow Ag(s)$

Reducing agent	Effective reduction change
Hydrogen	$H_2(g) \rightarrow 2H^+$
Carbon	$C(s) \begin{cases} \rightarrow CO(g) \\ \rightarrow CO_2(g) \end{cases}$
Carbon(II) oxide	$CO(g) \rightarrow CO_2(g)$
Hydrogen sulphide	$S^{2-}(g) \rightarrow S(s)$
Sulphur(IV) oxide	$SO_2(g) \rightarrow SO_4^{2-}(aq)$
Ammonia	$NH_3(g) \rightarrow N_2(g)$
Iron(II) salt	$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$
Potassium iodide	$2I^-(aq) \rightarrow I_2(g)$
Sodium and any metal atom high in the reactivity series	$Na(s) \rightarrow Na^+(aq)$

NOTE In general, metallic elements, being electropositive, tend to lose their electrons easily and so are good reducin agents, while non-metallic elements, being electronegative, are oxidizing agents.

EXAMPLE

Write a balanced ionic equation for the redox reaction between acidified potassium tetraoxomanganate(VII) and iron(II) tetraoxosulphate(VI).

Step 1

(a) Tetraoxomanganate(VII) ion is the oxidizing agent. It is reduced to manganese(II) ion.

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

(b) Iron(II) ion is the reducing agent. It is oxidized to iron(III) ion.

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

Step 2

(a) Reduction half-equation

(i) Balance the number of atoms first by adding the correct number of H^+ and H_2O on the appropriate sides of the equation.

$$MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

(ii) Next, balance the number of charges.
Total number of charges on left-hand side
= (–1) + (+8) = +7
Total number of charges on right-hand side
= +2

To balance the charges, we add $5e^-$ to the left-hand side. Thus, the balanced reduction half-equation is as follows:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

(b) Oxidation half-equation

(i) $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

The number of atoms is balanced in the above equation.

(ii) Balance the number of charges.
Total number of charges on left-hand side = +2
Total number of charges on right-hand side = +3

To balance the charges, we add one electron, e^-, to the right-hand side. Thus, the balanced oxidation half-equation is as follows:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

Step 3

(a) Reduction half-equation

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

(b) Oxidation half-equation
Multiply the half-equation by 5.

$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$$

Now, the number of electrons involved in the oxidation and reduction half-equations are the same. Combine both the half-equations to eliminate the electrons. The overall ionic equation for the redox reaction is as follows:

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

SUMMARY

- Chemical reactions are changes in which some new chemical substances are formed. They can be classif into the following.

Type of reaction	General equation	Explanation
Combination	$A + B \rightarrow AB$	Two substances combine to form one substance.
Decomposition	ABC heat $\xrightarrow{\text{heat}} AB + C$	One substance splits into two or more simpler substances. Usually, heat is required.
Displacement	$A + BY \rightarrow B + AY$	The ability of one element or group to displace another is determined by their relative positions in the electrochemical series.
Double decomposition	$AB + CD \rightarrow AD + CB$	Two reactants are both decomposed to form new substances b an exchange of radicals.
Catalytic reaction	$A + B \xrightarrow{\text{catalyst}} C$	A catalyst is used to speed up the reaction.
Reversible reaction	$A + B \rightleftharpoons C + D$	A reaction in which the products can react to give the reactan Conditions of the forward and backward reactions may be th same or different.
Thermal dissociation	$AB \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} A + B$	It is a reversible reaction. Forward reaction usually requires heating. Backward reaction involves cooling.
Redox reaction	$\underset{\text{O.A.}}{A} + \underset{\text{R.A.}}{B} \rightarrow C + D$	A reaction in which one reactant is oxidized and the other is reduced. Reactants are an oxidizing agent and a reducing agen

- Catalysts are substances that alter the rates of reactions. They remain unchanged in chemical nature an in mass at the end of the reactions.
- An oxidation, in modern terms, is a process of electron loss or an increase in the oxidation number. A reduction is a process of electron gain or a decrease in the oxidation number.
- Oxidation and reduction reactions must take place together since a substance cannot lose/donate electro unless another substance is present to gain/accept electrons. These reactions are known as redox reactio
- A redox reaction can be represented by the oxidation half-equation showing electron loss and the reducti half-equation showing electron gain.
- An oxidizing agent, being an electron acceptor, will become reduced or its oxidation number will b decreased. A reducing agent, being the electron donor, will become oxidized or its oxidation number w be increased.
- Tests for oxidizing agent (a) It oxidizes sulphide ions, S^{2-}, to a yellow precipitate of sulphur; (b) it oxidi green iron(II) chloride to brown iron(III) chloride.
- Tests for reducing agent (a) It reduces purple acidified potassium tetraoxomanganate(VII) ion MnO_4^- manganese(II) ion, Mn^{2+}; (b) it reduces orange acidified potassium heptaoxochromate(VI) ion, Cr_2O , to green chromium(III) ion, Cr^{3+}.
- To balance redox reactions:
  - (a) Write down the half-equations for oxidation and reduction.
  - (b) Balance the half-equations.
  - (c) Ensure that the electron gain in the reduction process is equal to the electron loss in the oxidatio process.
  - (d) Add the half-equations to eliminate the electrons and get the overall reaction.

1. The type of chemical reaction shown below in $H_3O^+ + OH^- \rightarrow 2H_2O$
   - A Hydrolysis
   - B Direct combination
   - C Oxonolysis
   - D Neutralization

2. In the reaction,
   $2Pb(NO_3)_2(s) \xrightarrow{heat} 2PbO(s) + 4NO_2g, + O_2(g)$
   - A lead (II) oxide is oxidized.
   - B NO_2 is isolated.
   - C $Pb(NO_3)_2$ is decomposed.
   - D $Pb(NO_3)_2$ is dissociated.

3. In employing MnO_2 in the reaction below
   $2KClO_3(s) \xrightarrow[\Delta]{MnO_2} 2KCl(aq) + 3O_2(g)$
   - A MnO_2 is catalysed.
   - B $KCLO_3$ is catalysed.
   - C the forward reaction is catalysed.
   - D the backword reaction is catalysed.

4. In the reaction
   $2SO_2(g) + O_2g \xrightarrow{V_2O_5(s)} 2SO_3(g)$
   It is an example of
   - A homogenous catalysis.
   - B heterogenous catalysis.
   - C inert catalysis.
   - D contact catalysis.

5. Promoters in chemical reactions
   - A improve the speed of chemical reactions.
   - B improve the efficiency of a catalyst.
   - C improve the stability of products.
   - D improve the stability of reactants.

6. Major difference between thermal dissociation and thermal decomposition is that
   - A thermal dissociation is not reversible.
   - B thermal decomposition is reversible.
   - C thermal dissociation is reversible.
   - D thermal decomposition is not reversible.

7. Oxidation reaction may be defined as follows except
   - A oxidation reaction is one in which electron is lost.
   - B oxidation reaction is one in which there is an increase in the oxidation number.
   - C oxidation reaction is one in which oxygen is gained.
   - D oxidation reaction is one in which hydrogen is gained.

8. From the reaction,
   $2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(s) + 2Fe^{2+}(aq)$
   who is the reducing agent
   - A I^-
   - B $2Fe^{3+}$
   - C I_2
   - D $2Fe^{2+}$

9. From $C(s) + ZnO(s) \rightarrow CO_2(g) + 2Zn(s)$
   The oxidation number of free carbon is
   - A –4
   - B +4
   - C zero
   - D +2

10. What is the oxidation number of chromium in sodium heptaoxo chromate (VI)
    - A +3
    - B +12
    - C +6
    - D +2

11. In balancing the above redox equation, the value of *x* is given as
    $MnO_4^-(aq) + 8H^+ag + X \rightarrow Mn^{2+}(aq) + 4H_2O\ l$
    - A 10e
    - B 2e
    - C 5e
    - D 4e

12. Which of the following does not define oxidation?
    - A Removal of electron(s)
    - B Addition of oxygen
    - C Removal of electronegative elements
    - D Increase of oxidation number in the positive direction
    - E Removal of hydrogen

13. $Cl_2 + 2KBr \rightarrow 2KCl + Br_2$
    In the above equation chlorine is
    - A an oxidizing agent.
    - B a reducing agent.
    - C an electron donor.
    - D an acid.
    - E a base.

14. The oxidation state of sulphur in tetraoxosulphate(VI) is

A $+5$. C $+6$. E $+2$.
B $+4$. D -2.

15. $2H_2 + O_2 \rightarrow 2H_2O$
In the above reaction, the oxidation number of hydrogen changes from

A $+2$ to $+1$. D 0 to $+2$.
B $+4$ to $+1$. E 0 to $+1$.
C $+1$ to $+2$.

16. Write short notes on the following reactions, giving examples in each case.

(a) Reversible reaction
(b) Oxidation-reduction (redox) reaction
(c) Double decomposition
(d) Thermal dissociation

17. Define accurately the term catalyst and give five characteristics of a catalyst.

18. (a) Define the following:
(i) Oxidizing agent (ii) Reducing agent
(b) Show that the following reactions are oxidation-reduction reactions, indicating with reasons the oxidizing and reducing agents.

(i) $2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$
(ii) $3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(l) + N_2$
(iii) $2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$
(iv) $2FeCl_2(aq) + Cl_2(g) \rightarrow 2FeCl_3(aq)$

19. (a) When hydrogen sulphide is burnt in oxyge to form sulphur(IV) oxide and water, ho does the oxidation number of sulphu change?

$$2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2SO_2(g$$

(b) Write down the half-equation whic represents the oxidation of iron(II).

20. Break up the following equations into two half equations — one for oxidation and one fo reduction.

(a) $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
(b) $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$
(c) $2Al(s) + 3Pb^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Pb(s$

ELECTRODE POTENTIALS • 11
ELECTROCHEMICAL SERIES • ELECTROLYSIS

ELECTRODE POTENTIAL

Metal ions/metal system

If we place a metal plate in a solution containing its ions (e.g. a solution of one of its salts), some of the atoms from the metal plate will ionize and go into solution as positively charged ions, leaving behind their valence electrons on the surface of the plate. For a univalent ion, we have

$$\underset{\text{plate}}{M(s)} \rightarrow \underset{\text{solution}}{M^{+}_{(1)}(aq)} + \underset{\text{plate}}{e^{-}} \qquad (1)$$

At the same time, some of the metallic ions in solution will take up electrons from the metal plate and deposit themselves as neutral atoms on the plate, leaving behind an excess of anions in the salt solution.

$$\underset{\text{solution}}{M^{+}(aq)} + \underset{\text{plate}}{e^{-}} \rightarrow \underset{\text{plate}}{M(s)} \qquad (2)$$

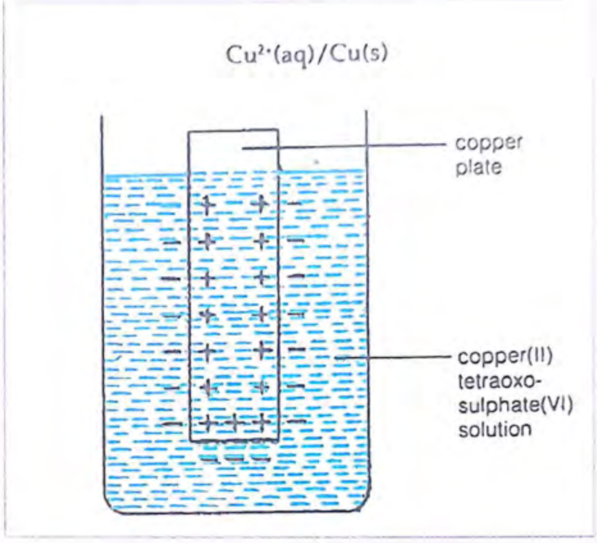
If reaction (1) is favoured, the metal plate or electrode becomes negatively charged with respect to the solution or electrolyte. If reaction (2) is favoured, the electrode becomes positively charged with respect to the electrolyte. A potential difference, known as the electrode potential for the metal ions/metal system is set up between the metallic electrode and the electrolyte solution.

Copper(II) ions/copper system When a copper plate is dipped into a copper(II) tetraoxosulphate(VI) solution, the net reaction is as follows:

$$\underset{\text{solution}}{Cu^{2+}(aq)} + \underset{\text{plate}}{2e^{-}} \rightarrow \underset{\text{plate}}{Cu(s)}$$

i.e. the positive copper(II) ions from the solution acquire two electrons each from the copper plate to become deposited as neutral metallic copper atoms on the plate. As a result,

Fig. 11.1 Electrode potential of copper



- the copper plate becomes positively charged on the surface due to a deficit of electrons; and
- the solution becomes negatively charged due to an excess of the negatively charged tetraoxosulphate(VI) ions, SO_4^{2-}.

The copper plate, thus, becomes positively charged with respect to the solution. A potential difference, known as the electrode potential of copper, is set up between the copper metal and the solution containing its ions.

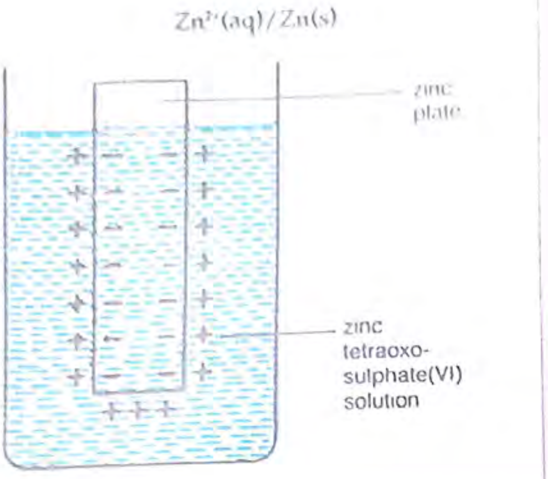
Zinc ions/zinc system If a zinc plate is dipped into a zinc tetraoxosulphate(VI) solution, the net reaction is as follows:

$$\underset{\text{plate}}{Zn(s)} \rightarrow \underset{\text{solution}}{Zn^{2+}(aq)} + \underset{\text{plate}}{2e^{-}}$$

i.e. the neutral zinc atoms on the plate give up electrons to the plate and go into solution as positively charged zinc ions. As a result,

- zinc plate becomes negatively charged on the surface due to an excess of electrons; and

Fig. 11.2 Electrode potential of zinc



- the solution becomes positively charged due to excess zinc ions.

The zinc plate, thus, becomes negatively charged with respect to the solution. A potential difference, known as the electrode potential of zinc, is set up between the zinc metal and the solution containing its ions.

Standard electrode potentials

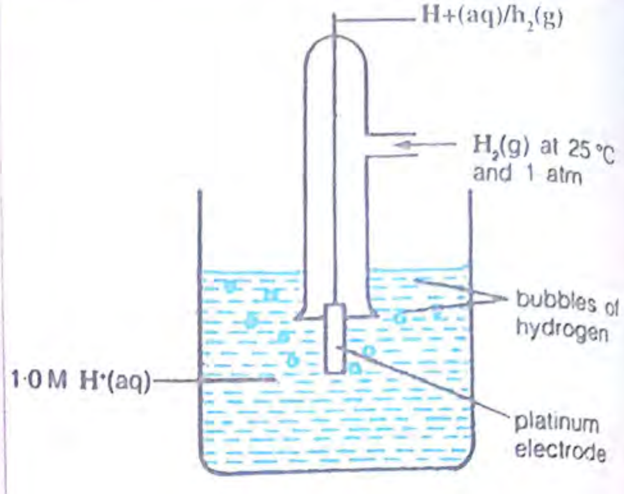
Electrode potentials vary from one metal ions/ metal system to another. The electrode potential of a given system depends on

- the overall energy change,
- the concentration of ions in the solution, and
- the temperature.

For comparing electrode potential values of different metal ions/metal systems, the *standard electrode potential* ($E^{\ominus}$) is used. This is the potential difference set up when a metal is in contact with a one-molar solution of its ions at 25 °C. It is not possible to measure the absolute value of an electrode potential directly; instead, it must be measured against some reference standard.

Hydrogen has been chosen internationally as an arbitrary standard, with an electrode potential value of zero at all temperatures. The standard electrode potential of a given metal ions/metal system is then expressed in terms of the potential difference (in volts) which exists between th metallic electrode and the standard hydrogen electrode. This is known as the standard electrode potential of the metal ions/meta system on the *hydrogen scale*. The electrode potentia value is

Fig. 11.3 Standard hydrogen electrode



- positive if electrons flow from the hydrogen electrode to the metal electrode; and
- negative if electrons flow from the metal electrode to the hydrogen electrode.

The standard hydrogen electrode consists of hydrogen gas at 25 °C and one atmospheric pressure, bubbling around an inert platinum electrode in contact with a one-molar solution of hydrogen ions, i.e. $2H^+(aq)/H_2(g)$ system.

The standard electrode potential of a metal ions/metal system is the potential difference set up between the metal and a one-molar solution of its ions at 25 °C (arbitrarily taking the standard electrode potential of the hydrogen ions/hydrogen gas system as zero volt).

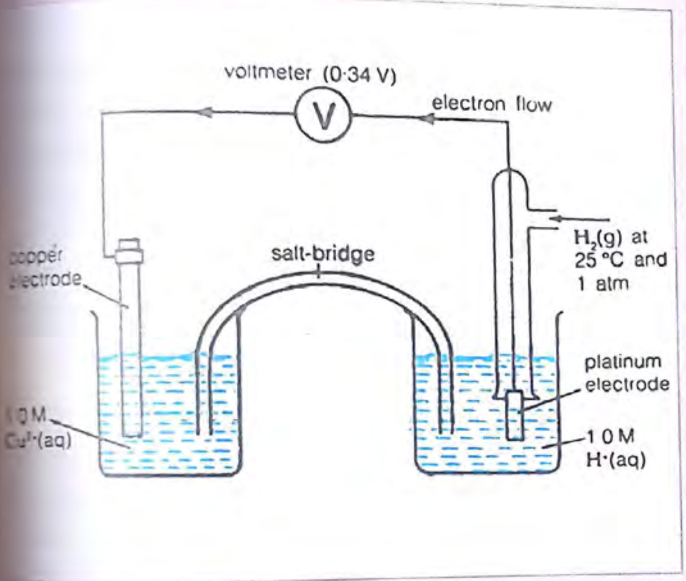
Measuring standard electrode potentials

We use the apparatus in fig. 11.4 to measure the standard electrode potential of a metal ions/metal system. Here, the standard electrode potential of copper, $Cu^{2+}(aq)/Cu(s)$ system, is being measured.

When the $Cu^{2+}(aq)/Cu(s)$ system or *half-cell* is connected to the $2H^+(aq)/H_2(g)$ system or half-cell by a salt bridge, the voltmeter shows a reading of 0.34 volts. This is the potential difference between the two half-cells, and is known as the *electromoti* e 11.1 Standard electrode potentials ($E^\ominus$) of some ommon metal ions/metal systems.

Metal ion/metal	$E^\ominus$
$K^+(aq)$ / K(s)	–2.92 V
$Ca^{2+}(aq)$ / Ca(s)	–2.87 V
$Na^+(aq)$ / Na(s)	–2.71 V
$Zn^{2+}(aq)$ / Zn(s)	–0.76 V
$2H^+(aq)$ / $H_2(g)$	0.00 V
$Cu^{2+}(aq)$ / Cu(s)	+0.36 V
$Ag^+(aq)$ / Ag(s)	+0.80 V
$Au^+(aq)$ / Au(s)	+1.68 V

11.4 Measuring standard electrode potential.



force or *e.m.f.* of the cell. As the electrode potential of hydrogen is taken to be zero, the standard electrode potential of copper is either +0.34 V or –0.34 V.

The half-cell reactions at the copper and hydrogen electrodes show that electrons flow from the hydrogen electrode to the copper electrode. The electrode potential of copper is, thus, +0.34 V (voltmeter needle deflects to the left).

At the platinum in hydrogen electrode

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- \quad \text{(Oxidation)}$$

At the copper electrode

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad \text{(Reduction)}$$

Overall reaction

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$$

ELECTROCHEMICAL CELLS

Producing an electric current

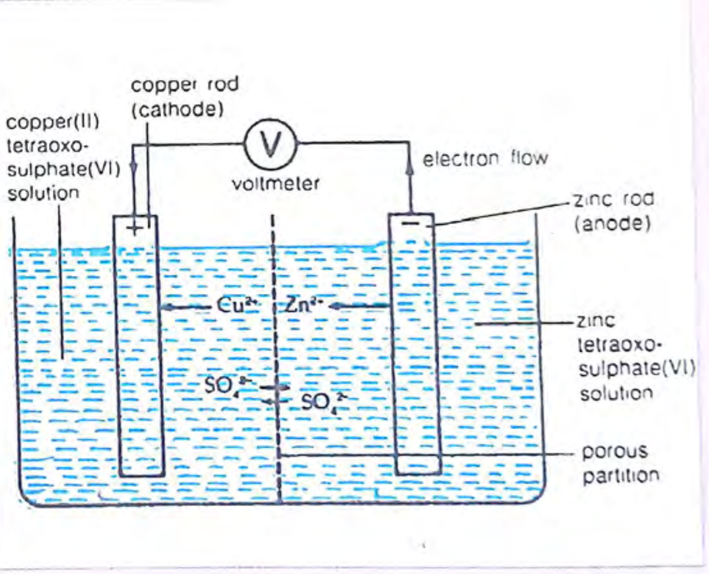
A flow of electrons (i.e. an electric current) can be set up between two electrodes which have different electrode potentials. The readiness and speed of this electron flow are determined by the magnitude of the difference between the two electrode potentials.

In fig. 11.5, metallic zinc is in contact with zinc ions, and metallic copper with copper(II) ions . An electric current flows through the wire which connects the two metals or electrodes outside the solution.

This device, in which chemical energy is converted to electrical energy, is called an *electrochemical cell*, *voltaic cell* or *galvanic cell.* It consists of two half-cells:

- an oxidation half-cell reaction occurs at the electrode in one half-cell, and
- a complementary reduction half-cell reaction occurs at the electrode in the other half-cell.

Fig. 11.5 Producing an electric current.



The overall redox reaction results in a flow of electrons, i.e. an electric current.

In fig. 11.5, the atoms at the zinc electrode undergo oxidation and lose two electrons each to form zinc ions which go into the solution. The zinc electrode becomes negatively charged and functions as the negative electrode or *anode*. The excess electrons on the zinc electrode are made to flow along the wire to the electron-deficient copper electrode where they are

are connected to an external circuit, it produces electricity by discharging.

At the anode (dicharging cell) During the process of discharging, the lead atoms release two electrons each to become oxidized to lead(II) ions, Pb^{2+}, which then combine with the tetraoxosulphate(VI) ions, SO_4^{2+}, in the electrolyte to become deposited on the anode as lead(II) tetraoxosulphate(VI), $PbSO_4$.

$$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$$
$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

The electrons released pass round an external circuit as an electric current to be used for starting the engine of a vehicle, for lighting the car lamps and so on before arriving at the cathode.

At the cathode (discharging cell) The electrons from the anode are accepted at the cathode where the lead(IV) oxide and the hydrogen ions from the electrolyte undergo reduction to produce lead(II) ions and water.

$$PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$$

The lead(II) ions then combine with the tetraoxosulphate(VI) ions from the electrolyte to become deposited at the cathode as lead(II) tetraoxosulphate(VI).

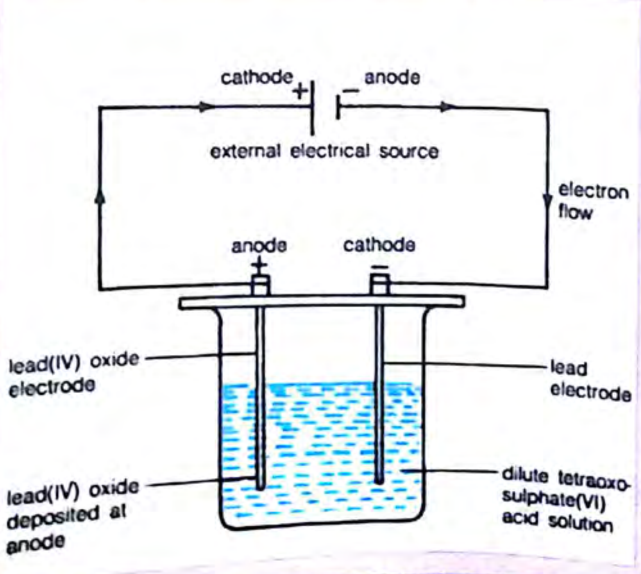


Fig. 11.10 Lead accumulator – recharging.

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

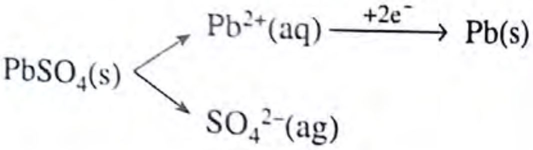
During the discharging process,

- the density of the acid decreases to 1.15 g c due to the absorption of hydrogen and tetrao sulphate(VI) ions from the electrolyte; and
- the e.m.f. of the cell drops to 1.8 V.

When both electrodes are completely covered lead(II) tetraoxosulphate(VI) deposits, the l accumulator will stop discharging a current. To m it produce a current again, it will have to be recharg

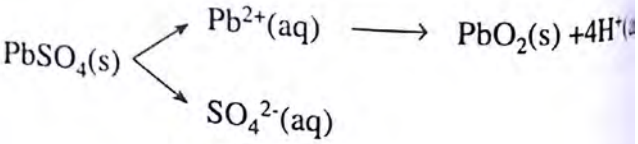
During the process of recharging, the re reactions at the respective electrodes in the cell reversed because it is an electrolysis. The electr which is the anode in the charged cell becomes cathode, while the cathode becomes the anode. T anode and the cathode of an external electrical sou are connected to the cathode and anode of recharging cell respectively. The reactions summarized as follows:

At the cathode (recharging cell)



$$\begin{tikzcd} & Pb^{2+}(aq) \arrow[r, "+2e^-"] & Pb(s) \\ PbSO_4(s) \arrow[ur] \arrow[dr] & & \\ & SO_4^{2-}(ag) & \end{tikzcd}$$

At the anode (recharging cell)



$$\begin{tikzcd} & Pb^{2+}(aq) \arrow[r] & PbO_2(s) +4H^+ \\ PbSO_4(s) \arrow[ur] \arrow[dr] & & \\ & SO_4^{2-}(aq) & \end{tikzcd}$$

After recharging,

- the density of the acid in the cell returns to initial value of 1.25 g cm^{-3} due to the release the same amount of ions (i.e. in the proportion $4H^+:2SO_4^{2-}$) into the solution; and
- the e.m.f. of the cell returns to 2.2 V.

ELECTROCHEMICAL SERIES

We have learnt how to find the standard electro potentials of metal ions/metal half-cells. In a simil way, we can also find the standard electrode potenti

Half-cell reactions Reduction → ← Oxidation		E° in volts	Significant properties Redox agents	Electro-negativity
$K^+ (aq) + e^-$	$\rightleftharpoons K (s)$	–2.92	Very strong reducing agents	Increasing electropositivity ↑
$Ca^{2+} (aq) + 2e$	$\rightleftharpoons Ca (s)$	–2.87		
$Na^+ (aq) + e^-$	$\rightleftharpoons Na (s)$	–2.71		
$Mg^{2+} (aq) + 2e$	$\rightleftharpoons Mg (s)$	–2.37		
$Al^{3+} (aq) + 3e^-$	$\rightleftharpoons Al (s)$	–1.66		
$Zn^{2+} (aq) + 2e$	$\rightleftharpoons Zn (s)$	–0.76		
$Fe^{2+} (aq) + 2e$	$\rightleftharpoons Fe (s)$	–0.44		
$Sn^{2+} (aq) + 2e^-$	$\rightleftharpoons Sn (s)$	–0.14	Increasing strength of reducing agents ↑ Increasing strength of oxidising agents ↓	
$Pb^{2+} (aq) + 2e^-$	$\rightleftharpoons Pb (s)$	–0.13		
$2H^+ (aq) + 2e^-$	$\rightleftharpoons H_2 (g)$	0.00		
$Cu^{2+} (aq) + 2e^-$	$\rightleftharpoons Cu (s)$	+0.34		
$O_2 (aq) + 2H_2O(l) + 4e^-$	$\rightleftharpoons 4OH^- (aq)$	+0.40		Increasing electronegativity ↓
$I_2 (s) + 2e^-$	$\rightleftharpoons 2I^- (aq)$	+0.54		
$Fe^{3+} (aq) + e^-$	$\rightleftharpoons Fe^{2+} (aq)$	+0.77		
$Ag^+ (aq) + e^-$	$\rightleftharpoons Ag (s)$	+0.80		
$Br_2 (l) + 2e^-$	$\rightleftharpoons 2Br^- (aq)$	+1.06		
$Cr_2O_7^{2-} (aq) + 14H^+(aq) + 6e^-$	$\rightleftharpoons 2Cr^{3+} (aq) + 7H^2O(l)$	+1.33		
$Cl_2 (aq) + 2e^-$	$\rightleftharpoons 2Cl^- (aq)$	+1.36	Very strong oxidising agents	
$MnO_4^- (ag) + 8H^+(aq) + 5e^-$	$\rightleftharpoons Mn^{2+} (aq) + 4H_2O(l)$	+1.52		
$F_2(g) + 2e^-$	$\rightleftharpoons 2F^- (aq)$	+2.87		

f non-metal/non-metal ions half-cells, such as $Br_2(l)$/ Br(aq), and ion/ion half-cells, such as $Fe^{3+}(aq)$/ e^{2+}(aq). These standard electrode potentials of the arious half-cells can be arranged in order, starting vith the most negative values, to give the *lectrochemical series.*

In the electrochemical series,

- the good reducing agents, i.e. strongly electropositive elements, are at the top, and
- the good oxidizing agents, i.e. strongly electronegative elements, are at the bottom.

Thus, the series is very useful since we can use it o predict the properties and chemical behaviour of elements and their respective compounds.

Significant features of the series

Current flow and e.m.f. of a cell The direction of the current flow from a simple electrochemical cell is dependent on the relative positions of the two metallic electrodes on the electrochemical series. The metal higher up the series will serve as the negative electrode while that lower down will serve as the positive electrode.

The electromotive force or e.m.f. of an electrochemical cell is given by the algebraic difference between the electrode potentials of the two metallic electrodes. A big e.m.f. means a powerful cell. So, if we want a powerful cell, the metals which serve as electrodes should be far apart in the electrochemical series.

Chemical reactivity of elements The electrochemical series is sometimes known as the activity series of metals. This is because the metals in the series are arranged in decreasing order of chemical reactivity. (The exception is calcium, which is above sodium but is less reactive.) Since reactivity of metals is related to their readiness to form positive ions, the strongly electropositive metals like sodium and potassium are more reactive than the weakly electropositive metals like silver and gold.

The non-metals in the series are arranged in increasing order of chemical reactivity. This is because reactivity of non-metals is related to their readiness to form negative ions. For example, a strongly electronegative non-metal like chlorine is more reactive than a less electronegative non-metal like iodine.

Two elements are more likely to form a stable compound if they are far apart in the series. Elements which are close to one another in the series will either not combine at all or form very unstable compounds. Hence, non-metals combine very readily with metals, while metals usually do not form stable compounds with one another.

Occurrence in nature The metals above hydrogen in the series do not occur in the free state in nature. Instead, they exist as compounds, e.g. trioxonitrates(V), trioxocarbonates(IV), chlorides, sulphides and oxides. This is because such metals are very reactive and form compounds readily with the non-metallic elements in their environment. Metals like copper, silver and gold, which are below hydrogen in the series, are inactive, and tend to occur uncombined, i.e. in the free state, in ores.

Displacement and redox reactions The series shows at a glance the order in which elements will displace one another. Metals will displace other metals which are below them in the series. For example, if a piece of zinc is placed in a copper(II) tetraoxosulphate(VI) solution, some of the zinc atoms tend to go into the solution as ions while the copper ions tend to come out of the solution and are deposited as metallic atoms on the surface of the zinc. This is because zinc is higher up the series than copper and has a greater tendency to exist as positive ions in solution.

$$Zn(s) + Cu^{2+}(aq) \rightarrow zn^{2+}(aq) + Cu(s)$$

The ease with which one metal can displace another is also dependent on their relative positions in the series. The further apart they are in the series, the easier it is for displacement reactions to occur. Thus, zinc easily displaces copper from copper(II) salt solution but lead which is only two elements above copper in the series will not displace the latter so readily.

A metal cannot displace another which is above it in the series. Copper and the metals below it in the series ca never displace hydrogen from acids.

Non-metals will displace other non-metals whic are above them in the series. For example, chlorin will displace bromine or iodine from solutions of the ions, as in the extraction of bromine from sea-wate

$$Cl_2(g) + MgBr_2(aq) \rightarrow MgCl_2(aq) + Br_2(g)$$

Ionically,

$$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(g)$$

Displacement reactions are also redox reaction From the electrochemical series, we can tell whic element will oxidize another, e.g. an element lik copper will oxidize another like zinc which is above it in the series. Alternatively, since the ability of a element to reduce another depends on its ability t donate electrons, we can say that

- the reducing power of elements decrease progressively down the series; while
- the oxidizing power increases down the same series.

This is why the electrochemical series is als known as the redox series.

Preferential discharge of ions in electrolysis
During electrolysis,

- a metal lower down in the series is usually discharged in preference to the one above it;
- a non-metal higher up the series is usually discharged in preference to the one below it.

These will be discussed later.

Limitations of the electrochemical seri

Although the electrochemical series gives us a lot of important information, it has its limitations. The series only tells us whether a certain redox reaction can take place. It cannot predict the rate at which the reaction will occur and the amount of materials reacting. Standard electrode potentials relate only to standard conditions, so the values are affected by changes in concentration, temperature and pressure. Such effec however, are generally small and negligible.

Corrosion as an electrochemical process

Most metals react with the oxygen and moisture in the surrounding air to form oxides. As a result of such reactions, the metals gradually deteriorate. This process is known as *corrosion.*

Corrosion is of great economic importance. This is because many things around us such as vehicles and parts of buildings are made of metals.

Iron is the most common metal that is found around us. Therefore, its corrosion is of special significance. The corrosion of iron is known as *rusting.* Rusting is actually an electrochemical process. Let us see how this process occurs.

Iron rusts when it comes into contact with air and water because electrochemical cells are set up at the surface of contact.

At the anode At the anode or anodic region, iron is oxidized to give iron(II) ions, Fe^{2+}.

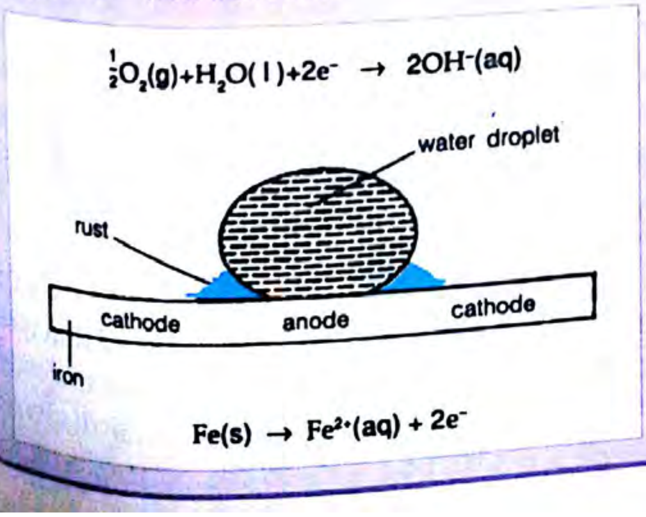
$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

At the cathode Oxygen from the air dissolves in the water layer. At the cathodic region, the oxygen concentration in the water is higher. The oxygen is reduced by the electrons from the anode to give hydroxide ions, OH^-.

$$\frac{1}{2}O_2(aq) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$$

The iron(II) and hydroxide ions diffuse away from the anodic and cathodic regions and settle down as iron(II) hydroxide, $Fe(OH)_2$. This is further oxidized by the dissolved oxygen to form brown hydrated iron(III) oxide, $Fe_2O_3.xH_2O$, or rust. Rust is soft and breaks off easily and the metal below continues to rust.

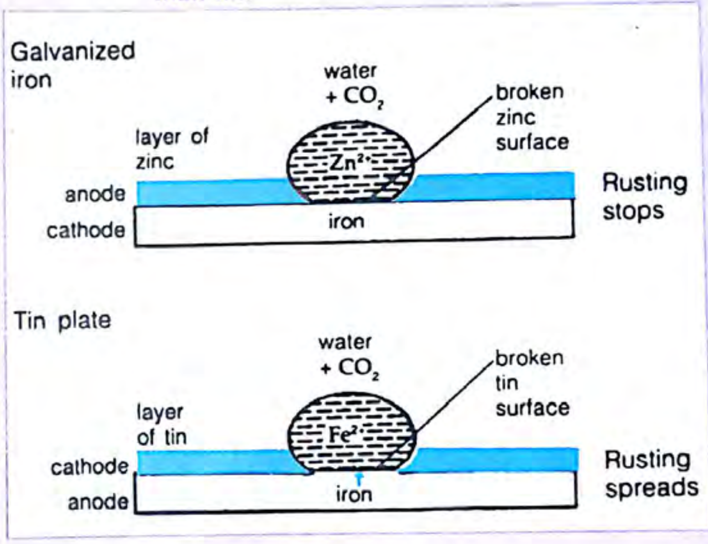
Fig. 11.11 How iron rusts.



Prevention of rnsting by cathodic protection

We can protect an object made of iron from rusting by coating it with another metal that does not corrode so easily. Both zinc and tin are used to coat iron objects. A tin-plated iron container, however, corrodes much faster than a galvanized iron container when they have both been subjected to the same amount of handling. This can be explained by using the electrochemical series.

Fig. 11.12 Zinc is a better protective covering for iron than tin.



Tin-plated iron is a sheet of iron coated with a thin layer of tin while galvanized iron is coated with zinc. During the course of handling, parts of the tin or zinc coat may become broken. The holes in them then become filled with trioxocarbonate(IV) acid, formed by the dissolving of carbon(IV) oxide in atmospheric moisture. As a result, simple electrochemical cells are set up as follows:

	Anode	Electrolyte	Cathode
Tin-plated iron	Iron	Dilute acid	Tin
Galvanized iron	Zinc	Dilute acid	Iron

In tin-plated iron, the iron, being above tin in the electrochemical series, serves as the anode. When the tin layer is broken, the iron ionizes and goes into the solution, thereby bringing about its rusting.

The metal parts of this vessel have to be painted regularly to protect them from corrosion.

In galvanized iron, the zinc, being above iron in the series, serves as the anode. When the zinc layer is broken, the zinc dissolves instead of the iron, which being the cathode, remains intact. Rusting of iron will only set in after all the zinc has corroded. Thus, zinc forms a more efficient protective covering for iron than tin.

ELECTRIC CHARGES AND CURRENT

Electric charges

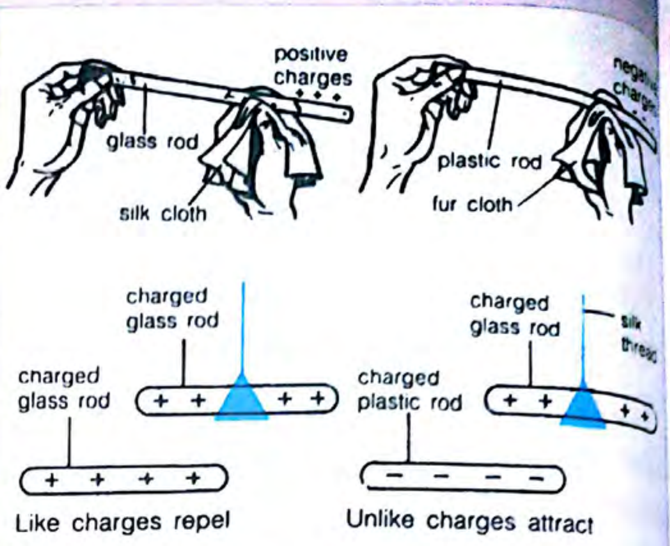
Matter is made up of atoms. An atom consists of positively-charged protons, neutrons and negatively-charged electrons. The electrical property of matter is due to the charges on these atomic sub-particles.

An atom is neutral, i.e. it has an equal number of protons and electrons. When two materials are rubbed together, however, electrons from the atoms of one material can be transferred onto the other material. The material that loses the electrons becomes positively charged, while the one that gains the electrons becomes negatively charged.

When objects made of certain materials gain or lose electrons, they become charged. Such objects exhibit *static electricity*. The charges on them remain stationary i.e. there is no electron flow. Charged objects attract uncharged objects. Objects with like charges repel one another and those with unlike charges attract one another.

We can show the presence of static electricity by rubbing a plastic ruler against the sleeve of a shirt. The ruler acquires a charge and is able to attract small bits of paper. When a glass rod is rubbed with a silk cloth and suspended by a silk thread, it repels another glass rod which has also been rubbed with a silk cloth. This repulsion is due to the presence of like (positive) charges on both the glass rods.

Fig. 11.13 Electrification by friction.



A glass rod rubbed with a silk cloth attracts a plastic rod that has been rubbed with a fur cloth. This attraction is due to the presence of unlike charges on the rods, since the glass rod is positively charged and the plastic rod, negatively charged.

Electric current and circuits

An electric current is a flow of electrons. The complete continuous path taken by these electrons is called an *electric circuit*. Some important effects are associated with such a flow of electrons (current) around an electric circuit. They are the heating, lighting, magnetic and chemical effects.

A simple electric circuit may consist of a source of electric energy (e.g. dry cell or an accumulator) connected by wires to a load (e.g. an electric bulb) and a switch. If the wires are not disconnected at any point along an electric circuit, we say that the circuit has a complete conducting path. Such a circuit is called a closed circuit. An open circuit is one which has one or more gaps along its conducting path.

In the electric circuit shown in fig. 11.14, the cell provides an e.m.f. which sets up a potential difference across the bulb and drives an electric current through it. Electrons flow from the negative terminal of a cell through a connecting wire to the positive terminal

Fig. 11.14 Simple circuits.

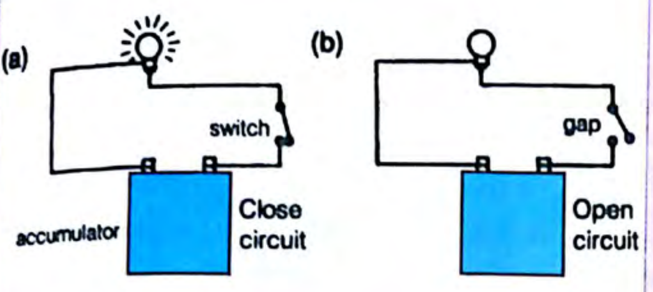
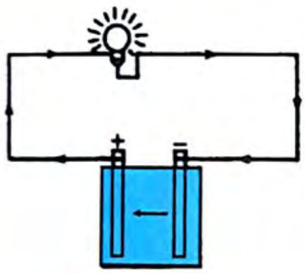


Fig. 11.15 Conventional direction of current.



Current flows from the positive to the negative terminal.

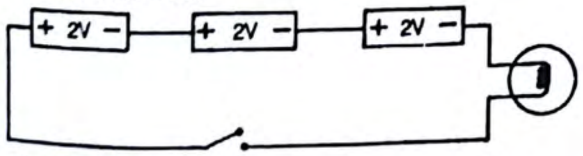
By convention, however, an electric current flows in the opposite direction, i.e. from the positive terminal (higher electrode potential value) to the negative terminal (lower electrode potential value) of the cells.

In electrical circuits, cells can be arranged in series or in parallel.

Fig. 11.16 Arrangement of cells in circuits.

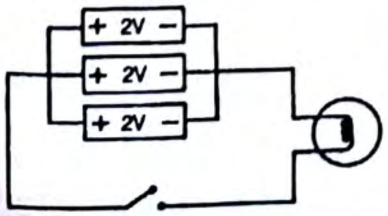
(a) Series arrangement

The resultant potential difference across the circuit is 2V + 2V + 2V = 6V.



(b) Parallel arrangement

The resultant potential difference across the circuit is only 2V.



Sources of electricity

An electric current can be produced by simple cells, batteries (where a number of simple cells are connected in series) and accumulators. All these devices produce only small amounts of electricity by chemical action.

A dynamo produces electric current by using a magnet. Large amounts of electricity can be produced by huge dynamos called generators.

The current produced by a dynamo is different from that produced by a cell. In a dynamo, the electric current is always changing its direction. The passage of current is first in one direction, then it changes to the opposite direction. Such a current is called an alternating current (a.c.). Cells produce direct current (d.c.) which does not change its direction of flow.

Solar energy is a possible important source of electricity in the future.

Conductors and Insulators

Substances which conduct electricity are called *conductors*. There are two types of conductors:

- *metallic conductors*, like metal wires, graphite and mercury, and
- *electrolytic conductors* (*electrolytes*) like fused lead(II) bromide, sodium chloride solution and dilute hydrochloric acid.

Non-conductors or *insulators* are substances that do not conduct electricity. They are either pure solids or liquids (non-electrolytes). Water, earth, moist air

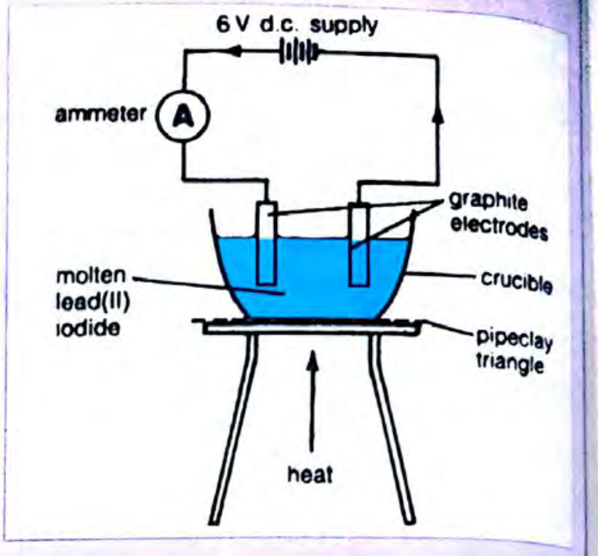
Experiment 11.1 To investigate the conduction of electricity in a molten substance.

Method Place some lead(II) iodide crystals in a crucible and dip two graphite electrodes into it. Connect the two electrodes to a 6-volt d.c. supply and an ammeter. Note any deflection of the ammeter needle. Start heating the solid lead (II) iodide crystals strongly and observe what happens to the ammeter needle.

Result When the lead(II) iodide melts, the ammeter needle becomes deflected.

Conclusion Solid lead(II) iodide does not conduct electricity but molten lead(II) iodide does.

Fig. 11.17 Molten lead(II) iodide conducts electricity.



and the human body are poor conductors of electricity. Metalloids such as germanium and silicon (known as *semi-conductors*) are also poor conductors of electricity.

ELECTROLYSIS

In electrochemical cells, electricity is generated by a chemical change. The reverse is also possible, i.e. an electric current can be used to bring about a chemical change.

Some common terms used in electrolysis are as follows:

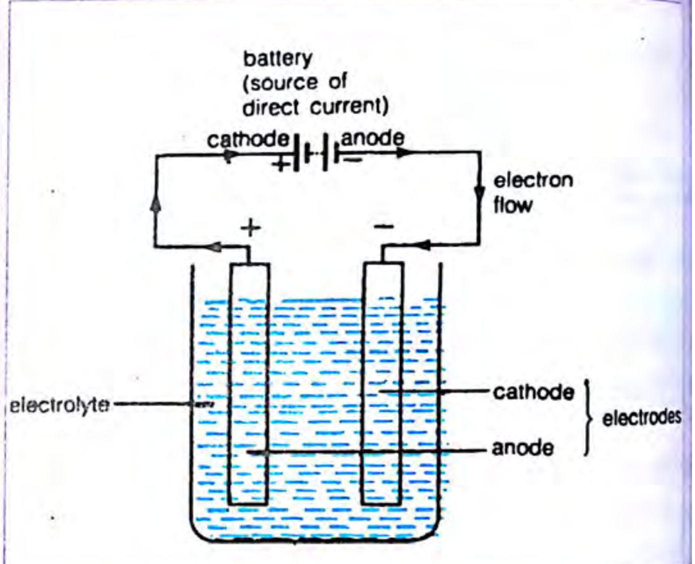
Electrolysis This is the chemical decomposition of a compound brought about by a direct current passing through either a solution of the compound or the molten compound.

Electrolyte This is a compound which conducts electricity and is decomposed in the process. To behave as an electrolyte, the compound must be in a liquid form, either as the molten compound or an aqueous solution of the compound. A non-electrolyte does not conduct electricity in this manner.

Electrodes These are conductors in the form of wires, rods or plates through which an electric current enters or leaves the electrolyte.

Anode This is the positive electrode by which the conventional current enters the electrolyte (or by which electrons leave an electrolyte). It is the electrode which is joined to the positive terminal of the electric supply.

Fig. 11.18 A simple electrolytic cell.



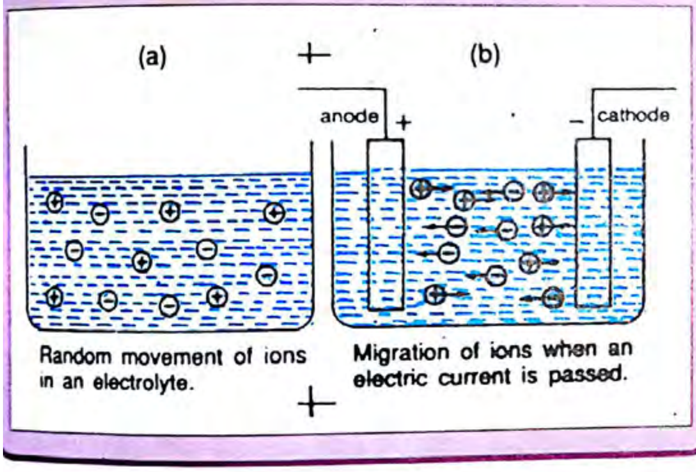
Cathode This is the negative electrode by which the conventional current leaves the electrolyte (or by which electrons enter the electrolyte). It is the electrode which is joined to the negative terminal of the electric supply.

Electrolytic cell This is an assembly of two electrodes in an electrolyte, and is used for the electrolysis of a substance. In the earlier days, this set up was known as a *voltameter.* In an electrolytic cell, oxidation occurs at the anode (positive electrode) and reduction at the cathode (negative electrode).

Ionic Theory

The ionic theory was first presented by Arrhenius in 1887 to explain electrolysis. The theory proposed that when an electrolyte is melted or dissolved in water, some, if not all, of the molecules of the substance dissociate into freely-moving charged particles called *ions*. The process of dissociation into ions is known as *ionization*. The metallic ions, ammonium ions and hydrogen ions are positively charged while the non-metallic ions and hydroxide ions are negatively charged. The number of electrical charges carried by an ion is equal to the valency of the corresponding atom or group. Due to the electronic charges carried by these ions, their properties are quite different from those of their corresponding atoms which are electrically neutral.

Fig. 11.19 Behaviour of ions in an electrolyte.



Random movement of ions in an electrolyte.

Migration of ions when an electric current is passed.

When we pass an electric current through an electrolyte, the free ions lose their random movement. The positive ions become attracted to the cathode (negative electrode) and are known specifically as cations (i.e. cathode ions). The negative ions move towards the anode (positive electrode) and are called anions (i.e. anode ions). Therefore, the current through the electrolyte is carried by the movement of ions to the electrodes, and not by a flow of electrons in the electrolyte.

Arrhenius' version of the ionic theory has been modified since X-ray diffraction studies show that salts and strong alkalis consist of oppositely charged ions even in the solid state. The modern theory proposes that the ions in such solids are pulled away from one another either as a result of the heat energy applied when the solid melts, or with the help of the solvent molecules when the solid dissolves. Thus,

Arrhenius' theory $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

Modern theory $Na^+Cl^-(s) \rightarrow Na^+(aq) + Cl^-(aq)$

Table 11.3 Some electrolytes and their ions

Electrolyte	Cation	Anion
$NaCl$	Na^+	Cl^-
KOH	K^+	OH^-
$Pb(NO_3)_2$	Pb^{2+}	$2NO_3^-$
Na_2CO_3	$2Na^+$	CO_3^{2-}

Although the second equation is a more accurate representation of what takes place, for simplicity, we still use equations of the first type to show the dissociation of ionic compounds in solution.

Some covalent compounds, e.g. acids and weak bases, can also dissociate into ions although they exist as molecules and not ions in the solid state. They do so by reacting with water or other solvents to form hydroxonium ions, H_3O^+, or other ions. For example, the ionization of hydrochloric acid is represented as

$$H_2O(l) + HCl(g) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

although we usually represent it as a simple dissociation:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

We can prove the existence of ions during electrolysis (experiments 11.2 and 11.3) by

- using a compound wih a coloured cation and/or a coloured anion, and showing the migration of the coloured ions;
- showing the formation of a coloured compound when the migrating ions meet.

Table 11.4 Coloured compounds and ions.

Compound/ion	Colour
Tetraoxomanganate(VII) ion, MnO_4^-	Purple
Tetraoxochromate(VI) ion, CrO_4^{2-}	Yellow
Silver tetraoxochromate(VI), Ag_2CrO_4	Red
Tetraammine copper(II) ion, $Cu(NH_3)_4^{2+}$	Blue

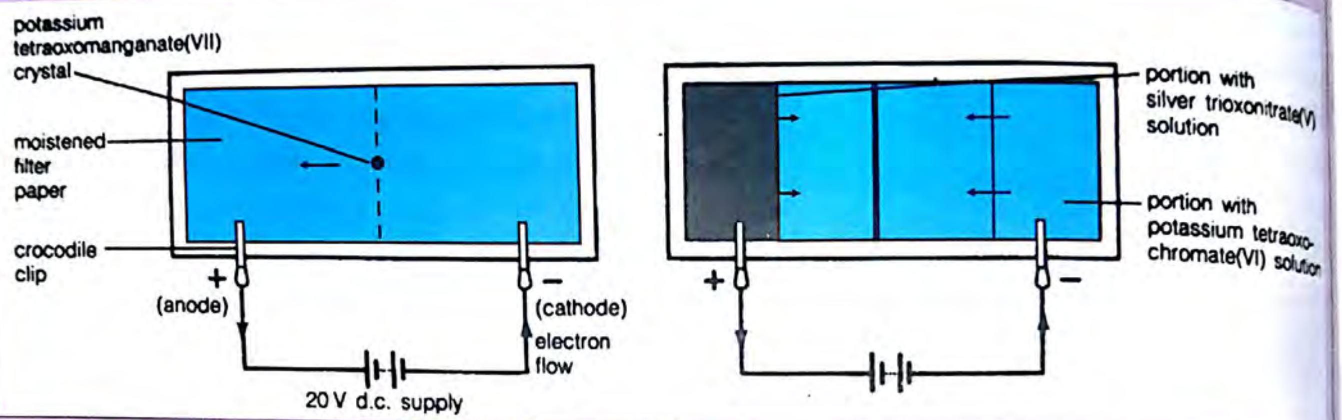
NOTE During electrolysis, positive ions migrate to the negative electrode (cathode) and the negative ones migrate to the positive electrode (anode).

Experiment 11.2 To observe the migration of coloured ions during electrolysis using a filter paper.

Method (a) Place a wet strip of filter paper on top of a microscopic slide and secure it at both ends with crocodile clips. Connect the clips to a battery as shown. Put a small speck of potassium tetraoxomanganate(VII), KMnO4, in the centre of the filter paper. Observe the filter paper for about ten minutes.

(b) Replace the filter paper with a fresh moist one. Moisten one end of the paper with silver trioxonitrate(V), $AgNO_3$, solution as shown, and the other end with potassium tetraoxochromate(VI), K_2CrO_4, solution. Observe what happens at the centre line of the filter paper.

Fig. 11.20 Migration of coloured ions using filter paper strips.



Result (a) A purple colour first appears at the central line of the filter paper as the crystal of tetraoxomanganate(VII) dissolves in the water. Then a streak of purple will slowly move towards the anode (positive electrode). This is due to the migration of the purple tetraoxomanganate(VII) ion, MnO_4^-. The colourless potassium ion, K^+, which is not visible, travels in the opposite direction.

(b) After several minutes, a red colour appears at the centre of the filter paper. This is due to the formation of insoluble red tetraoxochromate(VI), Ag_2CrO_4, when the silver ions, Ag^+, migrating to the cathode (negative electrode) meet the tetraoxochromate(VI) ions, CrO_4^{2-}, migrating to the anode.

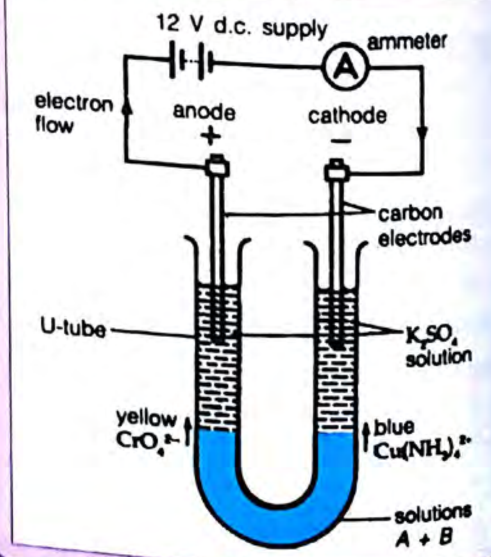
Conclusion The migration of coloured ions prove the existence of ions in electrolysis.

Experiment 11.3 To observe the migration of coloured ions during electrolysis using a gelatin medium.

Theory Potassium tetraoxochromate(VI), K_2CrO_4, provides the yellow-coloured tetraoxochromate(VI) anions, CrO_4^{2-}. The deep blue-coloured tetraammine copper(II) cations, $Cu(NH_3)_4^{2+}$, are furnished by reacting a copper(II) salt solution with excess aqueous ammonia.

Method Solution A is made by mixing 25 cm³ of saturated potassium tetraoxochromate(VI) solution, 50 cm³ 1 M copper(II) tetraoxosulphate(VI) solution and 100 cm³ 5 M aqueous ammonia solution. Solution *B* is made by dissolving 20 g of gelatin in 200 cm³ hot water.

Fig. 11.21 Migration of ions using a gelatin medium.



The two solutions are mixed while warm. The mixture is stirred and poured into a U-tube. When the gelatin sets, a saturated solution of potassium tetraoxosulphate(VI) is poured into each limb of the U-tube to the same level and an electrolytic cell is set up.

Result After some time, a yellow-coloured band can be seen to move towards the anode, while a blue coloured band moves towards the cathode. Gradually, the colours at both electrodes deepen, showing an increase in ion concentration.

Conclusion During electrolysis, the positively charged, blue tetraammine copper(II) ions, $Cu(NH_3)_4^{2+}$ migrate to the negative electrode or cathode, while the negatively charged, yellow tetraoxochromate (VI) ions, CrO_4^{2-}, migrate to the positive electrode or anode. The visible migration of these ions establish the existence of ions in electrolytes.

Electrolytes and Non-electrolytes

Both metallic conductor and electrolyte can carry an electric current. A metallic conductor, however, conducts electricity, both in solid or liquid states, by the movement of electrons from atom to atom. An electrolyte conducts electricity only when molten or in solution as a result of the movement of its ions to the electrodes and their subsequent reactions at the electrodes.

Electrolytes vary in their ability to conduct electricity. Strong electrolytes like salts conduct large currents since they are composed entirely of free moving ions. Weak electrolytes ionize only slightly and so do not conduct electricity readily. For example, ethanoic acid, a weak electrolyte, shows only 0.48%, ionization, i.e. out of every 1 000 molecules present, only four are ionized.

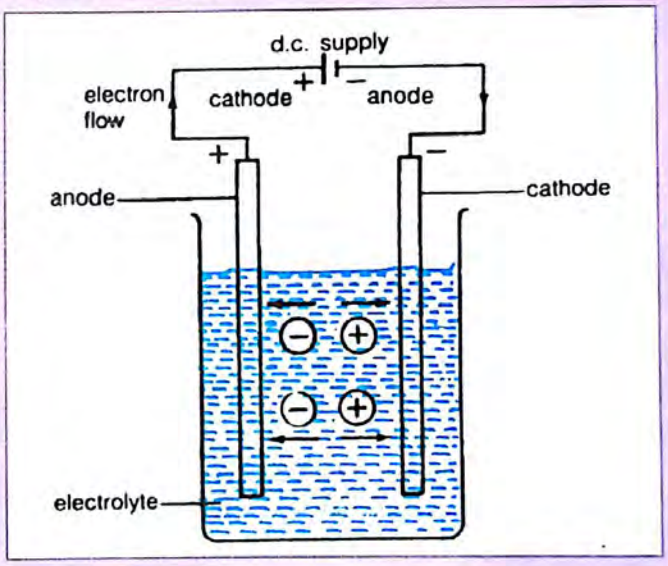
Non-electrolytes do not conduct electricity since they do not ionize. They are covalent and are mainly organic compounds. Examples include urea, ethanol, benzene, trichlcoromethane, cane sugar, ether and tetrachloromethane.

Mechanism of Electrolysis

Electrolysis is the chemical change brought about by the passage of a direct current through an electrolyte via electrodes.

Before the passage of current, the ions move about randomly in the electrolyte. When electrolysis begins, the battery or generator of electric current pumps electrons from its negative terminal (anode) to the cathode of the electrolytic cell. The negatively charged cathode then attracts cations in the electrolyte to itself. The cations accept electrons to become electrically neutral and are eventually discharged. The positive terminal (cathode) of the battery draws electrons from the anode of the electrolytic cell. Anions in the electrolyte are then attracted to the positively charged anode, where they give up their electrons to become electrically neutral and are also finally discharged. Hence, an electric current passes through the complete circuit.

Fig. 11.22 Mechanism of electrolysis.



Electrolytic reactions

Electrolytic reactions are redox reactions since they involve the transfer of electrons. Oxidation occurs at the anode where the anions lose electrons. This reaction at the anode is known as the *anodic half-reaction*. The *cathodic half-reaction* which takes place simultaneously at the cathode is a reduction reaction since the cations gain electrons here. The overall reaction is obtained by the algebraic addition of the two half-reactions.

As a result of the chemical reactions that occur during electrolysis, certain products are formed at each electrode. In general, metals or hydrogen gas are discharged at the cathode while non-metals (except hydrogen) are discharged at the anode.

Preferential discharge of ions

During the electrolysis of a given electrolyte, the products formed at the electrodes depend on the nature of the electrolyte. Where the electrolyte is a solution, the electrolytic products formed at the electrodes may vary because the solvent, which is usually water, will also ionize. In such a case, the cations and anions of both the electrolyte and the solvent will migrate to the cathode and the anode respectively where they will compete with one another to be discharged. The product which is formed at an electrode will depend on which ions are preferentially discharged – the ions from the electrolyte or those from the solvent.

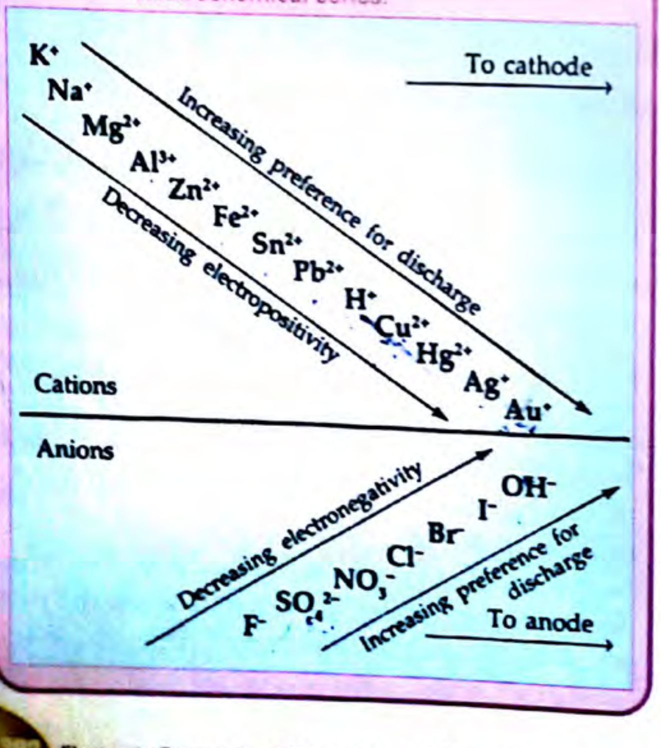
The discharge of ions is governed by three conditions, namely,

- the position of the ions in the electrochemical series;
- the concentration of the ions in the electrolyte;
- the nature of the electrode.

Relative position of ions in the series The position of ions in the electrochemical series is similar to that of the corresponding elements.

If all other factors are constant, a cation which is lower in the series (less electropositive) will show a greater tendency to be discharged than another w is higher up (more electropositive). This is beca the former gains electrons more readily from th cathode and so becomes discharged as a neutral ato while the latter tends to persist in solution as a positi ion. For example, K^+, Na^+ and Ca^{2+} are nev discharged at all from aqueous solutions since H^+ wi always be preferentially discharged. Only when the is no competition with H^+ or other ions will the strongly electropositive elements be discharged. Suc a situation occurs during the electrolysis of the molte salts of these metals.

Fig. 11.23 Relative position of ions in the electrochemical series.



An anion which is higher in the series (les electronegative) is discharged in preference to anothe which is lower down the series (more electronegative as the former loses electrons more readily. Fo example, SO_4^{2-} and NO_3^- are never discharged fron an aqueous solution due to the preferential discharg of OH^-.

Concentration of ions If other conditions are equal, increasing the concentration of a given ion tends to promote its discharge from solution. The influence of concentration, however, is effective only when the two competing ions are closely positioned in the electrochemical series. The effect of concentration becomes less important as the positions of the competing ions become further apart in the series.

We can illustrate this by considering what happens during the electrolysis of a concentrated solution of sodium chloride. In this solution, there are four types of ions as shown:

	NaCl	H_2O
Cations	$Na^+(aq)$	$H^+(aq)$
Anions	$Cl^-(aq)$	$OH^-(aq)$
Concentration of ions	High	Low
Position in electrochemical series	Na^+ are higher in the series than H^+. Cl^- are slightly lower in the series than OH^-	

At the cathode H^+ are preferentially dischar although the concentration of Na^+ is far greater. Her the great distance between the positions of Na^+ an H^+ in the series makes the effect of concentration les important.

At the anode Cl^- are preferentially discharged. The effect of concentration is important in this case because the positions of Cl^- and OH^- are close to one another in the series.

Nature of electrodes Electrodes which take no part in the electrolytic reaction are described as inert electrodes. Platinum and carbon (graphite) usually behave as inert electrodes, although platinum is attacked by liberated chlorine and carbon by liberated oxygen. Some electrodes which have strong affinity for certain ions may influence ionic discharge. For example, in the electrolysis of aqueous sodium chloride using platinum electrodes, H^+ are preferentially discharged. If a mercury cathode is used, however, the mercury will tend to associate with the Na^+ to form sodium amalgam, Na/Hg, so that the discharge of Na^+ requires less energy than that of H^+, and so occurs in preference.

$$Na^+(aq) + Hg(l) + e^- \rightarrow Na/Hg(l)$$

$$H^+(aq) + e^- \rightarrow H; \qquad H + H \rightarrow H_2(g)$$

Other electrodes may also influence the ionic discharge because they possess characteristics similar to those of the ion in the electrolyte. For example, if a copper anode is used in the electrolysis of a solution of copper(II) tetraoxosulphate(VI), neither the SO_4^{2-} nor the OH^- will be discharged. Instead, the copper atoms from the anode will go into solution as Cu^{2+} because these atoms will give up their electrons more readily than SO_4^{2-} or OH^-. This principle is made use of in the extraction and purification of some metals.

SOME EXAMPLES OF ELECTROLYSIS

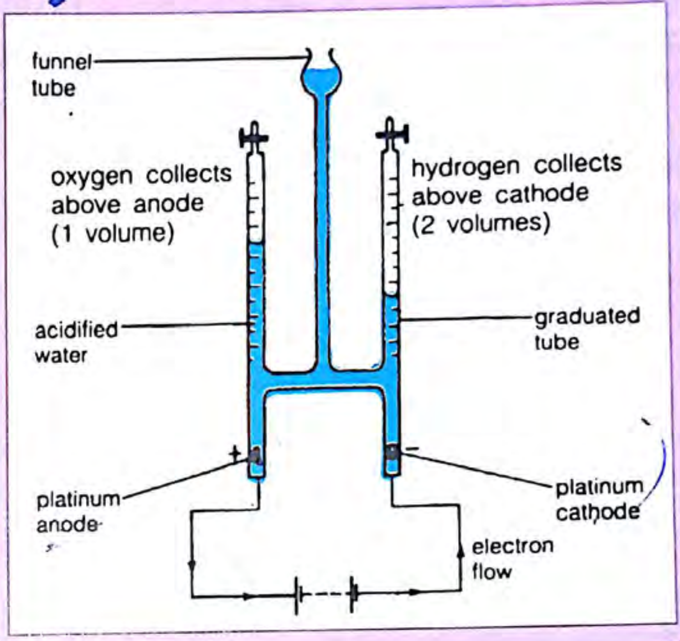
Electrolysis of acidified water

Acidified water is made by adding a few drops of tetraoxosulphate(VI) acid to water. The electrolysis of acidified water is the same as the electrolysis of dilute tetraoxosulphate(VI) acid.

The electrolytic cell used is designed for the collection of gaseous products at the two electrodes. Both the electrodes used are platinum foils. Acidified water contains the following ions:

	H_2SO_4	H_2O
Cations	$2H^+(aq)$	$H^+(aq)$
Anions	$SO_4^{2-}(aq)$	$OH^-(aq)$
Concentration of ions	High	Low
Position in electro chemical series	OH^- are higher in the series than SO_4^{2-}.	

Fig. 11.24 Electrolysis of acidified water.



At the cathode The H^+, which are the only cations present, migrate to the cathode where they acquire an electron each to form neutral hydrogen atoms. These atoms then combine in pairs to produce the diatomic molecules of gaseous hydrogen.

$$H^+(aq) + e^- \rightarrow H$$

$$H + H \rightarrow H_2(g)$$

At the anode Both SO_4^{2-} and OH^- migrate to the anode, where OH^- are preferentially discharged. Each OH^- loses its electron to the anode to become a neutral – OH group. Two – OH groups react to form one molecule of water and one atom of oxygen. Gaseous oxygen is produced when the oxygen atoms combine in pairs to form diatomic molecules.

$$OH^-(aq) \rightarrow OH + e^-$$

$$OH + OH \rightarrow H_2O(l) + O$$

$$O + O \rightarrow O_2(g)$$

Summary

Cathodic half-reaction	$4H^+(aq) + 4e^- \rightarrow 2H_2(g)$
Anodic half-reaction	$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$
Overall reaction	$4H_2O(l) \rightarrow 4H^+(aq) + 4OH^-(aq)$ $\rightarrow 2H_2(g) + O_2(g) + 2H_2O(l)$ $2H_2(l) \underset{OR}{\rightarrow} 2H_2(g) + O_2(g)$

The electrolysis of acidified water yields 2 volumes of hydrogen at the cathode and 1 volume of oxygen at the anode, i.e. the ratio of hydrogen to oxygen by volume is 2 :1 respectively.

Although the percentage of ionization of water is very low, the discharge of OH^- during electrolysis disturbs the ionic equilibrium of water. To restore the equilibrium, more water molecules ionize.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The total amount of acid in the solution remains unchanged at the end of the electrolysis, but its concentration increases due to the removal of water molecules.

Electrolysis of copper(II) tetraoxosulphate (VI) solution (using different anodes)

The electrolytic cell used is designed to collect solid copper deposits at the cathode and a gas at the anode. The electrolyte contains the following ions:

	$CuSO_4$	H_2O
Cations	$Cu^{2+}(aq)$	$H^+(aq)$
Anions	$SO_4^{2-}(aq)$	$OH^-(aq)$
Concentration of ions	High	Low
Position in electrochemical series	Cu^{2+} are just below H^+ in the series. OH^- are higher in the series than SO_4^{2-}.	

At the cathode Both Cu^{2+} and H^+ migrate to the cathode where Cu^{2+} are discharged preferentially. The Cu^{2+} acquire two electrons each from the cathode to be deposited as metallic copper on the cathode as a result the cathode gradually grows thicker. This reaction is the same whether a platinum, carbon or copper cathode is used.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

At the anode (carbon or platinum) Both SO_4^{2} OH⁻ migrate to the anode, where OH^- are preferenti discharged as oxygen gas. Here, the positions of ions in the series are more important than th concentrations.

$$OH^-(aq) \rightarrow OH + e^-$$
$$OH + OH \rightarrow H_2O(l) + O$$
$$O + O \rightarrow O_2(g)$$

Summary

Cathodic half-reaction	$2Cu^{2+}(aq) + 4e^- \rightarrow 2Cu(s)$
Anodic half-reaction	$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e$
Overall reaction	$2Cu^{2+}(aq) + 4OH^-(aq)$ $\rightarrow 2Cu(s) + O_2(g) + 2H_2O(l)$

The electrolysis of aqueous copper(II tetraoxosulphate(VI), using carbon or platinum electrodes, yields copper deposits at the cathode and oxygen at the anode.

As the Cu^{2+} and OH^- are gradually discharged the solution becomes acidic with tetraoxosulphate(VI acid due to the H^+ and SO_4^{2-} which remain in the solution. This change is seen by the gradual fading away of the blue colour of copper(II) tetraoxosulphate(VI). If we continue to pass a current through the solution, subsequent electrolysis of this dilute acid will occur, yielding hydrogen at the cathode

Fig. 11.25 Electrolysis of copper(II) tetraoxosulphate(VI) solution using carbon or platinum anode.

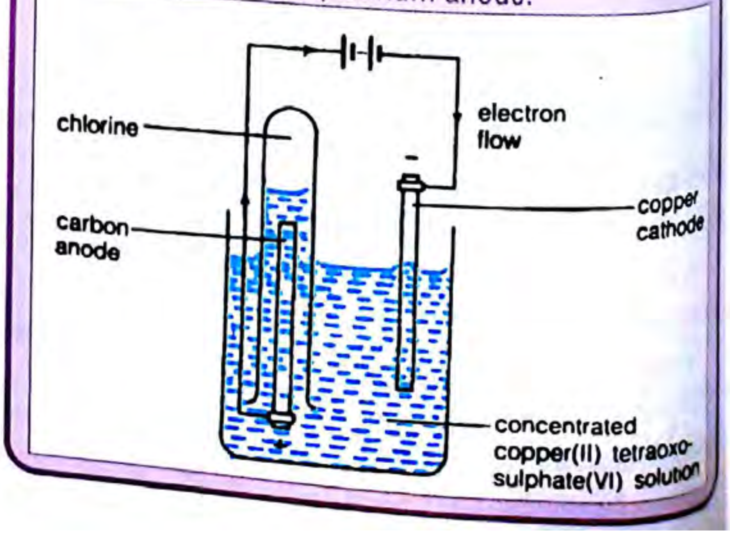
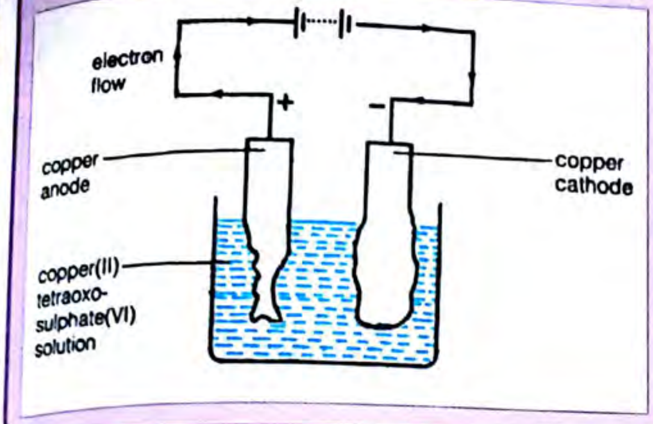


Fig. 11.26 Electrolysis of copper(II) tetraoxosulphate(VI) using copper anode.



and oxygen at the anode.

At the anode (copper) If a copper rod is used as the anode, electrons can be supplied through the anode to the external circuit by three ways.

- the SO_4^{2-} ions in the solution could be deposited as salt, i.e. sulphation of the anode.

$$SO_4^{2-}(aq) \rightarrow SO_4(s) + 2e^-$$

- the OH^- ions in the solution could be discharged as gaseous oxygen and water.

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$$

- the metallic atoms on the anode surface might dissolve in the solution as ions, leaving their electrons behind.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

In this case, the conversion of copper atoms to ions is favoured as it requires the least energy, so no ions are discharged. Instead, for each atom of copper deposited at the cathode, one atom of copper is dissolved from the anode to form Cu^{2+}. There is no change in the composition of the electrolyte since copper is merely transferred from the anode to the cathode during electrolysis.

Anode		*Electrolyte*		*Cathode*
$Cu(s)$	$\xrightarrow{-2e^-}$	$Cu^{2+}(aq)$	$\xrightarrow{+2e^-}$	$Cu(s)$

Summary of the electrolysis of some common electrolytes

In general, during the electrolysis of aqueous solutions of sodium and potassium salts, only H^+ are discharged at the cathode as hydrogen gas because of the relatively high electropositivity of Na^+ and K^+. During the electrolysis of aqueous solutions of trioxonitrate(V) and tetraoxosulphate(VI) salts, only OH^- are discharged as oxygen gas at the anode because of the relatively high electronegativity of NO_3^- and SO_4^{2-} consequently, the electrolysis of aqueous solutions of the trioxonitrates(V) or tetraoxo-sulphates(VI) of potassium or sodium yield

- hydrogen at the cathode, and
- oxygen at the anode.

FARADAY'S LAWS OF ELECTROLYSIS

The quantity of products liberated at the electrodes during an electrolysis is dependent on

- the magnitude of the steady current passed;
- the time of flow of the steady current;
- the ionic charge of the liberated element.

These quantitive aspects of electrolysis were investigated by Faraday, who put forward two laws in 1833 to describe these relationships.

Faraday's First Law of Electrolysis

Faraday's First Law of Electrolysis states that the mass (m) of an element discharged during an electrolysis is directly proportional to the quantity of electricity (Q) passing through it.

From the definition, we get

$$m \propto Q$$

The unit of quantity of electricity, Q is the coulomb. This is not measured directly but is derived from the measured rate of flow of electricity, i.e. the current I (in amperes), and the time of flow of the current, t (in seconds), i.e.

$$Q = I \times t$$

Electrolyte	Cathode	Product discharged at cathode	Anode	Product discharged at anode	Effect on lectrolyte
Acidified water (dilute tetraoxo-sulphate(VI) acid	Platinum	Hydrogen gas (2 volumes)	Platinium	Oxygen gas (1 volume)	Concentrations of H^+ and SO_4^{2-} increase as water is removed making electrolyte more acid
Concentrated copper(II) chloride solution	Copper	Copper deposits	Carbon	Chlorine gas	Removal of $Cu2^+$ and Cl^- dilutes electrolyte.
Dilute copper(II) chloride solution	Copper	Copper deposits	Carbon	Oxygen gas	Concentrations of H^+ and Cl^- increase, making electrolyte acidic.
Concentrated copper(II) chloride or copper(II) tetraoxosulphate(VI) solution	Copper	Copper deposits	Copper	Copper anode dissolves	Concentration of electrolyte remains unchanged.
Concentrated copper(II) tetraoxosulphate(VI) solution	Copper	Copper deposits	Platinium	Oxygen gas	Concentrations of H^+ and SO_4^{2-} increase, making electrolyte acidic.
Concentrated hydrochloric acid	Carbon	Hydrogen gas (1 volume)	Carbon	Chlorine gas (1 volume)	Removal of H^+ and Cl^- dilutes electrolyte, making it less acidic
Concentrated sodium chloride solution (brine)	Carbon	Hydrogen gas (1 volume)	Carbon	Chlorine gas (1 volume)	Concentrations of Na^+ and OH^- increase, making electrolyte alkaline.
Molten sodium chloride	Carbon	Sodium	Carbon	Chlorine gas	Concentration remains unchanged.
Concentrated sodium hydroxide solution	Platinium	Hydrogen gas (2 volumes)	Platinium	Oxygen gas (1 volume)	Concentrations of Na^+ and OH^- increase as water is removed, making electrolyte more alkaline

The First Law of Electrolysis can also be stated as follows: *the mass of an element discharged during an electrolysis is directly proportional to*

- *the magnitude of the current; and*
- *the time of flow of the current.*

According to Faraday's First Law,

$$m \propto I \times t$$

or $m = E I t$ (where E is a constant)

When m is expressed in grams, the constant E, is the mass in grams of the substance liberated by the passage of 1 coulomb (C) of electricity (i.e. a current of 1 ampere passed for 1 second) and is known as the electrochemical equivalent of the substance.

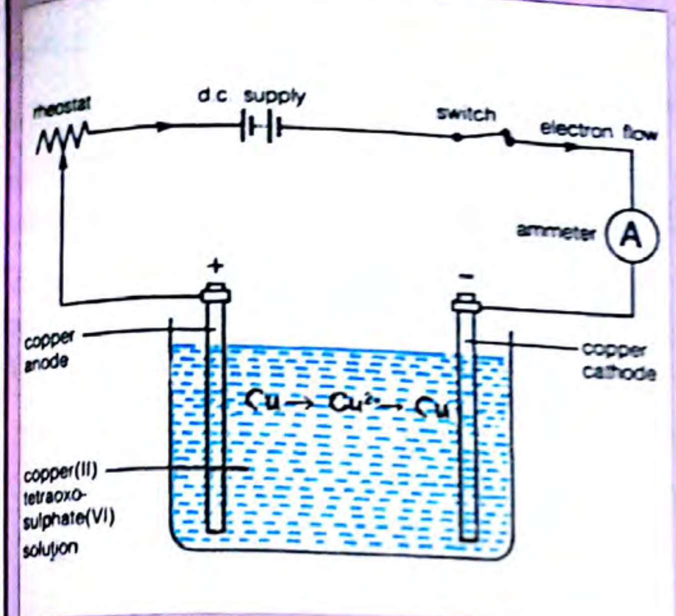
To verify Faraday's First Law of Electrolysis, set up an electrolytic cell as shown in fig. 11.27. When an electric current is passed through the electrolyte, copper atoms are deposited on the cathode.

Weigh the copper cathode at the beginning of the experiment. Pass a steady current of 1 A for 10 minutes. Switch off the current supply. Weigh the copper cathode again and find the gain in mass. Repeat this procedure, using different time intervals.

Plot a graph of the gain in mass against time. A straight line graph passing through the origin is obtained showing that the mass of copper deposited is directly proportional to the time duration of current flow.

Repeat the experiment, but this time pass currents of different magnitudes through the electrolyte for a fixed period of time. Plot a graph of gain in mass

Fig. 11.27 Verification of Faraday's First Law of Electrolysis.



against the magnitude of the current. A straight line graph passing through the origin is obtained showing that the mass of copper deposited is directly proportional to the magnitude of current flow.

Faraday's Second Law of Electrolysis

Faraday The minimum quantity of electricity required to liberate one mole of singly-charged ions, such as hydrogen or chloride ions, is 96 500 coulombs. This quantity of electricity is called the faraday and is denoted by F.

The discharge of one mole of singly-charged ions, i.e.

$$M^+ + e^- \rightarrow M$$
$$\text{or} \quad A^- \rightarrow A + e^-$$

involves the transfer of one mole of electrons, which contains Avogadro's Number (6.02×10^{23}) of electrons. Therefore,

> *one faraday = one mole of electrons*

If one faraday discharges one mole of ions of a univalent element such as hydrogen, sodium, silver and chlorine, it follows that two faradays will be needed to discharge one mole of ions of a divalent element or radical such as zinc or tetraoxosulphate(VI), i.e.

Fig. 11.28 Gain in mass ∝ duration of current.

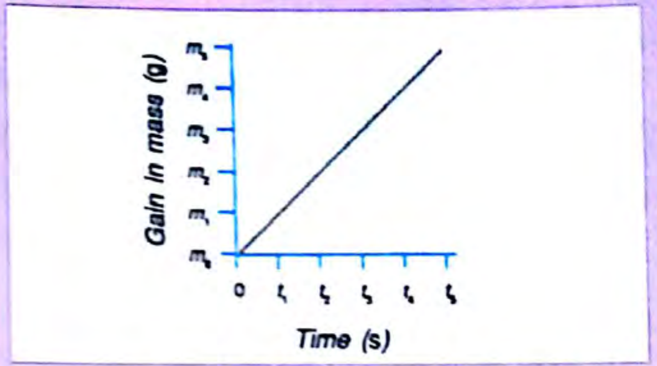
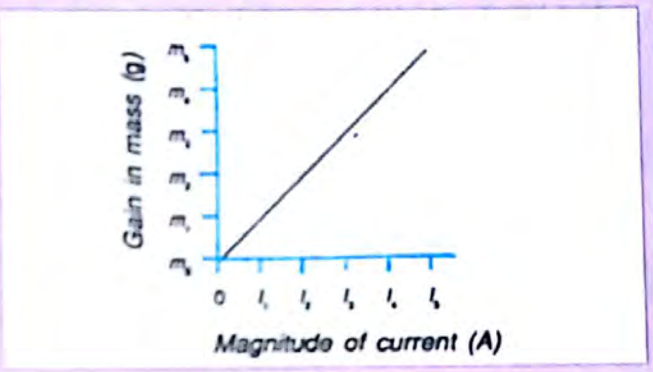


Fig. 11.29 Gain in mass ∝ magnitude of current.



$$M^{2+} + 2e^- \rightarrow M$$
$$\text{or} \quad A^{2-} \rightarrow A + 2e^-$$

F ~ 96500

This is in accordance with Faraday's Second Law of Electrolysis.

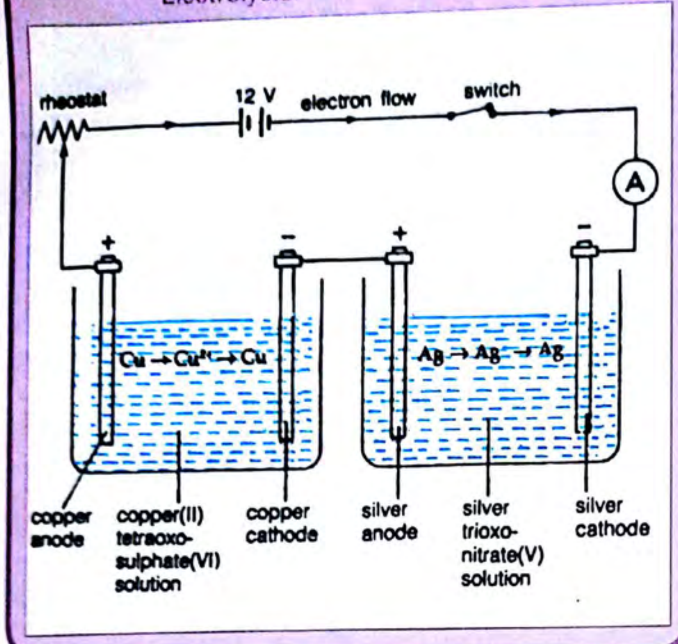
> *Faraday's Second Law of Electrolysis states that when the same quantity of electricity is passed through different electrolytes, the relative number of moles of the elements discharged are inversely proportional to the charges on the ions of the elements.*

To verify Faraday's Second Law of Electrolysis, set up two electrolytic cells as shown in fig. 11.30,

- one with copper electrodes immersed in copper(II) tetraoxosulphate(VI) solution; and
- the other with silver electrodes immersed in silver trioxonitrate(V) solution.

When a current is passed through this set-up, copper will be deposited on the copper cathode and silver on the silver cathode.

Fig. 11.30 Verification of Faraday's Second Law of Electrolysis.



Weigh the copper and silver cathodes before beginning the experiment. Pass a steady current of 1 A through the solutions for 20 minutes. Switch off the current, and find the gain in the mass of each cathode.

Although the same amount of electricity was passed through the two electrolytes, the number of moles of silver deposited is double that of the copper, i.e. if

x moles of copper are deposited, then
2x moles of silver are deposited.

The charge on the copper ion is +2, while that on the silver ion is +1.

Thus, the numbers of moles of copper and silver deposited are inversely proportional to the charges of their ions.

EXAMPLES

1 *Calculate the mass of silver deposited when a current of 2.6 A is passed through a solution of a silver salt for 70 minutes. (Ag = 108; 1 faraday = 96 500 C)*

Quantity of electricity used = It = (2.6 × 70 × 60) C

$$\underset{108\text{ g}}{Ag^+(aq)} + \underset{1F}{e^-} \rightarrow \underset{108\text{ g}}{Ag(s)}$$

96 500 C liberate 108 g of Ag.

$$(2.6 \times 70 \times 60)\text{ C will liberate } \frac{2.6 \times 70 \times 60 \times 108}{96\,500}$$

$$= 12.22\text{ g}$$

∴ the mass of silver deposited is 12.22 g.

2 *Calculate the volume of oxygen evolved at 285 K and 0.91 × 10⁵ N m⁻² when a current of 2.5 A is passed through acidified water for 1.5 min. (Molar volume of a gas is 22.4 dm³; standard pressure = 1.01 × 10⁵ N m⁻²; 1 faraday = 96 500C)*

Table 11.6 Faraday requirements for the discharge of ions.

I mole of ions discharged	Number of moles of electrons involved		Number of moles of atoms or groups liberated	Number of moles of electrons involved	Number of faradays required
At the cathode					
$H^+(aq)$	$+ e^-$	→	H		1F
$Na^+(l)$	$+ e^-$	→	Na(s)		1F
$Ag^+(aq)$	$+ e^-$	→	Ag(s)		1F
$Ca^{2+}(l)$	$+ 2e^-$	→	Ca(s)		2F
$Al^{3+}(l)$	$+ 3e^-$	→	Al(s)		3F
At the anode					
$Cl^-(aq)$		→	Cl(g)	$+ e^-$	1F
$OH^-(aq)$		→	OH(g)	$+ e^-$	1F
$SO_4^{2-}(aq)$		→	$SO_4(s)$	$+ 2e^-$	2F
$PO_4^{3-}(aq)$		→	$PO_4(s)$	$+ 3e^-$	3F

Quantity of current used = It = (2.5 × 1.5 × 60) C

$$4OH^-(aq) \rightarrow 2H_2O(l) + \underset{\substack{22.4\ dm^3 \\ \text{at s.t.p.}}}{O_2(g)} + \underset{4\ F}{4e^-}$$

$4 \times 96\,500$ C electricity liberate 22.4 dm^3 oxygen at s.t.p.

∴ (2.5 × 1.5 × 60) C electricity liberate

$$= \frac{2.5 \times 1.5 \times 60 \times 22.4}{4 \times 96\,500}\ dm^3$$

$$= \frac{2.5 \times 1.5 \times 60 \times 22\,400}{4 \times 96\,500}\ cm^3$$

$$= 13.06\ cm^3 \text{ at s.t.p.}$$

Convert the volume at s.t.p. to its volume at 285 K and $0.91 \times 10^5\ N\ m^{-2}$

$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ where p_1 = s.p. = $1.01 \times 10^5\ N\ m^{-2}$;

$V_1 = 13.06\ cm^3$; $T_1 = 273$ K;
$p_2 = 0.91 \times 10^5\ N\ m^{-2}$; $T_2 = 285$ K.

$$V_2 = \frac{p_1V_1T_2}{p_2T_1} = \frac{1.01 \times 10^5 \times 13.06 \times 285}{0.91 \times 10^5 \times 273}\ cm^3$$

$$= 15.13\ cm^3$$

[the volume of oxygen evolved at $0.91 \times 10^5\ N\ m^{-2}$ and 285 K is 15.13 cm^3.

USES OF ELECTROLYSIS

Electrolysis is of great importance in industry. Some of the main applications of electrolysis are listed below.

1 Extraction of elements: Many metals (e.g. Na, K, Mg, Ca, Al, Zn) and non-metals (e.g. H_2, F_2, Cl_2) are obtained either by electrolysis of their ores or by the electrolysis of their fused compounds or their aqueous solutions.

2 Purification of metals (e.g. Cu, Hg, Ag, Au).

3 Electroplating of one metal by another.

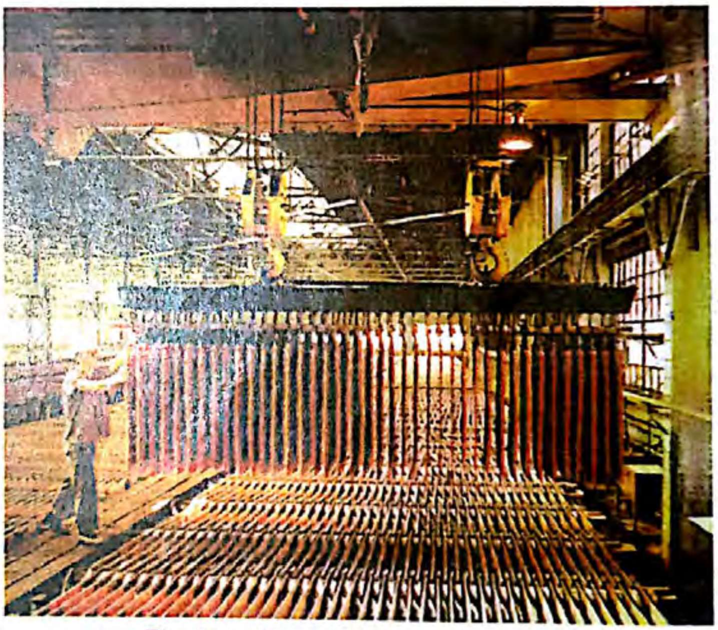
4 Preparation of certain important compounds, such as sodium hydroxide and sodium trioxo-chlorate(V).

Extraction and purification of metals

Very electropositive metals like potassium, sodium, calcium, magnesium and aluminium occur as compounds in natural ores. Such ores are purified and the pure metal is extracted from them by electrolysis. An example is the extraction of aluminium from purified bauxite (Al_2O_3).

The less electropositive metals, e.g. copper, mercury, silver and gold, tend to occur in the uncombined form in ores. These ores are usually contaminated with impurities such as sand, limestone and iron compounds. An example is the extraction of copper from copper ore.

In this process, an electrolytic cell is used in which the impure ore serves as the anode and a pure copper plate serves as the cathode. The electrolyte can be any soluble copper salt, such as copper(II) tetraoxo-sulphate(VI).



Electrolytic purification of copper

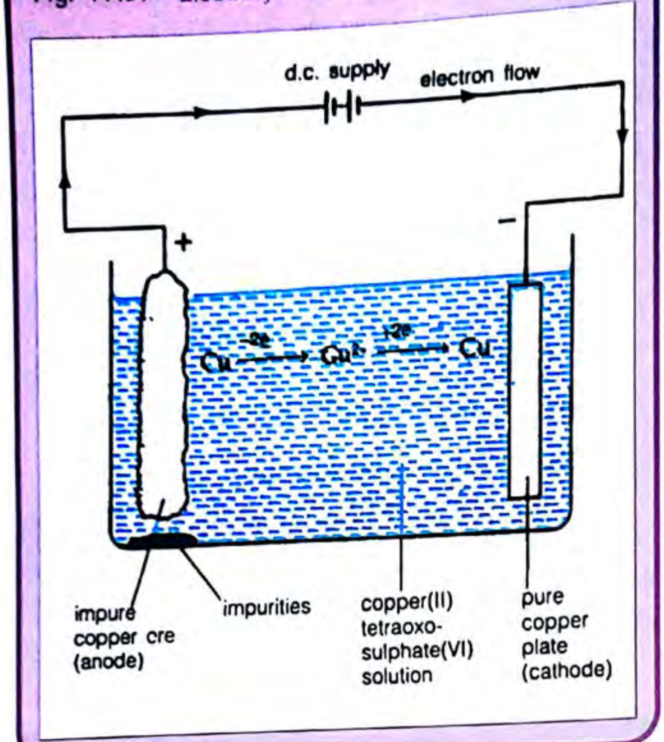
At the anode The metallic copper atoms in the ore give up two electrons each to go into solution as copper ions.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

At the cathode The copper ions in the solution are attracted to the cathode where they receive two electrons each from the cathode to become neutral copper atoms which are then deposited on the cathode.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Fig. 11.31 Electrolytic extraction of copper.



The net result is that pure copper atoms are transferred from the impure ore (anode) to the cathode. Similar arrangements are used in the extraction and purification of silver, mercury and gold. In all cases, the electrolyte is soluble salt of the metal being extracted or purified, the anode is the metallic ore or impure metal, while the cathode is a pure piece of the metal on which the pure metallic atoms can be deposited.

Electroplating

Electroplating is a method of coating the surface of one metal with another metal, usually copper, silver, chromium, nickel or gold, by means of electrolysis, for decoration or protection against corrosion. Articles which are usually plated include table-ware, cutlery, jewellery, and iron or steel objects, such as the metallic parts of motor-cars.

The arrangement of the electrolytic cell is essentially the same as that used in the extraction of metals. The cathode is the metallic object which is to be coated or plated; the anode, a strip of the plating metal; and the electrolyte, a salt of the plating metal. Thus, in silver-plating a spoon,

- the cathode is the spoon,
- the anode is a silver rod, and
- the electrolyte is a soluble silver salt, usually silver trioxonitrate(V) solution.

As the current is passed through the cell, the plati metal dissolves at the anode, and the ions produc migrate to the cathode, where they are discharg and deposited as a layer on the object. For exampl

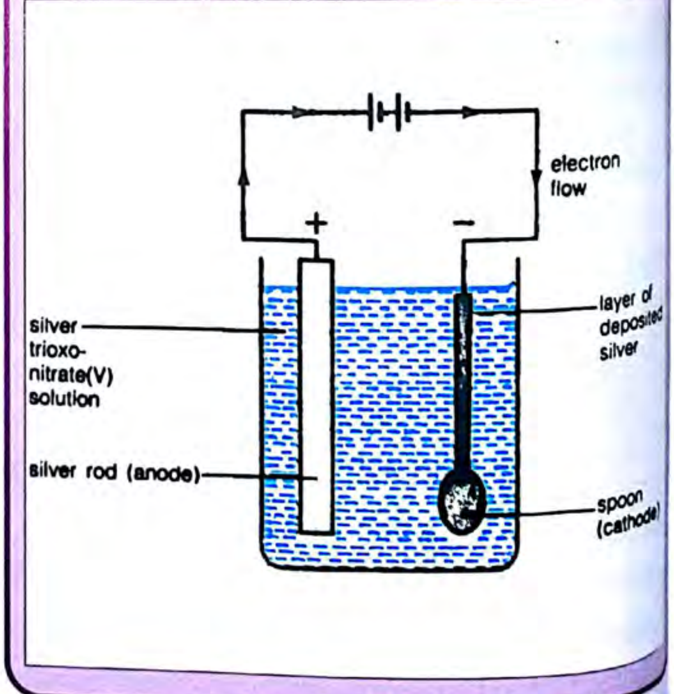
	At anode	**In solution**	**At cathod**
Silver-plating	$Ag(s) \xrightarrow{-e^-}$	$Ag^+(aq) \xrightarrow{+e}$	$Ag($
Copper-plating	$Cu(s) \xrightarrow{-2e^-}$	$Cu^{2+}(aq) \xrightarrow{+2e^-}$	$Cu($

Usually many articles (i.e. cathodes) are plated the same time. The thickness of the plating may b controlled by adjusting the magnitude of the curren and the duration of the process.

Sometimes, a series of platings may be necessar For example, chromium does not adhere well to stee and allows moisture to pass through it so it i eventually stripped off. In this case, steel is

- first coated with copper which provides adhesion, then
- with a layer of nickel for protection against corrosion, and
- finally with a layer of chromium for a tarnish-free finish.

Fig. 11.32 Silver plating.



Electrolysis of brine

The electrolysis of brine yields hydrogen and chlorine at the electrodes, and a concentrated solution of sodium hydroxide. This process has now been modified and adapted for the industrial preparation of these three important products.

The electrolytic cell in the industrial electrolysis of brine is known as the Kellner-Solvay cell. The anode consists of a series of graphite (carbon) rods dipped into brine contained in a tank. Fresh brine enters one end of the tank while used brine overflows from the other end. A layer of mercury flowing in at the base of the tank, in the same direction as the brine, acts as the cathode. Since brine is less dense than mercury, it floats on top of the mercury layer.

At the anode Chlorine is discharged as follows:

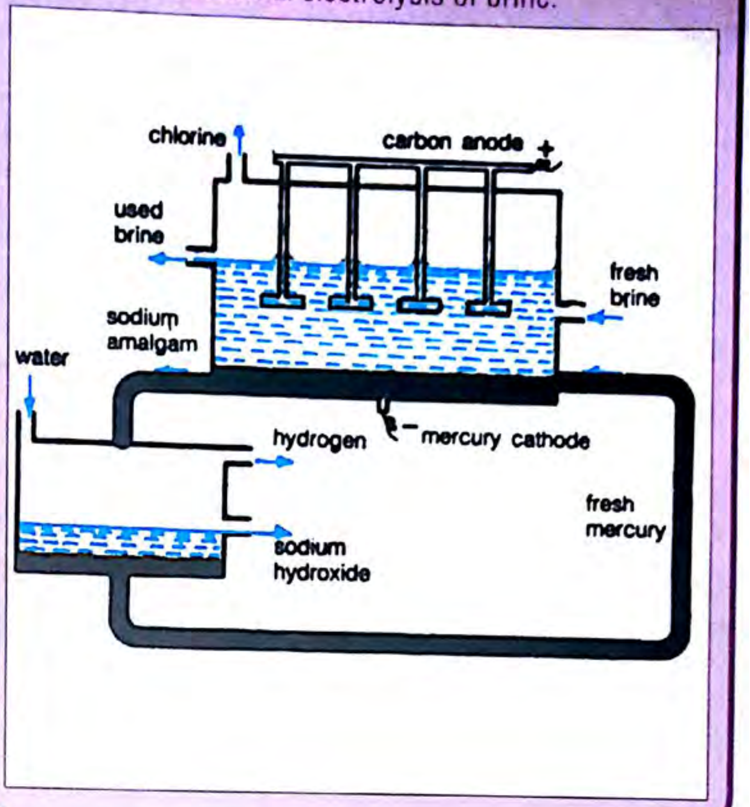
$$Cl^-(aq) \rightarrow Cl + e^-$$
$$Cl + Cl \rightarrow Cl_2(g)$$

At the cathode The sodium ions which are attracted to the cathode form a loose association with the mercury to produce sodium amalgam. The amalgam is drained from the cell at one end and led to a second tank, while fresh mercury is continuously supplied to the cell from its other end.

In the second tank, the amalgam is treated with water, whereupon it decomposes to produce sodium hydroxide, hydrgen and mercury. The latter is recycled to the cell for use again.

$$2Na/Hg(l) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + 2Hg(l)$$

Fig. 11.33 Industrial electrolysis of brine.



The electrolysis of brine is important not only because of the usefulness of the three products,

- sodium hydroxide,
- hydrogen, and
- chlorine,

but also because it is a very economical process. Brine is very easily available from sea water and although the initial cost of mercury is high, it can be reused. Thus, this process is widely employed, especially in places where electricity is cheap.

SUMMARY

- When a metallic plate M (electrode) is placed in a solution (eletrolyte) of its salt, M^+A^-, it will becom either negatively or positively charged. The potential difference set up between the metal and solutio is called the electrode potential for that metal ions/metal system.
- The standard hydrogen electrode consists of hydrogen gas at 25 °C and one atmospheric pressure, bubbling around and inert platinum electrode which is in contact with one-molar solution of hydrogen ions. This $2H^+(aq)/H_2(g)$ system provides a reference against which the standard electrode potentials of other elements are measured.
- The standard electrode potential of metal ions/metal system is the potential difference set up between the metal and a one-molar solution of its ions at 25 °C, taking the standard electrode potential of the hydrogen ions/hydrogen gas system as zero volt.
- A flow of electrons constituting an electric current can be set up between two electrodes which have different electrode potentials.
- An electrochemical cell (or voltaic or galvanic cell) converts chemical energy to electrical energy. It consists of two half-cells. Oxidation takes place at the anode (negative electrode) of the electrochemical cell and reduction at the cathode (positive electrode). Electrons flow from the anode to the cathode, giving rise to an electric current.
- The standard electrode potentials of elements, arranged in increasing order, gives the electrochemical series. From this series, the following information can be deduced.
  (a) The ease with which different elements gain or lose electrons.
  (b) The direction of current flow and the expected e.m.f. of a electrochemical cell.
  (c) The chemical reactivity of elements and the form of occurence of metals in nature.
  (d) The end products in displacement and redox reactions.
  (e) The preferential discharge of ions in electrolysis.
- Corrosion is an electrochemical process in which metals react with the oxygen and moisture in the surrounding air to form oxides. An example is the rusting of iron. Rusting can be prevented by cathodic protection, whereby iron is coated with another metal higher in the electrochemical series such as zinc. Zinc gives up its electrons more readily than the iron and so when galvanized iron, i.e. iron coated with zinc, is scratched, zinc will dissolve in water in preference to iron, thus arresting the process of rusting.
- In a closed circuit, electrons flow from the negative terminal of an electrochemical cell through a connecting wire to the positive terminal, but by convention, we say that electric current flows in the opposite direction, i.e. from the positive to the negative terminal.
- The modern Ionic Theory states that at electrolyte consists of ions which are set free when the electrolyte is melted or dissolved in water. Cations are positively charged ions which are attracted to the cathode while anions are negatively charged ions which are attracted to the anode.
- Electrolysis is the chemical change brought about by the passage of a direct current through an electrolyte. During electrolysis, electrons flow from the battery to the cations at the cathode. The cations are then reduced and deposited or discharged at the cathode. Anions give up electrons to the anode, become oxidized and deposited or discharged at the anode, while the electrons flow to the battery. As a result of this redox reaciton, there is a flow of electrons through the circuit.
- In an electrolytic cell, oxidation occurs at the anode (positive electrode) and reduction at the cathode

(negative electrode). The anode and the cathode of the cell are connected to the positive and negative terminals of the battery (electrochemical cell) respectively.

- The preferential discharge of ions is governed by the '
  (a) position of the ions in the electrochemical series;
  (b) concentration of the ions in the electrolyte; and
  (c) nature of the electrodes.
- Faraday's Laws of Electrolysis enable us to determine the quantity of electricity needed and the amount of substances deposited over a certain period of time during the electrolysis of a given electrolyte. The quantity of electricity, Q, (in coulombs) can be found by multiplying the current, I, (in amperes) by the time, t, (in seconds), i.e. $Q = It$. The quantity of products formed during electrolysis depends on
  (a) the magnitude of the current;
  (b) the time flow of the current; and
  (c) the ionic charge of the liberated element.
- A faraday of electricity (96 500 coulombs), denoted by the symbol F, is the flow of one mole (i.e. 6.02 × 10^{23}) of electrons. One faraday discharges one mole of an univalent element while two faradays will be needed to discharge one mole of a divalent element.

EXERCISES

1. Potential difference set up between metal and its solution is called
   A metal voltage.
   B back e.m.f.
   C electrode potential.
   D electrode potential of the metal.

2. Potential difference set up when a metal is in contact with one molar solution of its ions at 25°C is called
   A inert standard potential.
   B standard electrode potential.
   C electrochemical cell.
   D Galvanic cell.

3. Electrode potential value of pure hydrogen at all temperatures is
   A 1
   B zero
   C 2
   D 0.5

4. These are factors affecting standard electrode potential except
   A pressure.
   B overall energy change.
   C the concentration of ions in the solution.
   D temperature.

5. Half cell electrode of copper system is represented conventionally as
   A $Cu_{(s)}|Cu^{2+}_{(aq)}$
   B $Cu^{2+}_{(aq)}|Cu_{(s)}$
   C $Cu^{2+}_{(aq)}\|Cu_{(s)}$
   D $Cu\|Cu^{2+}$

6. Two half cells which are capable of converting chemical energy to electrical energy is called
   A a cell.
   B electrochemical cell.
   C chemical potential.
   D metallic potential.

7. Which of the electrodes does oxidation occur?
   A At the cathode.
   B At the anode.
   C At the electrolyte.
   D At the half electrode.

8. The overall redox reactions occurring at the electrodes is represented as (in copper | zinc cell) $Cu^{2+}_{(aq)}|Cu_{(s)}\|Zn_{(s)}|Zn^{2+}_{(aq)}$, the double represents
A capacitor.
B battery.
C salt bridge.
D inert conductor.

9. The major function of a salt bridge in cell is to
A smoothen the electron flow.
B to provide electrolyte.
C to complete the electric circuit.
D to provide adequate driving force.

10. Lead and accumulator is an example of secondary cell therefore, it must be charged by passing
A direct current.
B stabilized current.
C alternating current.
D back current.

11. Electrolyte in the dry Leclanche cell is
A anhydrous ZnSO4.
B pasty MnO_2
C NH_4CL paste.
D muslin bag.

12. Electromotive force of an electrochemical cell is given by
A algebraic product between the electrode potentials of the electrodes.
B algebraic difference between the electrode potentials of the electrodes.
C algebraic sum between the electrode potentials of the electrodes.
D algebraic zero between the electrode potentials of the electrodes.

13. In the activity series of metals, metals higher up will serve as
A cathode.
B anode.
C salt bridge.
D none of the above.

14. Corrosion in iron is called
A tarnishing.
B rusting.
C electrode corrosion.
D galvanization.

15. Corrosion in metals is an example of
A electrochemical process.
B half-cell reaction.
C metal-plating device.
D metal coupling device.

16. Flow of current in electrolytes is due to movement of
A electrons.
B holes and electrons.
C ions.
D charges.

17. What are products of the electrolysi concentrated calcium chloride solution?
A Ca, Cl_2
B Ca, O_2
C H_2, Cl_2
D Ca, H_2, Cl_2

18. What quantity of electricity is consumed 10 amperes was consumed in 1 hour d electrolysis?
A 36 kilo coulombs
B 3600 coulombs
C 7200 coulombs
D 72 kilo coulombs

19. Calculate the mass of aluminium deposited a current of 3.0 amperes is passed throug aluminium electrolyte for 2 hours (Al = 1 Faraday = 96 500 cm)
A 1.0 g B 6.04 g
C 4.04 g D 2.02 g

20. In electrolytic purification processes, the in metal to be purified is used as
A anode. B cathode.
C electrolyte. D salt bridge.

21. One faraday is equal to
A 9 650 coulombs.
B 96 500 coulombs.
C one mole of electrons.
D two a mole of electrons.
E half a mole of electrons.

22. In the electrolysis of brine, the anode must be carbon because

A carbon is a reducing agent.
B chlorine does not reduce carbon.
C carbon induces the discharge of chlorine.
D carbon is very reactive with chlorine.
E chlorine attacks other elements but not carbon.

23. (a) Define the electrode potential of a metal.
(b) Using a diagram, describe what happens in an electrochemical cell containing copper and zinc rods immersed in solutions of their respective ions, the solutions being separated by a porous partition. Give the redox reactions that take place at the electrodes.

24. Describe the structure of
(a) the Daniell cell,
(b) the Leclanche' cell,
and give the chemical reactions taking place in them respectively.

25. The reactions taking place inside a lead accumulator (or car battery) are said to be redox reactions. Describe the chemical reactions and justify the statement.

26. (a) Write briefly on the electrochemical series.
(b) Explain why copper reacts with concentrated trioxonitrate (V) acid but not with hydrochloric acid.
(c) Some metals are found to occur freely in nature while others occur only as compounds. Explain these occurrences with examples of each type of metal.
(d) When a galvanized dustbin and tin-plated dustbin have been subjected to an equal amount of rough handling, one of them is found to corrode much faster than the other. Which one corrodes faster and why?

27. Explain what happens when an electric current is passed through each of the following solutions
(a) Copper(II) chloride solution
(b) Aqueous sodium chloride
(c) Aqueous of tetraoxosulphate(VI) acid
Give a diagram of the apparatus you would use to collect the products in the case of (c).

28. (a) With the aid of a diagram, show how pure copper is extracted from an impure copper ore.
(b) How would you silver-plate a spoon?
(c) Describe the industrial preparation of chlorine from brine?
Explain the chemical reactions involved in the three processes above.

29. State Faraday's Laws of Electrolysis and show how you would verify the laws.

30. Calculate the amount of gold deposited when a current of 5 A is passed through a solution of gold salt for 2 hours 15 minutes. If the same current is used, find the time taken for 6.0 g of gold to be deposited.
(Au = 197, 1 faraday = 96 500 C)

31. A current is passed through three electrolytic cells connected in series containing solutions of silver trioxonitrate(V), copper(II) tetraoxosulphate(VI) and brine respectively. If 12.7 g of copper are deposited in the second electrolytic cell, calculate
(a) the mass of silver deposited in the first cell,
(b) the volume of chlorine liberated in the third cell at 17 °C and 800 mm Hg pressure. (Ag = 108, Cu = 63.5, 1 F = 96 500 C, G.M.V. of gases at s.t.p. = 22.4 dm^3)

32. 0.222 g of a divalent metal is deposited when a current of 0.45 A is passed through a solution of its salt for 25 minutes. Calculate the relative atomic mass of the metal.

33. (a) Write the equations for the cathodic and anodic half-reactions which occur during the electrolysis of copper(II) tetraoxo-sulphate(VI) solution, using the following electrodes:
(i) Platinum electrodes
(ii) Copper electrodes
(iii) Copper cathode and carbon anode
(iv) Carbon cathode and copper anode
(b) In the electrolysis of a solution of copper(II) tetraoxosulphate(VI) using copper electrodes, these results are obtained.

Mass of copper anode before experiment = 14.40 g
Mass of copper anode after experiment = 8.00 g
Mass of copper cathode before experiment = 11.50 g

(i) What was the mass of the cathode after the experiment?

(ii) Explain what happened to the concentration of the solution during the electrolysis.

(iii) Given that one faraday is 96 500 C and that the current used to carry out the electrolysis was 2 A, calculate how long it took to carry out the electrolysis.

34. (a) Explain why a crystal of sodium chloride is a poor conductor of electricity but its solution in water readily conducts electricity.

(b) Write the equatioin which represents the dissociation in solution of the salt formed from a trivalent cation X and a bivalent anion Y.

35. During a practical lesson, a student was asked t electroplate a stainless steel spoon using a bras rod as the electrode and copper(II) tetraoxo-sulphate(VI) solution as the electrolyte. The following were the results he obtained:

Mass of spoon	= 107.35 g
Mass of copper-coated spoon	= g
Mass of brass rod	= 50.3 g
Current	= 0.45 A
Time taken	= 27 minutes

(a) Draw a diagram of the set-up the students had used to electroplate the spoon. Which electrode should the spoon be?

(b) The student had forgotten to fill up one of the values in his results sheet. Find that value, and fill it in the empty space.

ENERGY AND CHEMICAL REACTIONS 12

WHAT IS ENERGY?

Energy is often defined as the ability to do work. It exists in different forms, such as

- potential or stored energy,
- kinetic energy or energy of motion,
- heat or thermal energy,
- light energy,
- electrical energy,
- sound or vibrational energy,
- chemical energy, and nuclear energy.

The various forms of energy are interconvertible. For example, the food we eat contains chemical energy. Inside our body, this energy is changed to heat energy that warms our body and to kinetic energy that enables us to do work.

We are not the only ones who can convert energy. An electric bulb converts electrical energy to heat energy and light energy.

When energy changes from one form to another, the total amounts of energy before and after the change are always the same. This is the Law of Conservation of Energy.

Energy can neither be created nor destroyed but it can be changed from one form to another.

ENERGY CHANGES IN REACTIONS

Energy changes occur in chemical reactions as reactants change to products. This is because the reactants and the products of a given chemical reaction possess different amounts of chemical energy.

We cannot measure the amount of chemical energy present in a substance, but we can observe the energy changes that accompany chemical reactions in the form of

- heat — when a strong acid and a strong base are mixed;
- light and heat — when magnesium is burned in air;
- sound and heat — when a mixture of hydrogen and oxygen is ignited.

Of these energy changes, we can only measure the changes in heat energy with ease.

Light and heat are given off by the oxy-ethyne flame.

Heat Content and Heat of Reaction

Every substance possesses a characteristic internal energy which is due to its structure and physical state. This is known as its *heat content* or *enthalpy*. Each mole of a substance has a characteristic heat content just as it has a characteristic mass.

In a chemical reaction, heat energy is either absorbsed or evolved because the heat contents of the substances involved in the reaction are different. The energy change which accompanies a chemical reaction is known as the heat of reaction. It is a constant for a given reaction carried out under a fixed set of conditions.

The standard heat of reaction is the amount of heat evolved or absorbed when a chemical reaction occurs between molar quantities of the substances as represented in the equation of reaction under standard conditions.

Units of energy It is not possible to measure the absolute heat content of any substance, but it is possible to measure the heat change when a substance is converted from one physical form to another or when a substance reacts to form another substance in a chemical reaction. Until recently, the basic unit for measuring heat change has been the kilocalorie (kcal) which is defined as *the amount of heat needed to raise the temperature of one kilogram of water by 1 °C*. (1 kilocalorie = 1 000 calories)

Since heat is a form of energy, the unit used for measuring heat change is also the joule (J). From accurate experiments, it has been established that,

$$\begin{aligned} 1 \text{ calorie} &= 4.18 \text{ joules (J)} \\ &= 4.2 \text{ J (to two significant figures)} \end{aligned}$$

Hence, 4.2 J of heat is required to raise the temperature of 1 g of water by 1 K or 1 °C. From this, we can define 1 J as follows:

One joule is the energy required to raise the temperature of 1 g of water by 0.239K (or °C)

Energy changes associated with chemical reactions are usually in thousands of joules. Therefore, the common unit for measuring heat energy is the kilojoule (kJ) where

$$1 \text{ kJ} = 1\,000 \text{ J}$$

To illustrate heat content and heat of reaction Tw moles of hydrogen combine with one mole of oxyge to form two moles of water. In this process, 571.1 kJ of heat energy is evolved because the heat conte of two moles of water is 571.16 kJ less than the tot heat content of the two reactants.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 571.16 \text{ kJ}$$

When one mole of water is formed, 285.58 kJ heat energy will be evolved. The heat of reaction f the formation of one mole of water is said to 285.58 kJ.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(1) + 285.58 \text{ kJ}$$

On the other hand, this same amount of energ must be supplied in order to decompose one mole water into hydrogen and oxygen. During th electrolysis of water, this energy is supplied in th form of electrical energy.

$$H_2O(1) + 285.58 \text{ kJ} \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

NOTE From the Law of Conservation of Energy, th heat absorbed in decomposing a compound is equ to the heat evolved in its formation under the sam conditions.

Heat of reaction is a very-broad term since ther are many different types of reactions such a neutralization, combustion, formation, etc. For th more important types of reactions, the heat of reactio is renamed accordingly, e.g. the heat of reaction whe

- a substance is burned completely in oxygen i renamed as heat of combustion;
- hydrogen ions from an acid neutralize hydroxide ions from an alkali to form water is renamed a heat of neutralization.

Exothermic and Endothermic Reactions

During a chemical reaction, heat can be evolved o absorbed depending on the relative heat content o the reactants and the products. When the total hea content of the products is less than that of the reactants the excess energy will be given off as heat to the surrounding as the reaction occurs. This type of reaction is said to be *exothermic*.

When the total heat content of the products is more than that of the reactants, heat energy must be absorbed from the surroundings for the reaction to proceed. Such a reaction is said to be *endothermic*.

An exothermic reaction is one during which heat is liberated to the surroundings. An endothermic reaction is one during which heat is absorbed from the surroundings.

The terms exothermic and endothermic apply not only to chemical changes but also to physical changes. Some examples of exothermic reactions are as follows:

1 Reaction between calcium oxide and water.

$$CaO(s) + H_2O(1) \rightarrow Ca(OH)_2(s)$$

2 Reaction between an acid and a base.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Some examples of endothermic reactions are as follows:

1 Thermal decomposition of calcium trioxocarbonate(IV).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

2 Thermal dissociation of ammonium chloride.

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

Representing Energy Changes

ΔH notation We represent the heat content of a substance by the letter *H*. The heat of reaction, i.e. the *change in heat content* during a reaction, then becomes ΔH, the Greek letter Δ (delta) signifying *change in*. Since the change in heat content during a reaction is the difference between the heat content of the products and that of the reactants, ΔH can be expressed mathematically as follows:

$$\Delta H = \begin{matrix}\text{Heat contents}\\\text{of products}\end{matrix} - \begin{matrix}\text{Heat content}\\\text{of reactants}\end{matrix}$$

Δ*H* is negative for an exothermic reaction since the products have a smaller heat content than the reactants. The negative sign also indicates that heat energy has been lost from the reacting system to the surroundings.

Equation 1

285.58 kJ of heat is evolved when 1 mole (2 g) of hydrogen gas combines with half a mole (16 g) of oxygen gas to form 1 mole (18 g) of water.

$$\underset{2\text{ g}}{H_2(g)} + \underset{16\text{ g}}{\frac{1}{2}O_2(g)} \rightarrow \underset{18\text{ g}}{H_2O(l)} \quad \Delta H = -285.58 \text{ kJ mol}^{-1}$$

Equation 2

The burning of carbon is exothermic. 408 kJ of heat is released when 1 mole (12 g) of coal combines with 1 mole (32 g) of oxygen.

$$\underset{12\text{ g}}{C(s)} + \underset{32\text{ g}}{O_2(g)} \rightarrow \underset{44\text{ g}}{CO_2(g)} \quad \Delta H = -408 \text{ kJ mol}^{-1}$$

From equations 1 and 2, we see that the magnitude of ΔH corresponds to the molar quantities as expressed in the equation of the reaction.

ΔH is positive for an endothermic reaction. The positive sign also indicates that during the reaction, the reacting system gains heat energy from the surroundings.

Equation 3

The decomposition of water into hydrogen and oxygen is an endothermic reaction. 285.58 kJ of heat is absorbed from the surroundings for every mole (18 g) of water which decomposes.

$$\underset{18\text{ g}}{H_2O(l)} \rightarrow \underset{2\text{ g}}{H_2(g)} + \underset{16\text{ g}}{\frac{1}{2}O_2(g)} \quad \Delta H = +285.58 \text{ kJ mol}^{-1}$$

Equation 4

180.6 kJ of heat is absorbed into the system when one mole (28 g) of nitrogen combines with one mole (32 g) of oxygen to yield nitrogen(II) oxide.

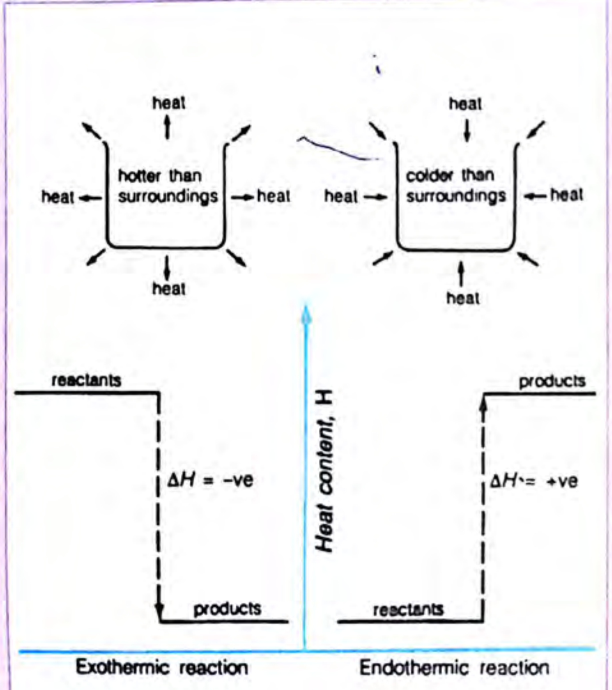
$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H = +180.6\ \text{kJ mol}^{-1}$$

28 g 32 g 60 g

Equations 1 to 4 are examples of *thermochemical equations*. In such equations, the ΔH value of each reaction is written beside the equation.

Energy level diagrams We can represent heat changes that occur in exothermic and endothermic reactions in diagrams.

Fig. 12.1 Exothermic and endothermic reactions explained in terms of heat content.



Heat of Reaction and Chemical Bonds

We have just learnt that energy change during a chemical reaction is due to the difference in the heat contents of the reactants and the products.

In a chemical reaction, the atoms and/or ion in the reactant particles regroup themselves to form particles of products. During this regrouping existing chemical bonds in the reactant particle are first broken down to give atoms and ions. New chemical bonds are formed between these ion and atoms to form particles of products. For *bond-breaking* and *bond-forming* to occur, there must be collision between the reactant particles.

The energy changes in chemical reactions come from the breaking or forming of chemical bonds which represent a form of energy known a *chemical energy*. To break a chemical bond, energy must be supplied to overcome the forces involved in the bond such as the electrostatic attraction in ionic compounds. Thus, bond-breaking is an endothermic change. On the other hand, energy is always evolved when a new bond is formed, i.e. bond-forming is an exothermic change.

During a chemical reaction, bonds are usually broken in the reactants and formed in the products.

Exothermic reaction (ΔH = -ve)	Bond-breaking energies (ΔH = +ve)	< Bond-forming energies (ΔH = -ve)
Exothermic reaction (ΔH = +ve)	Bond-breaking energies (ΔH +ve)	> Bond-forming energies (ΔH = -ve)

Measurement of the Heat of Reaction

If the heat of reaction is large, we can detect exothermic and endothermic reactions by feeling the temperature of the reaction vessel before and after the reaction. If the reaction is

- exothermic, there is a rise in temperature so the reaction vessel feels warm;
- endothermic, there is a fall in temperature so the reaction vessel feels cool.

To determine accurate values of ΔH, we use a *calorimeter*.

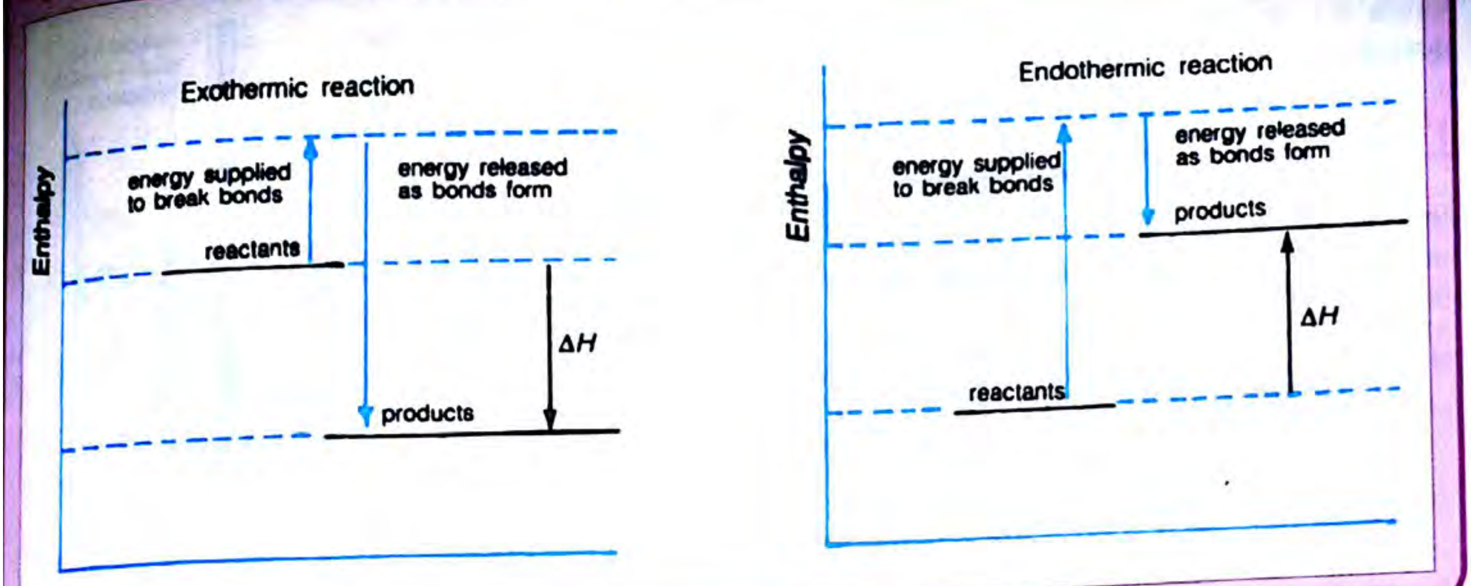
There are several types of calorimeters. The *bomb calorimeter* is very sensitive and is used in nutrition studies. The *glass calorimeter* is used to determine the ΔH of most chemical reactions. Reactants in stoichiometric amounts are placed in the calorimeter. As the reaction proceeds, the heat energy evolved or absorbed will either warm or cool the system. The temperatures of the system before and after the reaction are recorded.

Knowing

- the temperature change,
- the mass of reactants, and
- the specific heat capacity of the reaction mixture.

we can calculate the ΔH for the reaction.

Fig 12.2 Heat of reaction. Exothermic reaction



Standard conditions for measuring ΔH

The heat of reaction depends not only upon the mass of the reactants, but also upon the temperature and pressure of the reacting system. Another important factor is the physical state of the substances involved n the reaction, since heat change accompanies the rearrangement of certain bonds between particles when a substance changes from one physical state to another.

For example, we can represent the formation of water as follows:

(a) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286$ kJ mol^{-1}

(b) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -242$ kJ mol^{-1}

In (a) *liquid* water is formed, while in (b) water vapour is formed. Liquid water absorbs heat from the surroundings to form water vapour. The latent heat of vaporization of water is 44 kJ mol^{-1}.

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta H = +44 \text{ kJ mol}^{-1}$$

Therefore, the formation of water vapour requires less energy than the formation of liquid water. This is seen in the values of ΔH in (a) and (b) which differ by 44 kJ mol^{-1}

Besides the three states of matter, the existence of the reactants and products of a reaction in the aqueous state also affects the heat of reaction. For example, the heat evolved during the neutralization of a given amount of sodium hydroxide solution by hydrochloric acid is greater when hydrogen chloride gas is passed into the solution than when hydrochloric acid solution is used. This is because hydrogen chloride gas dissolves in water with the evolution of heat. The heat evolved when a substance is dissolved in water is known as the *heat of solution*. This is of considerable importance since a vast majority of reactions occur in aqueous medium.

We now see why it is so important to include the state symbols: solid (s), liquid (l), gas (g) or aqueous (aq) after each substance when writing a chemical equation.

Since the value of ΔH is affected by several factors, it is necessary to define standard conditions for its measurement. These conditions for determining ΔH are as follows:

1 The temperature must be 298 K (25 °C).
2 If gases are involved, the pressure must be at 1.01×10^5 Nm^{-2} (1 atm at 760 mm Hg).
3 If aqueous solutions are involved, their concentrations must be 1 mol dm^{-3}.

The heat of reaction or enthalpy change obtained under such standard conditions is given the special symbol, $\Delta H^\ominus$.

NOTE In practice, for many reactions, ΔH cannot be measured at 298 K. Experimental ΔH values are converted to values at 298 K, or the temperature at which a ΔH value is given is specified within parentheses.

Heat of Formation

The amount of heat evolved or absorbed when a substance is formed is known as the *heat of formation* (or enthalpy of formation).

The standard heat of formation of a substance, ΔH_f^θ, is the heat evolved or absorbed, i.e. the enthalpy change, when one mole of that substance is formed from its elements under standard conditions.

The equation for formation of 1 mole of liquid water is as follows:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -285.58 \text{ kJ mol}^{-1}.$$

Therefore, the standard enthalpy of formation of liquid water, ΔH_f^θ is –285.58 kJ mol^{-1}.

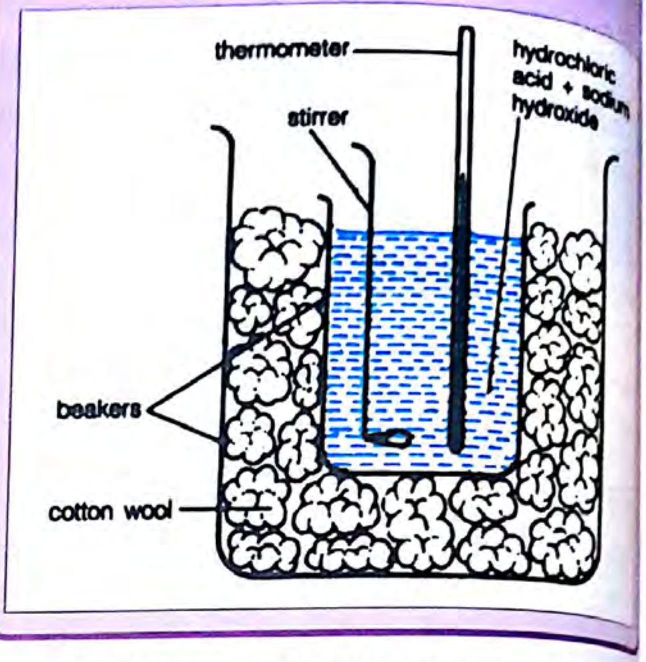
Heat of Neutralization

Neutralization is an exothermic reaction. The amount of heat evolved during a neutralization reaction in which one mole of water is formed is known as the *heat of neutralization* (or enthalpy change of neutralization).

The standard heat of neutralization, ΔH_n^θ, is the amount of heat evolved when 1 mole of hydrogen ions, H^+, from an acid reacts with 1 mole of hydroxide ions, OH^-, from an alkali to form 1 mole of water, under standard conditions.

In experiment 12.1, the dilute solutions of hydrochloric acid and sodium hydroxide are completely ionized. The only change that actually occurs is the formation of water molecules, H_2O. So, heat of neutralization is merely the heat of formation of one mole of water from its ionic components, and this is about –57.4 kJ mol^{-1}.

Fig. 12.3 Determination of the heat of neutralization.



$$\underset{\text{from acid}}{H^+(aq)} + \underset{\text{from base}}{OH^-(aq)} \rightarrow H_2O(l) \quad \Delta H = -57.4 \text{ kJ mol}^{-1}$$

Thus, the heat of neutralization of any strong acid and a strong base will be approximately the same. For example,

$$KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$$
$$\Delta H = -57.3 \text{ kJ mol}^{-1}$$

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$
$$\Delta H = -(2 \times 57.3) \text{ kJ mol}^{-1}$$

When weak acids or weak bases are involved, the heat of neutralization is less because the reactants are only partially dissociated into ions in solution. Energy is used up in drawing apart the undissociated ions before they can react. The heat of neutralization is only the net heat change, and is less than 57.4 kJ mol^{-1} by the amount of energy needed to bring about the dissociation of the weak acid or base. For example:

$$NH_3.H_2O(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$$
$$\Delta H = -51.5 \text{ kJ mol}^{-1}$$

Table 12.1 Standard heats of neutralization.

Acid	Alkali	ΔH_n^θ (kJ mol^{-1})
HCl	NaOH	–57.3
HNO_3	NaOH	–57.3
H_2SO_4	NaOH	–64.8
HCl	NH_3	–51.5
CH_3COOH	NaOH	–55.2
CH_3COOH	NH_3	–51.5

Experiment 12.1 To determine the heat of neutralization when sodium hydroxide reacts with hydrochloric acid.

Method Weigh a 250 cm^3 beaker which is to be used as a glass calorimeter. Pipette 100 cm^3 of 0.5 M hydrochloric acid into the glass calorimeter and 100 cm^3 of 0.5 sodium hydroxide solution into another beaker. Take the temperatures of the acid and the alkali solutions. Find the mean value of the two temperature readings. Place the glass alorimeter in a bigger beaker with pads of cotton wool between them to act as an insulator to reduce the heat loss from the system (see fig. 12.3).

As quickly as possible, add the sodium hydroxide solution to the acid in the calorimeter. Stir well to mix the solutions and record the highest temperature attained. Take the calorimeter out and weigh it together with the reaction mixture to find the mass of the reaction mixture.

Specimen result

Volume of 0.5 M hydrochloric acid = 100 cm^3
Volume of 0.5 M sodium hydroxide solution = 100 cm^3
Initial temperature of hydrochloric acid = 25.0 °C = 298.0 K
Initial temperature of sodium hydroxide solution = 25.2 °C = 298.2 K
Final (maximum) temperature of reaction mixture = 28.5 °C = 301.5 K

Calculation Within the limits of accuracy of the experiment, we may assume that

(a) Specific heat capacity of the reaction mixture = Specific heat capacity of pure water
= $4.2\ J\ g^{-1}\ K^{-1}$

(b) Total mass of the reaction mixture = 200 g
(The total volume of the reaction mixture is 200 cm^3 and it has an approximate mass of 200 g.)

(c) Initial temperature of the reaction mixture = Average temperature of the two reactant solutions

$$= \frac{298.0 \times 298.2}{2} = 298.1\ K$$

Temperature rise for the reaction mixture = 301.5 – 298.1 = 3.4 K

Total heat evolved = mass × specific heat capacity × temperature rise
$= 200\ g \times 4.2\ J\ g^{-1}\ K^{-1} \times 3.4\ K = 2\ 856\ J$

Equation of reaction

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

i.e. 1 mole hydrchloric acid reacts with 1 mole sodium hydroxide to produce 1 mole water.

100 cm^3 of 0.5M hydrochloric acid contain $\frac{100 \times 0.5}{1\ 000}$ = 0.05 mole acid.

Similarly, 100 cm^3 of 0.5 M sodium hydroxide contain 0.05 mole alkali.

[0.05 mole acid will react with 0.05 mole alkali to produce 0.05 mole water.

The production of 0.05 mole water evolves 2 856 J heat energy.

[the production of 1 mole water evolves $\frac{2\ 856}{0.05}$ = 57 120 J

= 57.1 kJ heat energy.

Conclusion The standard heat of neutralization of sodium hydroxide by hydrochloric acid is – 57.1 kJ mol^{-1}. The experimental value obtained here, though differing slightly from that in table 12.1, can be accepted as it is within experimental error

Heat of Combustion

Combustion is always accompanied by the evolution of heat. The amount of heat evolved when one mole of a substance is burned completely in oxygen is known as the *heat of combustion* (or enthalpy change of combustion).

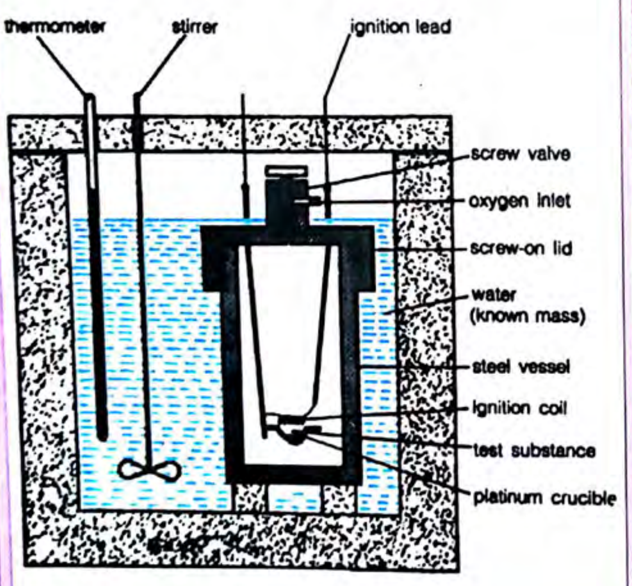
The standard heat of combustion of a substance, $\Delta H_c^{\ominus}$, is the heat evolved when one mole of the substance is burned completely in oxygen under standard conditions.

The heat of combustion is an important quantity since the combustion of fuels forms the main source of energy for industrial and domestic purposes. The energy used by the living body is also obtained from the biological combustion of food. For practical purposes, the relative effectiveness of a fuel is expressed more often in terms of its calorific value which is the amount of heat evolved per kilogram of the substance.

Table 12.2 *Standard heats of combustion and calorific values of common fuels and sugars.*

Fuels/ sugars	$-\Delta H_c^{\ominus}$ (kJ mol^{-1})	M_r	Calorific value (kJ g^{-1})
Methane	882	16	55.1
Butane	2 877	58	49.6
Petrol	5 460	≈114	47.9
Kerosene	8 400	≈198	42.4
Diesel	8 400	≈170	49.4
Charcoal	410	12	34.2
Glucose	2 816	180	15.6
Sucrose	5 644	342	16.5

Fig. 12.4 A bomb calorimeter.



A bomb calorimeter

A bomb calorimeter is usually used for the accurate determination of the heat of combustion. It consists of a strong cylindrical steel vessel or bomb usually lined with enamel to prevent corrosion. A known mass (about a gram) of the test substance is placed in a platinum crucible inside the bomb. The lid is screwed on tightly, and oxygen is pumped in through a valve until the pressure inside is about 2×10^6 N m^{-2}(20atm).

After closing the screw valve, the bomb is immersed in a known mass of water in a well-lagged calorimeter and left to attain a steady temperature. This initial temperature is measured using the thermometer in the calorimeter. The test substance is then ignited electrically by passing a current through the ignition coil. The temperature of the water, which is stirred continuously, is recorded at 30-second intervals in order to find the maximum temperature attained. From the heat capacity of the whole system (two calorimeters, water, thermometer and stirrer), the temperature rise and the heat generated by the ignition current, it is possible to calculate the heat of combustion.

Heat of Solution

When an ionic solid dissolves in water, a two-step process occurs, where each step is accompanied by a heat change. These steps are as follows:

1 The water molecules split up the ions in the crystal into free ions. This process needs energy known as *lattice energy.*

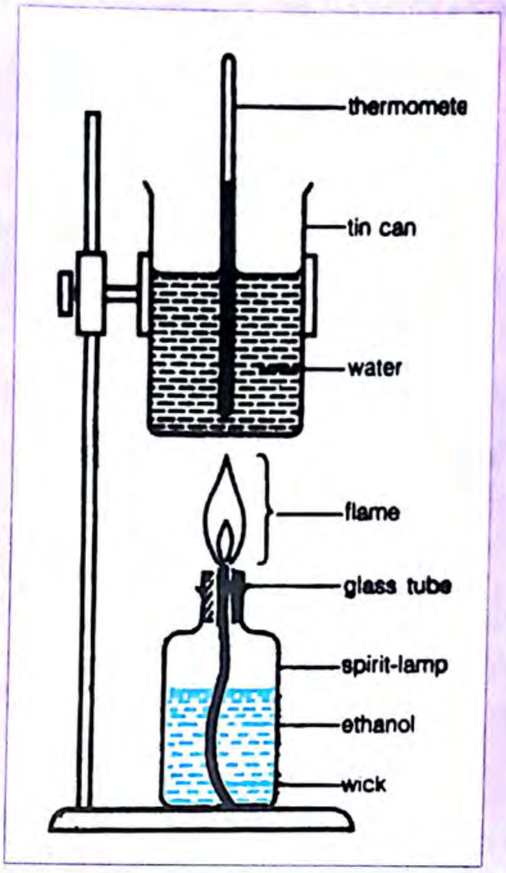
2 The free ions are then hydrated by water molecules. This process evolves energy known as *hydration energy.*

The resultant heat change of the two steps determines whether the dissolution is exothermic. It is known as the *heat of solution.*

Experiment 12.2 To find the heat of combustion of ethanol.

Method This experiment should be done in a draught-free area. The ethanol is burned in a spirit lamp or an improvised lamp as shown. The wick of the lamp is inserted through a glass tube held in the cork of the bottle so that it dips into the ethanol in the bottle. Weigh the lamp with the ethanol before the experiment. Put a known mass of water in a tin can clampled above the lamp. Record the initial temperature of the water. Light the lamp and heat the water in the can. Stir the waterfrequently. When the temperature of the water has risen by about 25 °C, record it, put out the flame and reweigh the lamp with the ethanol.

Fig. 12.5 Estimation of the heat of combustion.



Specimen result

Initial temperature of water = 25.2 °C
= 298.2 K
Final temperature of water = 50.0 °C
= 323.0 K
Mass of water in the can = 100.0 g
Mass of ethanol burned = 0.4 g

Calculation The amount of heat energy given off is that which raised the temperature of 100.0 g water (specific heat capacity = 4.2 J g^{-1} K^{-1}) from 298.2 K to 323.0 K.

Heat evolved = mass × specific heat capacity × temperature rise
= 100 × 4.2 × (323.0 – 298.2)
= 100 × 4.2 × 24.8 = 10 416 J

Mass of ethanol burned = 0.4 g
Relative molecular mass of ethanol, C_2H_5OH = 46

[number of moles of ethanol burned = $\frac{0.4}{46}$ = 0.0087 mole

Combustion of 0.0087 mole ethanol produces 10 416 J of heat energy.

[1 mole ethanol procduces $\frac{10\ 416}{0.0087}$ = 1 197 kJ of heat energy.

Conclusion The standard heat of combustion of ethanol is –1 197 kJ mol^{-1}.

Generally, when an ionic solute dissolves in a solvent, the overall heat change of the dissolution is as follows:

- Dissolution is exothermic if lattice energy $<$ hydration energy
- Dissolution is endothermic if lattice energy $>$ hydration energy

In hydrated salts where the ions are alread extensively hydrated before dissolution, the heat o hydration would be very small. Hence, the dissolutio of hydrated salts is endothermic.

The extent to which the solute particles becom separated and hydrated in aqueous solution varies wit the relative amounts of solute and solvent. The tw steps become complete only in dilute solution. If a concentrated solution is diluted, there will be a furthe heat change, the *heat of dilution*. This heat of dilutio

Experiment 12.3 To determine the heat of solution of sodium trioxothiosulphate (VI)-pentahydrate in water

Method Weigh a glass calorimeter, add about 500cm3 of warm distilled water (at 8-10°C above room temperature) into it and weigh it again. Note the temperature of the water, and immediately add finely-powered crystals of sodium trioxothiosulphate (VI)-pentahydrate into it, a little at a time, stirring vigorously until the temperature of the solution falls 8-10 °C below room temperature. Continue srirring until all the added crystals have just dissolved. Note the temperature again, and weigh the calorimeter and its contents.

Result

Mass of calorimeter = x g
Mass of calorimeter + water = y g
Mass of calorimeter + water + crystals = z g
Initial temperature of water = t_1°C
Final temperature of solution = t_2°C

Calculation Assume that the specific heat capacity of the sodium trioxothiosulphate (VI) solution is the same as that of pure water, i.e. 4.2 J g^{-1} K^{-1}

Total heat absorbed = mass x specific heat capacity x temperature fall
= $(y - x)$ x 4.2 x $(t_1 - t)$ J

Mass of trioxothiosulphate (VI) dissolved = (z - y) g
Relative molecular mass of $Na_2S_2O3_5H_2O$ = 248
[number of moles of trioxothiosulphate (VI) dissolved = $\frac{(z - y)}{248}$

[when 248 g (1 mol) of trioxothiosulphate (VI) are dissolved, the amount

$$\text{heat absorbed} = \frac{(y-x)\text{x}4.2\text{x}(t_1-t_2)}{(z-y)}\text{x}248\text{ J} = \frac{(y-x)\text{x}4.2\text{x}(t_1-t_2)}{(z-y)\text{x}1000}\text{x}248\text{ KJ}$$

Conclusion The dissolution of sodium trioxothiosulphate (VI)-pentahydrate crystals in water is accompained by a drop in temperature, indicating that the process is endothermic. (The calculation should give the heat of dissolution as a positive number. The actual value of the dissolution of sodium trioxothiosulphate (VI)-pentahydrate is +11.3 KJ mol^{-1})

gradually decreases so that eventually, increasing the dilution produces no further heat changes. In practice, this occurs when there are 800 – 1 000 moles of water to 1 mole of solute.

The standard heat of solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in so much water that further dilution results in detectable heat change.

Table 12.3 *Standard heats of solution of some common solutes in aqueous solution.*

Solute	Type of heat change	$-\Delta H_{sol}^{\theta}$ (kJ mol^{-1})
Ammonium chloride	Endothermic	+15.1
Sodium chloride	Endothermic	+3.8
Ammonium trioxonitrate(V)	Endothermic	+26.3
Sodium hydroxide	Exothermic	–43.0
Potassium hydroxide	Exothermic	–54.9
Sodium trioxocarbonate(IV)	Exothermic	–25.0

We can assess the solubility of an ionic solid from its heat of solution value. A solid with a positive heat of solution value is not as soluble as one with a negative value.

Since solubility varies with temperature, a substance which

- dissolves exothermically would be more soluble at lower temperatures, and
- substance which dissolves endothermically would be more soluble at higher temperatures.

This is in accordance with Le Chatelier's Principle (see page 256).

Some solutes, when added to water, will react with the water molecules to form entirely new products which then dissolve to form an aqueous solution (chemical solution). For example,

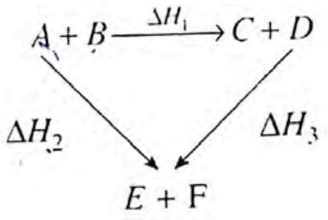
$$2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g) -\Delta H$$

The heat changes involved in such reactions would include the heat of the reaction between water and the solute, and the heats of solution of the new products.

Hess's Law and the Bron-Haber Cycle

The enthalpy change of a chemical reaction can be found experimentally. It can also be found theoretically from known values of enthalpy changes of related reactions. This is done by using *Hess's Law of Constant Heat Summation*. This law states that *the total enthalpy change of a chemical reaction is constant regardless of the route by which the chemical change occurs, provided that the conditions at the start of a reaction are the same as the final conditions.*

Using an energy cycle to represent Hess's Law



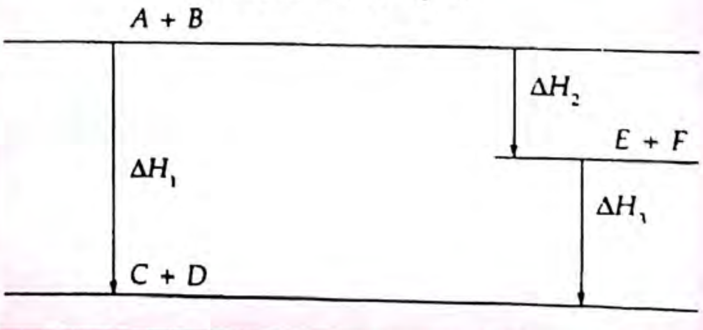
In this cycle,

heat change when
A + B → C + D = sum of heat changes when
(A + B → E + F) and
(E + F → C + D)

Hess's law can be illustrated by the above energy cycle diagram. This law is, thus, another form of the Law of Conservation of Energy.

Hess's Law can also be represented in the form of a *Born-Haber cycle,* which is the combination of an energy cycle and an energy level diagram.

A Born–Haber cycle



In this cycle, reactants A and B are placed at a higher level than the final products, C and D, to show that the former combination has more energy than the latter. To have the same amount of energy, A and B have to lose an amount ΔH_1. From the Born-Haber cycle, it can be seen that $\Delta H_1 = \Delta H_2 + \Delta H_3$, which agrees with Hess's Law.

EXAMPLE

Calculate the heat of formation of butane indirectly, using the Born–Haber cycle and Hess's Law, if the heats of combustion of carbon, hydrogen and butane are as follows:

ΔH_c^θ (graphite) = –393 kJ mol^{-1}

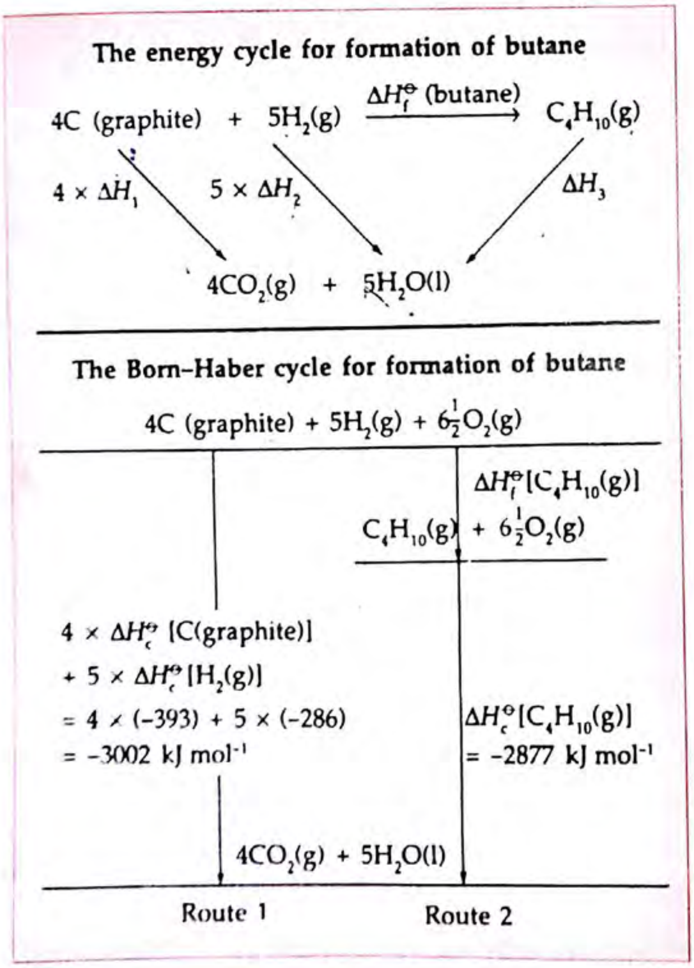
i.e. $C(s) + O_2(g) \rightarrow CO_2(g)$ (ΔH_1)

ΔH_c^θ (hydrogen) = –286 kJ mol^{-1}

i.e. $H_2(g) + .O_2(g) \rightarrow H_2O(g)$ (ΔH_2)

ΔH_c^θ (butane) = –2 877 kJ mol^{-1}

i.e. $C_4H_{10}(g) + 6\frac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$ (ΔH_2)



From here, we can see that

$-3\,002 = \Delta H_f^\theta$ (butane) $- 2\,877$

∴ the standard heat of formation of butane,

$\Delta H_f^\theta = (-3\,002 + 2\,877)$ kJ mol^{-1}

$= -125$ kJ mol^{-1}

BOND ENERGY

Energy changes in chemical reactions are due to the forming and breaking of bonds. The strength of a particular bond is usually measured by the amount of energy required to separate the atoms or ions held together by the bond. This is known as the *bond energy*. This is the energy that is absorbed when a particular bond is broken, or evolved when it is formed. Thus, it is the amount of energy associated with a particular bond in an element or a compound. For example,

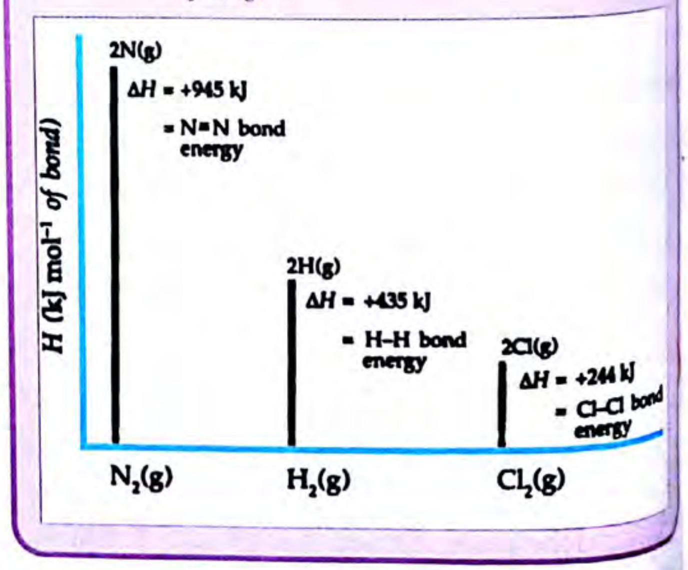
$$H_2(g) \rightarrow 2H(g) \qquad \Delta H = +435 \text{ kJ mol}^{-1}$$
$$H(g) + H(g) \rightarrow H_2(g) \qquad \Delta H = -435 \text{ kJ mol}^{-1}$$

We see that 435 kJ mol^{-1} of energy are absorbed when 1 mole of hydrogen bonds is broken in the gaseous state. The same amount of energy is also evolved when 1 mole of hydrogen bonds is formed from gaseous hydrogen atoms.

NOTE The bond energy evolved when a bond is formed and that absorbed when a bond is broken are the same only for homonuclear molecules, e.g. H-H, Cl–Cl; they are slightly different for heteronuclear molecules, e.g. H–Cl.

The average amount of energy associated with making or breaking 1 mole of a particular bond, in its gaseous state, is its bond energy.

Fig. 12.6 Bond energies of nitrogen, chlorine and hydrogen.



ble 12.4 *Average bond energies of some bonds.*

Bond	Bond energy (kJ mol^{-1})	Bond	Bond energy (kJ mol^{-1})
H-H	435	N≡N	945
Cl-Cl	244	N-H	389
C-C	347	O-H	464
C=C	611	H-Cl	431
C≡C	837	O-O	498
C-H	414	C-O	360
C-Cl	338	C=O	736

Bond energies indicate the strengths of the bonds. The higher the bond energy, the stronger the bond. Strong bonds are more difficult to break than weak ones since a large amount of energy is needed to break the former. Stable substances usually have high-energy bonds, while reactive substances have low-energy bonds. For example, nitrogen molecules, N≡N, with a bond energy of 945 kJ mol^{-1} is less reactive than hydrogen molecules, H–H, with a bond energy of 435 kJ mol^{-1} and chlorine molecules, Cl–Cl, with a bond energy of 244 kJ mol^{-1}.

EXAMPLE

Calculate the approximate heat of reaction of the following reaction from the bond values given in table 12.4.

$$H_2(g)\ \frac{1}{2} + O_2(g) \rightarrow H_2O(g)$$

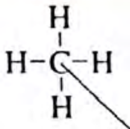
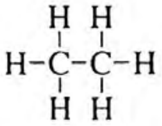
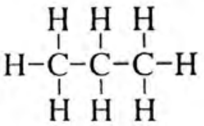
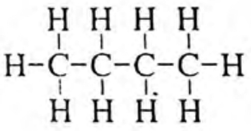
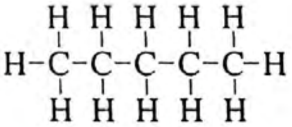
	***Energy change* (kJ)**
1 mole of H–H bonds broken	$1 \times (+435) = +435$
$\frac{1}{2}$ mole of O=O bonds broken	$\frac{1}{2} \times (+498) = +249$
1 mole of H–O–H bonds formed	$1 \times (-464) + 1\times(-464)$ $= -928$

$$\begin{aligned}\Delta H_{reaction} &= \text{total energy required} + \text{total energy evolved}\\ &= (+435 + 249)\text{ kJ} + (-928)\text{ kJ}\\ &= 684\text{ kJ} - 928\text{ kl}\\ &= -244\text{ kJ}\end{aligned}$$

∴ heat of reaction for the given equation is –244 kJ.

We can use bond energies to calculate the heat change or enthalpy change of a reaction. We can also explain why the heats of combustion of the alkanes increase regularly as we go down the series in terms of bond energies as follows: Each member in the alkane series differs from the one immediately above it by an extra $-CH_2$ group (see table 12.5). Each successive alkane has one extra C–C bond and two extra C–H bonds. During combustion, each successive alkane forms one extra CO_2 molecule and one extra H_2O molecule.

Table 12.5 Bond energies of some alkanes.

Alkane	Structural formula	ΔH_c^θ (kJ mol^{-1})	Diference $-\Delta H_c^\theta$ (kJ)
Methane		-890	
			670
Ethane		–1 560	
			660
Propane		–2 220	
			657
Butane		–2 877	
			643
Pentane		–3 520	

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

Therefore, during the combustion of each successive alkane,

1 extra C—C bond 2 extra C—H bonds	are broken
2 extra C = O bonds 2 extra O—H bonds	are formed

Since the extra bonds broken and formed are the same between the successive alkanes, there is a regular increase in the heats of combustion as we go down the series of alkanes.

Bond energies are difficult to measure. Usually, they are determined theoretically. For the calculation of a given bond energy, the simplest molecule containing the bond is generally used. To find the strength of the C–H bond, methane would be suitable as it contains only C–H bonds.

EXAMPLE

Find the average bond energy of the C–H bond in methane using the following data:
Heat of atomization of hydrogen,

$$\Delta H_{at}^{\theta}\,[H_2(g)] = 218 \text{ kJ mol}^{-1} \qquad (\Delta H_1)$$

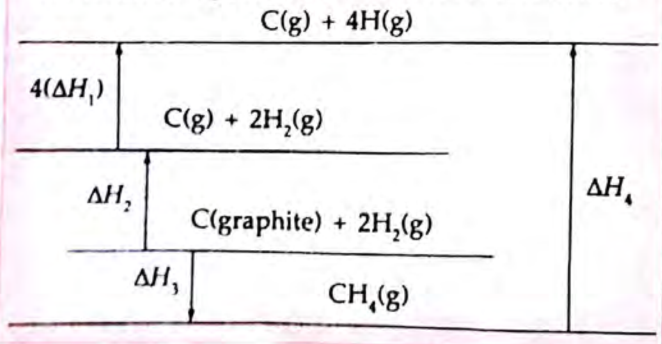
Heat of atomization of carbon,

$$\Delta H_{at}^{\theta}\,[C(graphite)] = 715 \text{ kJ mol}^{-1} \qquad (\Delta H_2)$$

Heat of formation of methane,

$$\Delta H_f^{\theta}\,[CH_4(g)] = -75 \text{ kJ mol}^{-1} \qquad (\Delta H_3)$$

NOTE *Heat of atomization of an element is the heat absorbed to form 1 mole of gaseous atoms from the element under standard conditions.*



Born-Haber Cycle for the formation of methane

From the diagram,

$$\Delta H_4 = 4(\Delta H_1) + \Delta H_2 - \Delta H_3$$
$$= 4(218) + 715 + 75 = 1\,662 \text{ kJ mol}^{-1}$$

ΔH_4 is 4 times the C–H bond energy.
The average C–H bond energy in methane
$= 1\,662 \div 4 = 415.5$ kJ mol^{-1}

LATTICE ENERGY

Bond energies help us to understand the stability molecular or covalent substances. In a similar w *lattice energies* help us to understand the stability ionic crystals.

The lattice energy of an ionic crystal is the heat of formation of one mole of ionic compound from widely separated gaseous ions under standard conditions.

Lattice energies, like bond energies, cannot measured experimentally. They can only determined theoretically.

CHEMICAL THERMODYNAMICS

Thermodynamics is the study of relationships between heat and other forms of energy. Heat is represented by the symbol q. All other forms of energy are referred to commonly as work in thermodynamics and are represented by w. The relationships between heat and work is expressed in the laws of thermodynamics.

The First Law of Thermodynamics

The First Law of Thermodynamics states that *energy may be converted from one form to another, but it cannot be created or destroyed.* This is actually the Law of Conservation of Energy.

The internal energy, U, of a chemical system is the sum of all the energies, such as the chemical or potential energy and bond energy of the system. When conditions of the system change, i.e.

- heat is evolved or absorbed, and/or
- if work is done on or by the system,

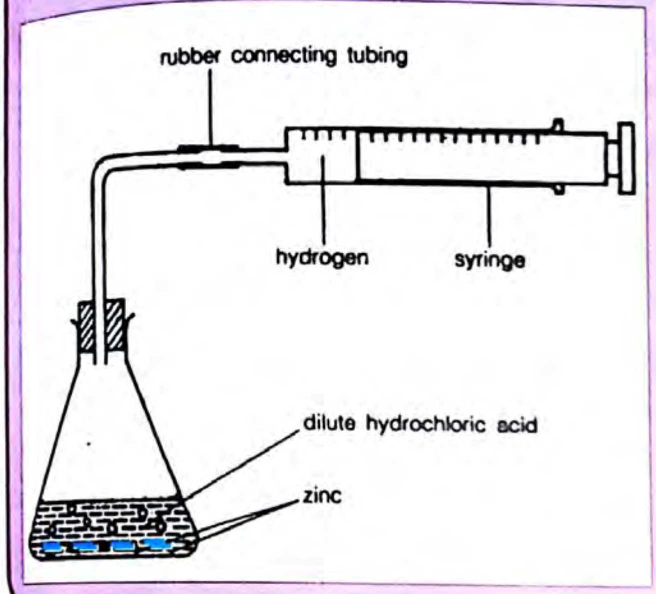
the internal energy of the system will change. From the First Law of Thermodynamics, such a change in the internal energy of a system may be represented by

Change in internal energy (ΔU)	=	Heat absorbed by the system (q)	+	Work done by the system (w)

The direction of energy flow is indicated by specifying the signs for q and w. Thus, when the system

- absorbs energy as heat from the surroundings, q is positive (+);
- evolves energy as heat to the surroundings, q is negative (–);

Fig. 12.7 To show work done by a system on its surroundings.



- absorbs energy by having work done on it by the surroundings, w is positive (+);
- evolves energy by doing work on the surroundings, w is negative (–).

When the system is gaseous, work done is given by $p\Delta V$, where p = pressure and ΔV = change in volume. We can illustrate this by considering what happens in the reaction between zinc and dilute hydrochloric acid using the apparatus shown in fig. 12.7.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

In this chemical system, the hydrogen gas evolved pushes the piston of the syringe to produce a change in volume, ΔV, against a constant pressure, p. Thus, the work done by the system on the surroundings is $p\Delta V$. Also, the heat absorbed by the system, q, at constant pressure, is equal to the change in enthalpy, ΔH. Therefore, we can say

$$\Delta U = (q) + (-w) = q - w$$
$$= \Delta H - p\Delta V$$

or

$$\Delta H = \Delta U + p\Delta V$$

From the above equation, it follows that in reaction where the volume change is small, ΔH and ΔU are approximately equal.

NOTE In a chemical system, work done is usually mechanical or electrical work.

The Second Law of Thermodynamics

Most exothermic processes occurs spontaneously. Such processes result in a decrease in the overall enthalpy of the system. Some endothermic processes also take place spontaneously. For example, crystals of ammonium trioxonitrate(V) dissolve spontaneously with the absorption of so much heat that the solution is noticeably cooled. Thus, enthalpy alone is not the only factor determining the spontaneity of a particular process. The other factors which exert an important influence on determining whether a process can occur spontaneously are

- the *entropy*, and
- the *free energy*,

of the system undergoing the change.

Entropy Entropy, S, is a property of a substance measured in J K^{-1} mol^{-1}. The simplest idea of entropy is to picture it as *a measure of the degree of disorder or randomness of a substance.* A perfectly ordered system at 0 K has an entropy of zero. There is no disorder or randomness in such a system and the units making up the perfect crystalline substance are in a neat array.

From this it follows that a crystalline substance with a highly-ordered structure usually has a low entropy, whereas a liquid has a higher entropy value due to the less ordered arrangement of molecules. In a gas, molecules are moving continuously and randomly; there is little order and the entropy is relatively large.

Generally, for a given substance, as temperature increases, the degree of disorder or entropy increases. However, fig. 12.8 shows that an increase in temperature alone has little effect on entropy. Large jumps in entropy occur when the solid melts and the liquid vaporizes.

The influence of entropy on a process is given by the Second Law of Thermodynamics which states that: *A spontaneous process occurs only if there is an increase in the entropy of a system and its surroundings.*

When a reversible chemical change occurs at a

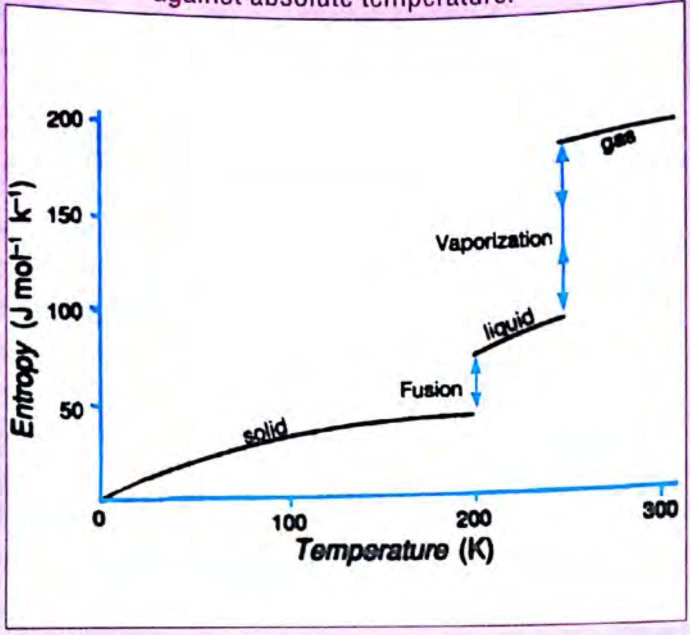


Fig. 12.8 Graph of molar entropy of ammonia against absolute temperature.

constant temperature, the change in entropy, ΔS, is equal to the heat absorbed or evolved, ΔH, divided by the absolute temperature, T, at which the process occurs.

$$\Delta S = \frac{\Delta H}{T}$$

If heat is absorbed, ΔS is positive and there is an increase in entropy. If heat is evolved, ΔS is negative and there is a decrease in entropy.

EXAMPLE

Calculate ΔS for the conversion of one mole of liquid water to vapour at 100 °C, given that the heat of vaporization of water = 2 260.87 J g^{-1}.

Mass of 1 mole of water = 18 g

Heat of vaporization of 1 mole of water

$$= 2\,260.87 \times 18 = 40\,695.70 \text{ J}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{40\,695.70}{(100+273)}$$

$$= 109.10 \text{ J K}^{-1} \text{ mol}^{-1}$$

The positive value shows that the entropy of water increases as it passes from the liquid to the vapour state.

Free energy Another factor that determines whether a process will occur spontaneously or not is the change in free energy of a chemical system.

The free energy of a chemical system, G, i energy which is available for doing work. Thi driving force that brings about a chemical ch Now,

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$$

and $\Delta S_{surroundings} = \dfrac{-\Delta H}{T}$

then $\Delta S_{total} = \qquad + \Delta S_{system}$

Multiplying throughout by T,

$$T\Delta S_{total} = -\Delta H + T\Delta S_{system}$$

or $$-T\Delta S_{total} = \Delta H - T\Delta S_{system}$$

The quantity $(-T\Delta S_{total})$ is called the free en change, ΔG;

$$\therefore \Delta G = \Delta H - T\Delta S_{system}$$

CONDITIONS FOR SPONTENEI OF REACTIONS USING ΔG

For a chemical change to occur spontaneou

- ΔS_{total} must be positive as the total entropy increase.

Since $\Delta G = -T\Delta S_{total}$ for ΔS_{total} to be positive,

- ΔG must be negative.

Thus, for all spontaneous changes, ΔG mus negative.

If ΔG is positive, the reaction will not take p unless some condition is altered to make ΔG nega Usually supplying heat to the system, i.e. raising temperature, makes ΔG negative and enables reaction to occur.

If a reaction is exothermic and also results in g disorder, the combined changes in the enthalpy entropy will lead to a large decrease in free ene making the reaction spontaneous.

If a reaction is endothermic and involves a los entropy, the reaction will not be spontaneous as resultant ΔG is positive. Such a reaction, howe will be spontaneous if the resultant of the two oppos influences, the enthalpy and the entropy of the reac system, leads to a net decrease in free energy.

If ΔG is zero, then the chemical system is i state of equilibrium. This happens when both ΔH ΔS are negative or positive.

Industrial application of the law

1 The formation of water gas is represented by

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \qquad \Delta H = +131 \text{ kJ mol}^{-1}.$$

This reaction is strongly endothermic. At room temperature, $T\Delta S$ is small relative to ΔH. Thus, ΔG is positive and the reaction is not spontaneous. At 700 °C, however, $T\Delta S$ becomes so large that it exceeds the positive value of ΔH. ΔG is negative under these conditions, resulting in a spontaneous reaction.

2 The synthesis of ammonia is exothermic.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

The formation of ammonia results in a decrease in ΔS. At room temperature, the enthalpy term, ΔH, predominates the $T\Delta S$ value, leading to a decrease in the value of ΔG, making it negative. Thus, the reaction is spontaneous, and a good yield of ammonia is obtained at room temperature. At 600 °C, however, the ΔS value becomes so significant that the $T\Delta S$ value now predominates the enthalpy term, ΔH, resulting in an increase in the value of ΔG, i.e. ΔG becomes positive. Thus, above 600 °C, the synthesis of ammonia is not spontaneous.

SUMMARY

- The Law of Conservation of Energy states that energy can be changed from one form to another, but it can neither be created nor destroyed.
- Energy changes accompanying chemical reactions can be observed as heat, light or sound.
- Each mole of a particular substance has a characteristic heat content or enthalpy. During a chemical reaction, heat is either absorbed or liberated because of the different heat contents of the reactants and products.
- The unit for heat change is the joule(J) or the kilojoule(kJ). The heat change of any reaction is represented as ΔH where $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- Standard conditions for measuring ΔH are at a pressure of 1.01×10^5 N m^{-2}, temperature of 298 K and concentration of 1 mol dm^{-3}.
- Standard heat of reaction is the amount of heat evolved or absorbed when a chemical reaction occurs between molar quantities of the reactants as represented in the equation of reaction under standard conditions.
- An exothermic reaction has a negative ΔH value indicating that heat energy has been lost to the surroundings. An endothermic reaction has a positive ΔH value indicating that heat energy has been absorbed from the surroundings.
- The energy changes in reactions actually come from the breaking and forming of chemical bonds. When more energy is required to break than form bonds, it is an endothermic reaction ($+\Delta H$). When less energy is required to break than form bonds, it is an exothermic reaction ($-\Delta H$)

- The standard heat of formation of a substance, ΔH_f^θ, is the heat evolved or absorbed when one mole that substance is formed from its elements under standard conditions.
- The standard heat of neutralization, ΔH_n^θ, is the amount of heat evolved when one mole of hydrogen ion H^+, from an acid reacts with one mole of hydroxide ions, OH^-, from an alkali to form one mole of wate under standard conditions.
- The standard heat of combustion of a substance, ΔH_c^θ, is the heat evolved when one mole of the substanc is completely burned in oxygen under standard conditions.
- The standard heat of solution is the amount of heat absorbed or evolved when one mole of a substanc is dissolved in such a large amount of water that further dilution results in no detectable heat change.
- Hess's Law of Constant Heat Summation states that the total enthalpy change of a chemical reaction constant regardless of the route by which the chemical change occurs provided that the initial and fina conditions are the same.
- The average amount of energy associated with one mole of a particular bond is its bond energy. The highe it is, the stronger the bond.
- The lattice energy of an ionic crystal is the heat of formation of one mole of ionic compound from widely separated gaseous ions under standard conditions.
- The First Law of Thermodynamics states that energy can be converted from one form to another, but it cannot be created or destroyed. Thus, during a chemical process,

$$\underset{(\Delta U)}{\text{Change in internal energy of system}} = \underset{(q)}{\text{Heat absorbed by system}} + \underset{(w)}{\text{Work done by system}}$$

- Enthalpy, entropy and free energy are the three factors which play a role in determining whether a reaction occurs spontaneously.

(a) Entropy, S, is a measure of the degree of disorder or randomness of a substance. A perfectly ordered system at 0 K has an entropy of zero. The change in entropy of a system, ΔS, is given by

$\Delta S = \Delta H/T$, where ΔH is the enthalpy change, T is the absolute temperature.

The Second Law of Thermodynamics states that a spontaneous process occurs only if there is an increase in the entropy of a system and its surroundings, i.e. the change in the total entropy of the system, ΔS_{total}, must be positive.

(b) Free energy, G, of a system is that energy which is available for doing work. The change in free energy of the system, ΔG, is given by $\Delta G = \Delta H - T\Delta S$. For all spontaneous processes, ΔG must be negative.

EXERCISES

1. Welding converts
   A electric energy to heat energy.
   B electric energy to light energy.
   C electric energy to both heat and light energies
   D chemical energy to heat energy.

2. Heat content of matter is sometimes called
   A entropy.
   B joule.
   C enthalpy.
   D ergs.

3. Heat content difference between the products and reactants of a chemical reaction is called
   A entropy change.
   B endothermic reaction.
   C exothermic reaction.
   D enthalpy change.

4. From the reaction $2H_2O_{(l)} \rightarrow 2H_2(g) + O_2g \Delta H =$ 285.58 Kj mol^{-1} it means that
   A 285.58 kilojoules of energy was absorbed from the surrounding.
   B 285.58 kilojoules of energy was released into the surrounding.
   C 285.58 is the entropy change of the reaction.
   D none of the above.

5. Endothermic reaction may be defined as except
   A reaction in which heat is absorbed.
   B reaction in which heat is released.
   C reaction in which ΔH = positive.
   D reaction in which the energy of the product is higher than energy of the reactant.

6. The notation ΔH_f^θ represents
   A enthalpy change of formation.
   B heat change of formation.
   C standard heat change of formation.
   D standard enthalpy of formation.

7. [A] $OH^-(aq) + H^+(aq) \rightarrow H_2Ol$
   [B] $2OH^-(aq) + 2H^+(aq) \rightarrow 2H_2O(l)$

   From reactions A and B, if the ΔH of A = -57.3 kJ mol^{-1}. Then the ΔH of B is
   A $\frac{-57.3}{2}$ kJ mol^{-1}
   B -57.3×2 kJ mol^{-1}
   C $(-57.3)^2$ kJ mol^{-1}
   D $2(-57.3)^2$ kJ mol^{-1}

8. Precautions taken when measuring heat of combustion of a specimen are except
   A the use of well lagged calorimeter.
   B use of volumes of water but continuously stirred.
   C Both water and the bomb must attain steady temperature before igniting the bomb.
   D temperatures of the ignited bomb is taken every 30 second interval until a steady temperature is attained.

9. The energy spent on disorganizing the regular structure of ions in a molecule is called
   A conformation energy.
   B lattice energy.
   C ionization energy.
   D electron affinity.

10. Substances which dissolve endothermically would dissolve more at
    A lower temperature.
    B any temperature provided not below freezing point.
    C higher temperature.
    D any isolated temperature.

11. From the 1st law of thermodynamics

$$\underset{\left(\text{change in internal energy}\right)}{\Delta U} = \underset{\left(\text{Heat absorbed}\right)}{q} + \underset{\left(\text{work done by the system}\right)}{w}$$

(Change in internal energy) (Heat absorbed)
(Work done by the system)
How is this equation given for a gaseous system?
A $\Delta U = q + wv$ B AU = zero
C $\Delta U = q + Pv$ D $\Delta U = q + P\Delta v$
(P = pressure, V = volume)

12. Which of these presents decrease in entropy?
- A Melting of ice.
- B Decomposition of calcium hydrogen trioxocarbonate IV.
- C Addition of cold water to starch solutions.
- D Addition of hot water to starch solution.

13. If ΔG (free energy) is used to determine spontaneity of a chemical reaction, what is the nature of reaction of ΔG = zero.
- A The reaction is static.
- B The reaction is exothermic.
- C The reaction is endothermic.
- D The reaction is at equilibrium.

14. From, $\Delta G = \Delta H - T\Delta S$, these will make ΔG negative except
- A decreasing the temperature.
- B decreasing the enthalpy change.
- C increasing the temperature.
- D making ΔH and $T\Delta S$ equal.

15. Calculate the ΔH of a chemical system when the entropy is 218.2 jK^{-1} mol^{-1} and the temperature is 100°C.
- A 81388.6 J q^{-1}
- B 40694.3 J q^{-1}
- C 122082.9 J q^{-1}
- D 132082.9 J q^{-1}

16. When ΔH is negative, the reaction is said to be
- A exothermic.
- B endothermic.
- C ionic.
- D reversible.
- E catalytic.

17. Which of these processes is endothermic?
- A Slaking of quicklime.
- B Formation of ammonia.
- C Combustion of graphite.
- D Dissolution of potassium trioxonitrate(V) in water.
- E Dilution of concentrated tetraoxosulphate(VI) acid with water.

18. Define the following:
- (a) Heat of formation
- (b) Heat of neutralization
- (c) Heat of combustion
- (d) Heat of solution

19. Explain the terms *exothermic* reaction and *endothermic* reactions. What is the sign of ΔH in each of the reactions?

20. (a) Explain why the heat of neutralization between strong acid and strong alkali pairs is of an approximate value of –57 kJ mol^{-1}.

(b) The heat of neutralization between ethanoic acid and sodium hydroxide solution is –55.5 kJ mol^{-1}. Is the ionizatin of ethanoic acid exothermic or endothermic? Give reasons.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

21. Using the average bond energy values given below, calculate the total bond energy of ethanol, C_2H_5OH.

C–C = 347 kJ mol^{-1} C–H = 414 kJ mol^{-1}
H–O = 464 kJ mol^{-1} C–O = 360 kJ mol^{-1}

22. Draw an energy level diagram for each of the following reactions:
- (a) $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$ $\Delta H = -770$ kJ mol^{-1}
- (b) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -480$ kJ mol^{-1}
- (c) $H_2(g) + I_2(s) \rightarrow 2HI(g)$ $\Delta H = +53.6$ kJ mol^{-1}
- (d) $C(s) + 2S(s) \rightarrow CS_2(l)$ $\Delta H = +105$ kJ mol^{-1}

23. State the laws of thermodynamics. Give the conditions for a chemical change to occur spontaneously.

24. Calculate
- (a) q when a system does 72 J of work and its internal energy decreases by 90 J.
- (b) ΔU for a gas that releases 35 J of heat and has 128 J of work done on it.

25. Define lattice energy and bond energy. Explain with examples why some bonds are more stable than others.

RATES OF REACTIONS 13

RATE OF A CHEMICAL REACTION

The speeds or rates of chemical reactions differ greatly. Some reactions are fast while others are slow. There are many reactions that occur at intermediate speeds. A white precipitate of silver chloride forms almost immediately when silver trioxonitrate(V) solution is added to hydrochloric acid. The rusting of an iron nail in air is a slow process that takes several days.

A given reaction can also occur at different rates if the conditions of the reaction are different. A big piece of marble reacts slowly with a dilute acid. If powdered marble is used, the reaction is rapid. A piece of calcium reacts slowly with cold water, but more rapidly with warm water.

The rates of chemical reactions and their control are important in industry as they are, often, the deciding factors that determine whether a reaction may be used economically or not.

Combustion of fuels is a very rapid reaction.

Meaning of rate of reaction

Zinc reacts with a dilute hydrochloric acid in the following way:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$$

As the reaction proceeds, zinc and the acid, i.e. the reactants, are used up while zinc chloride and hydrogen, i.e. the products, are formed. The rate of reaction is the speed at which reactants are used up or products are formed.

The rate of a chemical reaction is the number of moles of reactant converted or product formed per unit time.

We can measure the rate of the above reaction by

(a) taking a given mass of zinc,
(b) adding an excess of hydrochloric acid to it, and
(c) noting the time taken for all the zinc to react.

The reaction rate is given by:

$$\text{Rate of reaction} = \frac{\text{Amount of zinc (mol dm}^{-3}\text{)}}{\text{Time taken (min)}}$$

Most methods for determining reaction rates involve a change in the concentration of one of the components of the reaction with time.

$$\text{Reaction rate} = \frac{\text{Change in concentration of reactant / product}}{\text{Time taken for the change}}$$

The concentration of the reactant or product is expressed in mol dm^{-3} or g dm^{-3}. The time it takes to undergo the complete reaction can be in seconds, minutes or even years for slow reactions.

EXAMPLES

1 When 0.5 g of calcium trioxocarbonate(IV) was added to excess dilute hydrochloric acid, carbon(IV) oxide was evolved. The entire reaction took 5 minutes. What was the rate of reaction?

$$\text{Rate of reaction} = \frac{\text{Mass of reactant (i.e. } CaCo_3\text{)}}{\text{Time taken for the change}}$$

$$= \frac{0.5 \text{ g}}{5 \text{ min}} = 0.1 \text{ g min}^{-1}$$

0.1 g of calcium trioxocarbonate(IV) was converted to the product in 1 minute.

2 When a dilute solution of "20-volume" hydrogen peroxide solution was heated, the total volume of oxygen collected was 120 cm³ in just 15 minutes. What was the rate of formation of oxygen?

$$\text{Rate of reaction} = \frac{\text{Volume of product (i.e. } O_2\text{)}}{\text{Time taken for the change}}$$

$$= \frac{120 \text{ cm}^3}{15 \text{ min}} = 8 \text{ cm}^3 \text{ min}^{-1}$$

8 cm³ of oxygen was produced in 1 minute.

Ways of measuring reaction rates

We determine a reaction rate by measuring the rate at which the mass or concentration of a

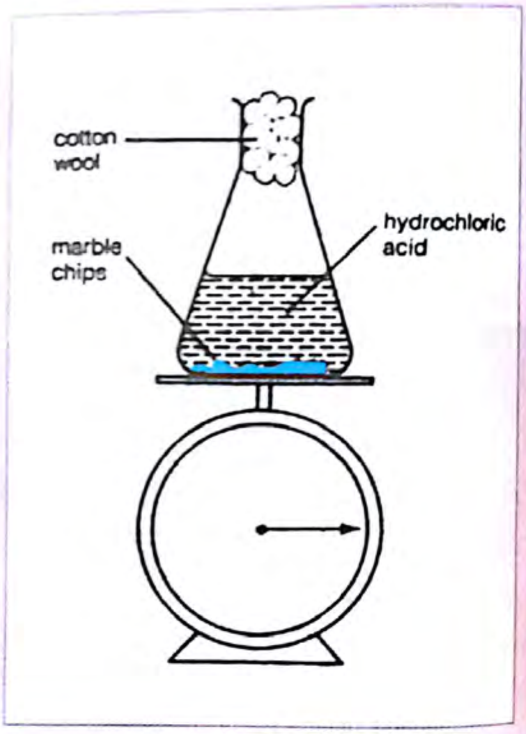
- reactant is decreasing, or
- product is increasing.

Experiment 13.1 To study how the rate of a reaction varies with time.

Theory When dilute acid is added to marble chips, carbon(IV) oxide is given off. The gas escapes resulting in a loss in the mass of the reaction system which is used to measure the rate of reaction.

Method Place 10 g of marble chips in a conical flask. Add about 100 cm³ of 1 M hydrochloric acid to the marble chips and plug the mouth of the flask loosely with cotton wool. Place it on a balance and start a stop-clock at once. Record the mass of the reaction mixture at one-minute intervals until the reaction is completed, i.e. until no further loss in mass is detectable. Calculate the losses in the mass of the reaction mixture and plot a graph of these values against time.

Fig. 13.1 Reaction rate varies with time.



Result There is a greater loss in mass per minute during the earlier stages of the reaction than during the later stages. The gradient of the graph decreases as the reaction proceeds, i.e. it is most steep at the beginning of the reaction when the concentration of the reactants is high and least steep at the end of the reaction when the concentration of the reactants is low. Fig. 13.2(a) and (b) show the types of graph obtained when loss in mass is plotted against time.

Conclusion The rate of a reaction is not constant but decreases as the reaction proceeds.

If we cannot do this, then we measure a property which changes proportionately with the mass of a reactant or product. Usually, we determine reaction rates by measuring the:

- decrease in the mass of the reaction system (e.g. due to the escape of a gaseous product)
- volume of a gaseous product;
- amount of precipitate formed;
- time taken to arrive at an easily seen stage;
- changes in intensity of colour;
- changes in pH; or
- changes in total gas pressure.

How reaction rate varies

When acid is added to zinc, we notice that the effervescence is more vigorous at the start of the reaction than at the end, i.e. the rate of a reaction is not constant during the course of the reaction.

For most irreversible reactions, the reaction rate decreases with time: being highest at the start, and decreasing gradually to zero.

Rate curve The graph in fig. 13.2(a), which shows the rate of reaction, is known as a rate curve. This curve passes through the origin because there is no loss in mass right at the start of the reaction. The gradient of the curve is steep at first because the rate of reaction is fast. Then, the gradient of the curve becomes less steep as the rate of reaction slows down. Finally the curve becomes horizontal. The point at which the curve becomes horizontal indicates the end point of the reaction, when one of the reactants (e.g. the marble chips, in experiment 13.1) is completely used up.

We can determine the following from a rate curve:

- Average rate of reaction.
- Rate at a particular instant during the reaction.

From the rate curve in fig. 13.2(b), the loss in the mass of the reaction system is equal to the mass of carbon(IV) oxide produced.

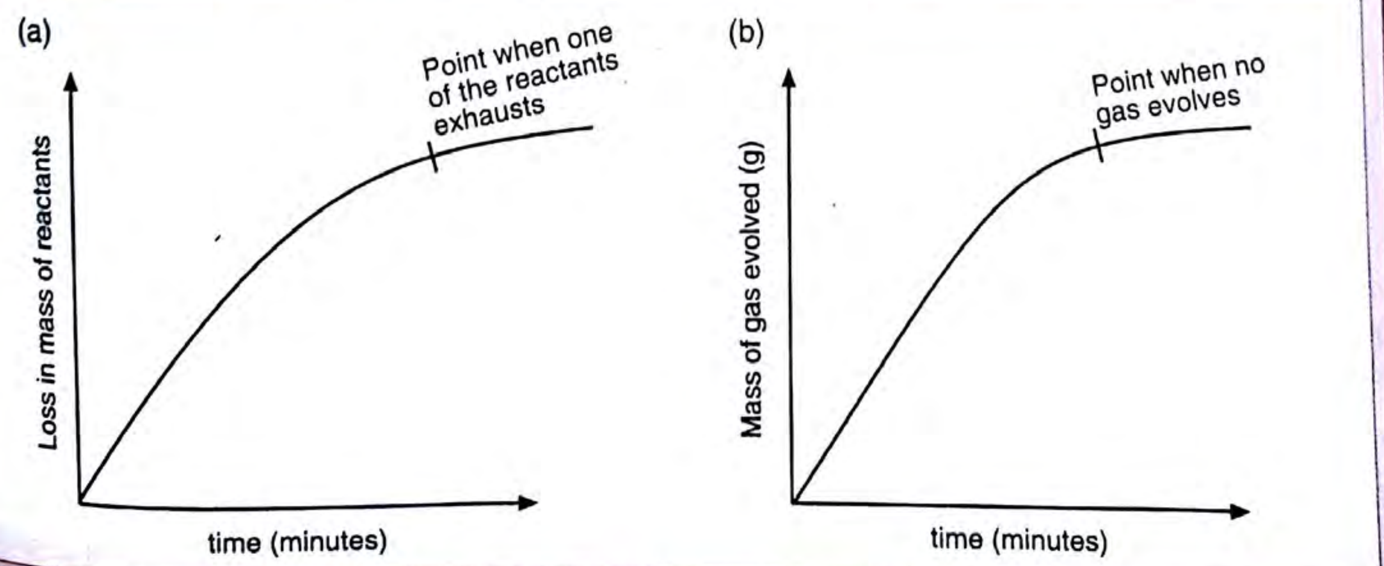
$$\text{Average rate of whole reaction} = \frac{\text{Total loss of mass}}{\text{Total reaction time}} = \frac{x \text{ grams}}{t_3 \text{ minutes}} = \frac{x}{t_3} \text{ g min}^{-1} \text{ of } CO_2 \text{ produced}$$

$$\text{Rate of reaction at } t_1 = \text{gradient of tangent at A} = \frac{x}{y}$$

$$\text{Rate of reaction at } t_2 = \text{gradient of tangent at B} = \frac{x_1}{y_1}$$

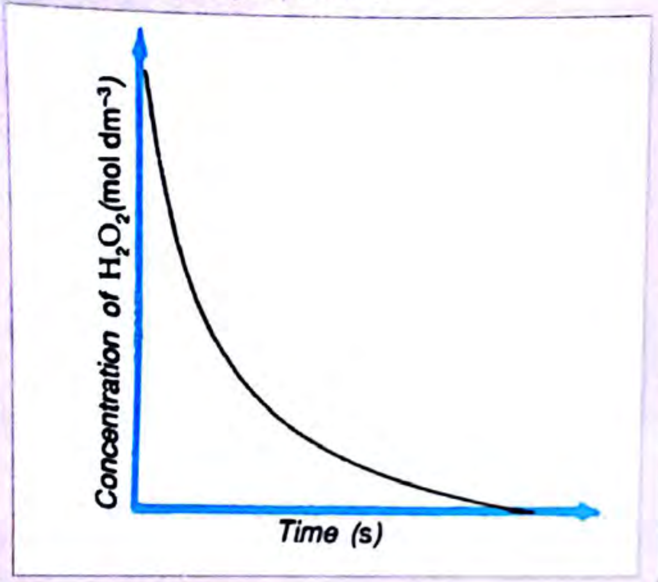
The gradient of the tangent at any point on the rate curve represents the rate of loss of carbon(IV) oxide, and therefore the rate of the reaction at that given instant. From the rate curve, we see that a larger

Fig. 13.2 Graphs of rate of reactions (Rate Curves)



Scanned by CamScanner

Fig. 13.3 Rate curve for decomposition of hydrogen peroxide.



gradient indicates a faster reaction rate while a smaller gradient indicates a slower one.

In general, a rate curve of quantity or concentration of product against time for a reaction has the shape shown in fig. 13.2. A rate curve for quantity or concentration of reactant against time has a different shape. When hydrogen peroxide decomposes as shown,

$$2H_2O_2(aq) \xrightarrow{\text{catalyst}} 2H_2O(l) + O_2(g)$$

its concentration decreases with time as the reaction proceeds. Fig. 13.3 shows the shape of the rate curve of concentration of hydrogen peroxide (reactant) against time.

The above observations may be summarized by stating that,

$$\boxed{\text{Rate of reaction} \propto [\text{concentration of A}]}$$

Where A is (i) amount in moles of products
(ii) amount in moles of disappeared reactants
(iii) volume of gas/es evolved

Therefore,

$$\boxed{\text{Rate of reaction} = K\ [\text{concentration of A}]}$$

K is called rate constant.

COLLISION THEORY

The *Collision Theory* assumes that there must be collisions between reactant particles for a chemical reaction to occur. Although there are many such collisions, only a small fraction of them result in a reaction; these are called *effective collisions*.

In a reaction system, particles move about a different speeds as they possess different amounts of energy. For a chemical reaction to occur, the colliding reactant particles must possess a certain minimum amount of energy, called *activation energy*.

In all chemical reactions, existing bonds in the reactant particles have to be broken first before new bonds can be formed to produce product particles. The breaking of bonds requires energy and is possible only if the reactant particles collide with sufficient energy to overcome this *energy barrier*. If the energy of the colliding reactant particles is less than the activation energy, they merely rebound from each other and no reaction occurs. Reaction occurs if the energy of the colliding reactant particles is equal to or more than the activation energy.

Every reaction has its own energy of activation. A reaction with a low activation energy will take place spontaneously at room temperature. A reaction with a high activation energy will only take place if energy is supplied, usually in the form of heat, light or electrical energy. The addition of a catalyst lowers the activation energy of a reaction.

Let us consider the synthesis of water (steam) from gaseous hydrogen and oxygen. Both hydrogen and oxygen gases exist as stable diatomic molecules. During the reaction,

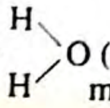
- the covalent bonds in the hydrogen and oxygen molecules are broken; respectively then
- new bonds are formed between the hydrogen and oxygen atoms to give molecules of water.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Bond-breaking : H–H → H + H (free atoms)

Bond-breaking : O–O → O + O (free atoms)

New bond forming: $2H + O \rightarrow$



$\mathrm{H{-}O{-}H}$ (water molecule)

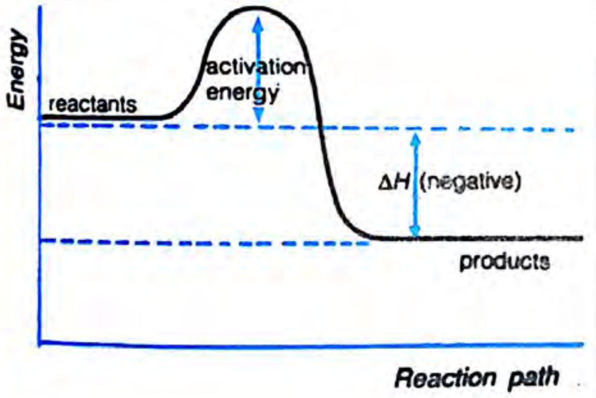
The breaking of the covalent bonds requires energy. An initial energy input is needed to activate the reactant molecules. This energy is the activation energy of the reaction. In this case, the energy is relatively high and a mixture of hydrogen and oxygen left undisturbed do not react under ordinary conditions. To overcome the energy barrier, energy must be supplied to the reaction system. This is usually provided by an electric spark. The net reaction of the formation of water is exothermic. Therefore, once the reaction begins, the heat energy evolved is enough to activate the rest of the reactant molecules.

The graphs in fig. 13.4 illustrate the concept of the energy of activation. From these, we see that

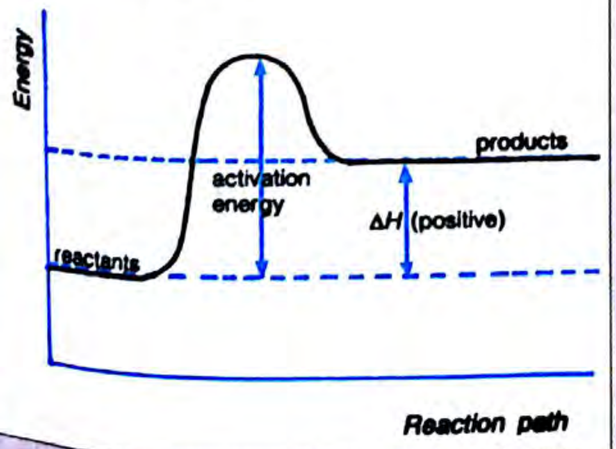
- both exothermic and endothermic reactions generally require an initial input of energy to overcome the activation energy barrier;
- exothermic reactions, once started, may evolve enough energy to activate more reactant particles so that the reaction can proceed without any further external energy supply;
- endothermic reactions have to be continually supplied with an external source of energy for activating the reactant particles as well as to form the products.

Fig. 13.4 Changes in energy content during the course of a chemical reaction.

(a) Exothermic reaction



(b) Endothermic reaction



FACTORS AFFECTING RATES OF REACTION

From the Collision Theory, we see that the rate of a reaction would depend on the frequency of effective collisions between reactant particles. The factors which influence

- the energy content of the particles,
- the frequency of collision of the particles, and
- the activation energy of the reaction

will also affect the rate of chemical reactions. Some of these important factors are as follows:

1 Nature of reactants.
2 Concentration/pressure (for gases) of reactants.
3 Surface area of reactants.
4 Temperature of reaction mixture.
5 Presence of light.
6 Presence of a catalyst.

Note When doing experiments to study the effect of one of the factors on rate of reaction, the other factors that also affect the rate of reaction must be kept constant. Only then can we assume that the changes in measurement that ocur are due, to the factor under study.

Effect of the Nature of Reactants

When a piece of iron is placed in dilute hydrochloric acid, there is a slow evolution of hydrogen gas; with a piece of zinc, hydrogen is evolved rapidly; and with a piece of gold, there is no evidence of a reaction. Thus, the rate of a chemical reaction is determined by the chemical nature of the reactants as different substances have different energy contents.

Effect of Concentration of Reactants

Reactant particles will collide more often if they are crowded in a small space, i.e. frequency of collision is dependent upon concentration. An increase (or decrease) in the concentration of the reactants will result in a corresponding increase (or decrease) in effective collisions of the reactants and hence in the reaction rate.

Pressure affects the concentration of gaseous reactants. For example, a mixture of hydrogen and chlorine gases will react twice as fast if the partial

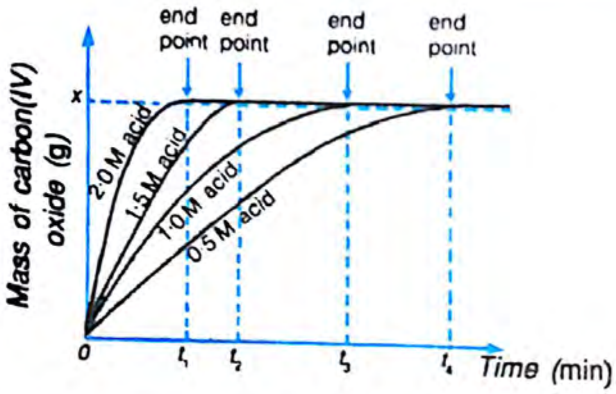
Experiment 13.2 To study the rate curves for different concentrations of hydrochloric acid in th reaction between the acid and calcium trioxocarbonate(IV).

Method Carry out the method described for experiment 13.1. Repeat the experiment wi same mass of marble chips each time but different concentrations of the acid, e.g 0.5 M, 1.0 M, 1.5 M and 2.0 M. Plot the rate curves for the different concentration of the acid on the same graph axes.

Result The rate of reaction is faster, especially at the beginning, if the acid is more concentrated. The reaction also completes faster if the acid is more concentrated However, the mass of carbon(IV) oxide formed is the same for all the four differen acid concentrations. This is because the same amount of marble chips (the limitin reactant) is used in each case.

Conclusion Rate of a reaction increases with increasing concentrations of the reactant.

Fig. 13.5 Graph of effect of concentration of a reactant on reaction rate.



Average rate of reaction, when

2·0 M acid is used = $\frac{x}{t_1}$ g min^{-1}

1·5 M acid is used = $\frac{x}{t_2}$ g min^{-1}

1·0 M acid is used = $\frac{x}{t_3}$ g min^{-1}

0·5 M acid is used = $\frac{x}{t_4}$ g min^{-1}

Experiment 13.3 To study the effect of the concentraion of acidified potassium iodide solution on the rate of production of iodine in the reaction with hydrogen peroxide.

Method Prepare acidified potassium iodide, A, and hydrogen peroxide B, as follows:

Solution A To 1 000 cm^3 of boiling water, add 1 g of starch powder, followed by 1 g of potassium iodide and stir. Then add about 2 cm^3 of concentrated tetraoxosulphate(VI) acid.

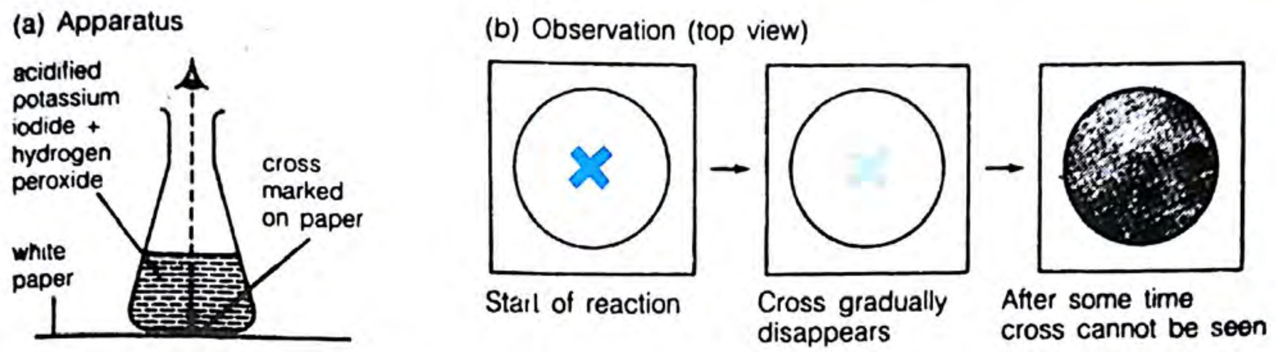
Solution B Mix 200 cm^3 of a "10-volume" commercial hydrogen peroxide with 800 cm^3 of distilled water.

Take ten 250-cm^3 conical flasks. Into five of these, labelled A_1 to A_5, add 100 cm^3, 80 cm^3, 40 cm^3 and 20 cm^3 of solution A respectively and make up the volume, where necessary, to a total of 100 cm^3 with distilled water. To each of the other five flasks, labelled B_1 to B_5, add 100 cm^3 of solution B.

Pour the solution from B_1 into A_1, shaking well to mix, while simultaneously starting the stop-clock. Record the time taken for a dark-blue colouration of certain intensity to develop. To determine this, stand the reaction vessel on a piece of

white paper marked with a cross, and observe the cross through the reaction mixture in the flask until the cross just becomes invisible.
Repeat the experiment using the other corresponding pairs of solutions. i.e. A_2 with B_2, A_3 with B_3, and so on.

Fig. 13.6 Effect of concentration on the rate of reaction.


(a) Apparatus

(b) Observation (top view)

Result The dark-blue colouration develops fastest in the A_1–B_1 reaction mixture, which has the highest concentration of potassium iodide. The time taken for the colour development becomes progressively longer as the concentration of potassium iodide decreases. The colour development is slowest in the A_5–B_5 reaction mixture, which has the lowest concentration of reactants.

Conclusion The rate of reaction is dependent on the concentration of the reactants; the more concentrated are the reactants, the faster is the rate of the reaction.

pressure of hydrogen or chlorine is increased from 0.5 to 1.0 atm. The concentration of solid and liquid reactants is unaffected by changes in pressure.

The following reactions are used to study the effect of concentration of reactants on the rate of reaction.

1 The reaction between hydrochloric acid and magnesium.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Hydrogen gas is given off. The reaction rate is obtained by measuring the duration of effervescence. The concentration of the acid is varied, while the mass of the metal is kept constant.

2 The reaction between a dilute acid and a trioxocarbonate(IV). (See experiment 13.2.)

3 The reaction between acidified potassium iodide and hydrogen peroxide (See experiment 13.3)

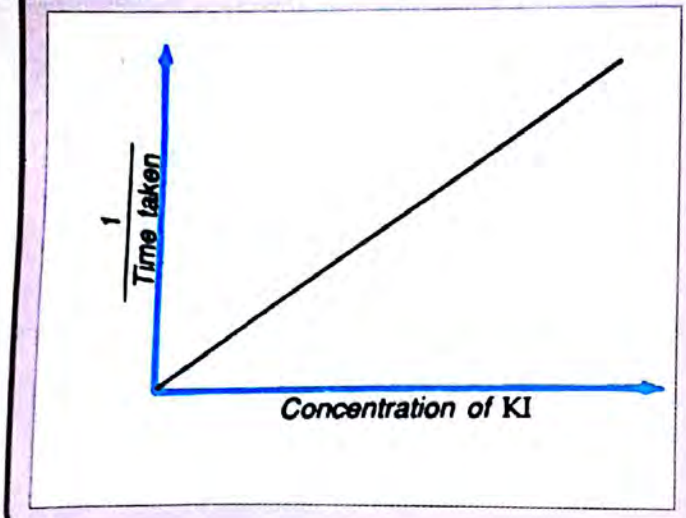
Iodine is liberated in this reaction. Starch is added to react with the iodine to form a dark-blue coloured complex. We measure the reaction rate by the time taken for a blue colour of a given intensity to develop.

$$2I^-(aq) + 2H^+(aq) + H_2O_2 \rightarrow 2H_2O(l) + I_2(g)$$

In the experiments on how the concentration of a reactant affects the reaction rate, we note that the time taken for the reaction to complete is inversely proportional to the rate of reaction. For example in experiment 13.3,

$$\text{Rate of reaction} \propto \frac{1}{\text{Time taken for cross to disappear}}$$

Fig. 13.7 Reaction rate increases with increasing concentration of a reactant.



If a graph is plotted as follows:

Vertical axis	$\dfrac{1}{\text{Time taken for cross to disappear}}$
Horizontal axis	Concentration of potassium iodide

we get a straight line passing through the origin (fig. 13.7). This shows that for this reaction, the rate is directly proportional to the concentration of potassium iodide, i.e. the reactant. For most reactions, the rate of reaction increases as the concentration of a reactant increases though the relationship may not be linear.

NOTE In general, reaction rate decreases with time. This is because as reaction goes on the reactants are being used up, so their concentrations keep on decreasing.

Effect of Surface Area of Contact

When a dilute acid is added to marble chips and to powdered marble, we notice a marked difference in the rate of reaction. The acid reacts more vigorously and faster with the powdered marble than with the marble chips. The powdered marble offers a greater area of contact with the acid than the marble chips so that more marble particles can react with the acid in a given time. This is a very important factor especially when one of the reactants is a solid, because only the particles on the surface of the solid are in contact and hence able to react with the other reacting particles.

To bring about greater contact between the reacting particles, the exposed surface area of the solid reactant must be increased by subdividing or breaking the solid into smaller pieces. The greater the surface area of the reactant, the higher is the rate of reaction. For example, zinc dust burns more quickly in oxygen or chlorine than zinc granules. Even lead burns in oxygen when it is in dust form.

In a reaction where the reactants are gases, liquids or solids dissolved in solution, the thoroughness of mixing is important to ensure maximum contact between the reactant particles. For example, liquids of different densities react slowly when they are immiscible, unless continually stirred. Similarly, in industrial processes, such as the Solvay process, elaborate devices are used to ensure thorough mixing of the gases with the liquids.

The efficiency of solid catalysts in increasing reaction rates depends on their surface areas. Catalysts in industrial processes are often prepared in a very finely divided form or are spread out on an inert support so that the largest possible surface area is exposed to the reacting particles. That is why we use

Experiment 13.4 To show that the rate of reaction of powdered marble with dilute hydrochloric acid is faster than that of marble chips with the acid.

Method Take two flasks and place 100 cm^3 of 2 M hydrochloric acid in each. At the same time, add 10 g of marble chips into one flask and 10 g of powdered marble into the other. Note the rate and duration of effervescence in the two flasks.

Result Effervescence is more vigorous and stops earlier in the case of the powdered marble than in that of the marble chips.

Conclusion Increasing the surface area of solid reactants increases the rate of reaction.

Fig. 13.8 Effect of surface area of reactant on reaction rate.

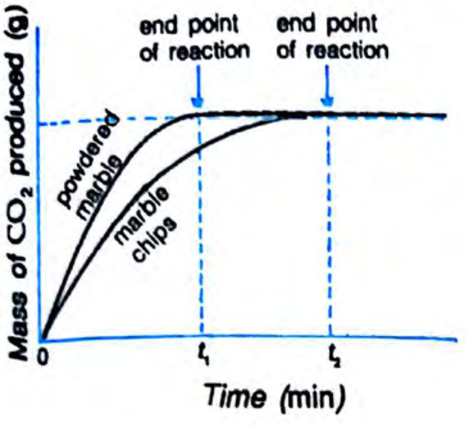
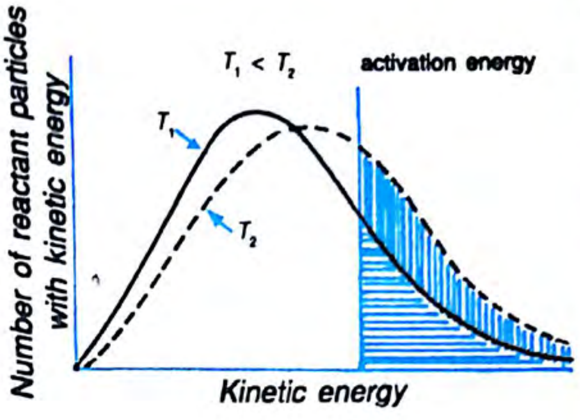


Fig. 13.9 Energy distribution among reactant particles at different temperatures.



platinum black (finely divided platinum powder appears black) and platinized asbestos (platinum deposited on asbestos support) but not a platinum block as the active catalyst.

If experiment 13.4 is done accurately, then rate curves can be drawn as in fig. 13.8. From these curves, we see that the average rate of reaction when

- powdered marble is used $= \frac{x}{t_1}$ g min^{-1}
- marble chips are used $= \frac{x}{t_2}$ g min^{-1}

The rate of reaction is faster, especially at the beginning, when powdered marble is used than when marble chips are used.

Effect of Temperature

We know that reactions are faster at high temperatures and slower at low temperatures for endothermic reactions. Many reversible reactions, if left at ordinary temperatures, would take years or even centuries to come to equilibrium. In general, the reaction rate doubles for each rise of 10 °C. The reverse effect of cooling a reaction in order to slow it down is true. For example, the refrigerator has low temperatures to slow down the chemical reactions that spoil food.

Increasing the temperature of a system can lead to an increase in reaction rate in two ways. When the temperature is raised, energy in the form of heat is supplied to the reactant particles, so that

Experiment 13.5 To show the effect of temperature on the rate of reaction between dilute hydrochloric acid and magnesium.

Method Maintain a water-bath at 40 °C. Pipette 10 cm^3 of 1 M hydrochloric acid into a test-tube and place it in the water-bath to attain the same temperature. Cut a 2-cm piece of magnesium ribbon, add it to the acid and note the rate of effervescence of hydrogen and the time taken for it to stop. Repeat the experiment at 45 °C, 50 °C and 55 °C.

Result Effervescence becomes more vigorous as the temperature increases while the duration of the effervescence becomes shorter.

Conclusion The rate of reaction is dependent on the temperature – the higher the temperature, the faster the rate of reaction.

- the number of particles with energies equal to or greater than the activation energy increases;
- the average speed of all the reactant particles increases due to the greater kinetic energy, leading to a higher frequency of collision.

As a result, the number of effective collisions increases and the reaction proceeds at a faster rate.

Fig. 13.9 shows the distributions of kinetic energy among the reactant particles of a given reaction at temperatures T_1 and T_2, (where $T_1 < T_2$). The shade area under each curve is proportional to the numbe of reactant particles having the activation energy, E or energy greater than E_a. We see that there are more reactant particles with sufficient energy to underg effective collisions at the higher temperature T_2, than at the lower temperature T_1.

Experiments 13.5 and 13.6 study the effect of temperature on the rate of reaction.

Experiment 13.6 To show that the rate of reaction between dilute hydrochloric acid and sodium trioxothiosulphate(VI) increases with increase in temperature.

Theory When dilute hydrochloric acid is added to a sodium trioxothiosulphate (VI) solution, a colloidal suspension of sulphur is formed.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l) + S(s)$$

The time taken for a given amount of sulphur to precipitate can be used to measure the rate of reaction.

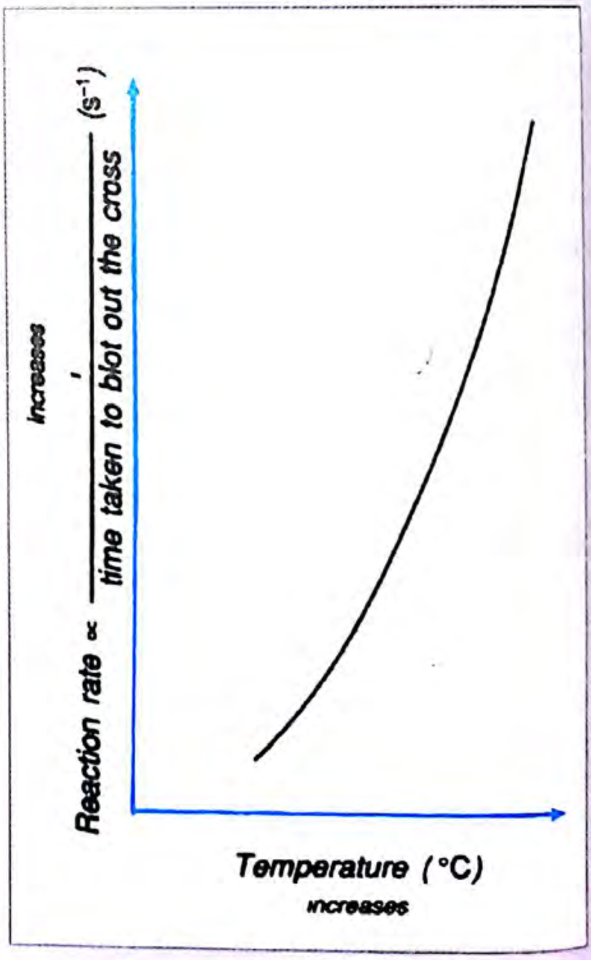
Method Dissolve 8 g of sodium trioxothiosulphate(VI) in 1 000 cm^3 of water. Pipette 50 cm^3 of this solution into a conical flask and heat it to 30 °C. Place the flask on top of a cross marked on a piece of white paper. Now add 10 cm^3 of 1 M hydrochloric acid to the flask and shake well to mix. Using a stop-clock, note the time taken for the cross to just disappear when viewed from above the solution.

NOTE The cross becomes invisible when a certain concentration of sulphur precipitate is present in the reaction mixture. Repeat the experiment at 35 °C, 40 °C, 45 °C, 50 °C and 55 °C. Plot a graph as shown.

Result As the temperature increases, the time taken for the cross to disappear becomes shorter, i.e. the rate of reaction becomes faster.

Conclusion The rate of reaction between the acid and sodium trioxothiosulphate (VI) solution increases with increase in temperature.

Fig. 13.10 Reaction rate increases with increasing temperature.



Effect of Light

Some reactions are influenced by light. The reaction etween hydrogen and chlorine, for example, is egligible in the absence of light, moderate in daylight nd explosive in bright sunlight. Such reactions are nown as photochemical reactions.

ther examples include

- the decomposition of hydrogen peroxide,
- the reaction between methane and chlorine
- photosynthesis in plants, and
- the conversion of silver halides to grey metallic silver (used in photography).

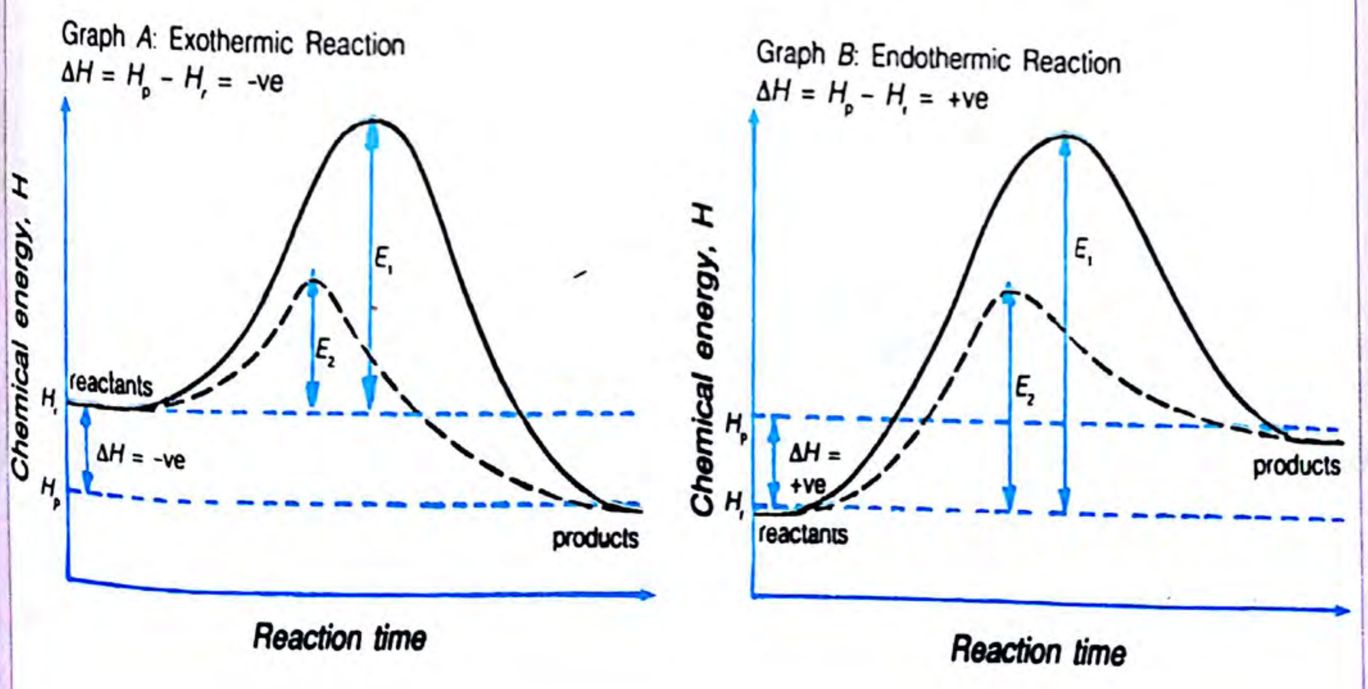
In these reactions, the reactant molecule become ctivated on absorbing light energy, and react rapidly gether in a series of chain reactions.

Effect of a Catalyst

A catalyst is a substance which alters the rate of a reaction but itself does not undergo any permanent change at the end of the reaction. In the preparation of oxygen by heating potassium trioxochlorate(V), in the presence of a small amount of the catalyst, manganese(IV) oxide, only moderate heat is needed to decompose potassium trioxochlorate(V). In the absence of the catalyst, potassium trioxachlorate(V) must be heated to a much higher temperature and for a longer time in order to obtain similar results.

A positive catalyst usually acts by lowering the energy barrier of a chemical reaction. Thus, in the presence of a catalyst, more reactant particles are able to react when they collide (see fig. 13.11).

Fig. 13.11 The lowering of the activation energy in catalyzed reaction.



Experiment 13.7 To examine the effect of the presence of manganese(IV) oxide on the decomposition of hydrogen peroxide to give water and oxygen.

Method Pour 50 cm^3 of water into a conical flask and then add 10 cm^3 of hydrogen peroxide solution. Place 2.0 g of granular manganese(IV) oxide in a small test-tube and lower it into the flask. Set up the apparatus as shown in fig. 13.12. Tilt the test-tube and empty the manganese(IV) oxide into the hydrogen peroxide solution. At the same time, start the stop-clock. Record the amount of oxygen evolved at one-minute intervals.

Repeat the experiment without the manganese(IV) oxide. Plot the rate curves on the same axes.

Result The decomposition of hydrogen peroxide is faster in the presence of the catalyst, manganese(IV) oxide, as depicted by the rate curves.

Conclusion Manganese(IV) oxide increases the rate of decomposition of hydrogen peroxide by acting as a positive catalyst.

Fig. 13.12 Effect of manganese(IV)oxide on the rate of decomposition of hydrogen peroxide.

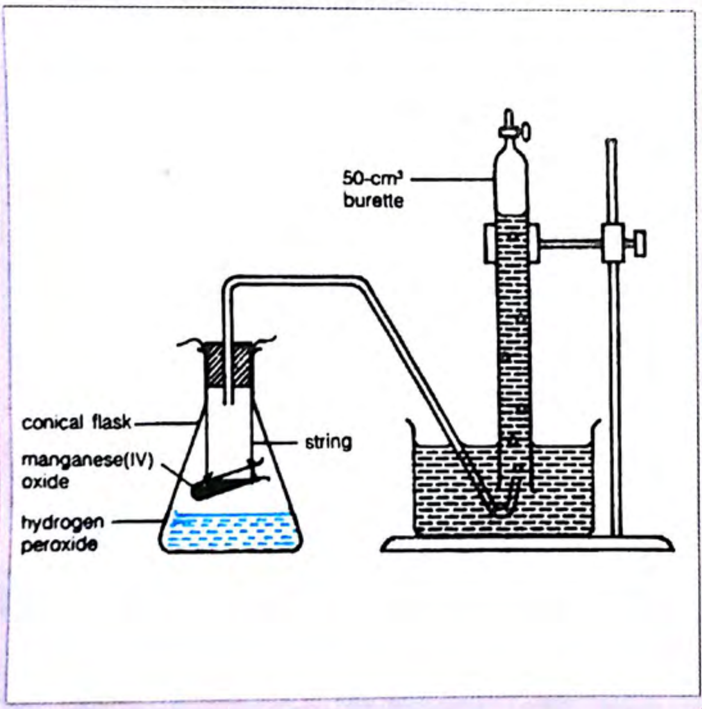
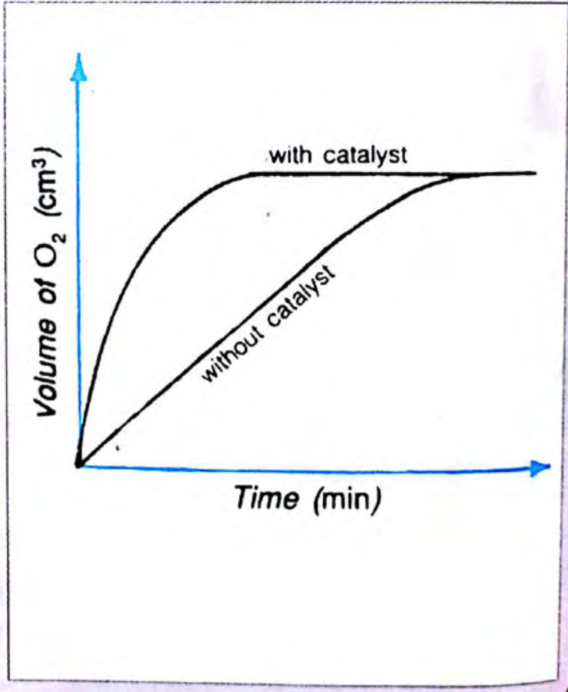
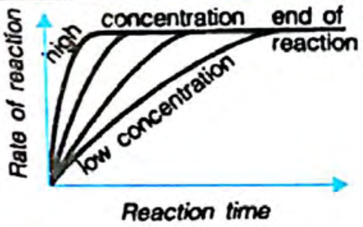
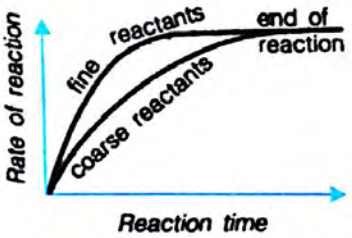
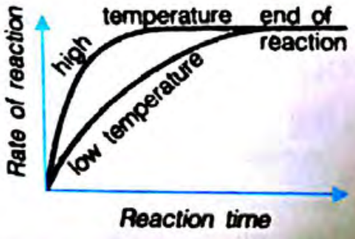
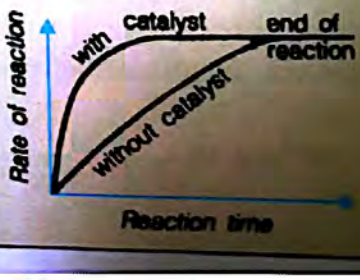


Fig. 13.13 Reaction rate increases in the presence of a catalyst.



SUMMARY

- The rate of a chemical reaction is the number of moles of reactant used up or product formed per unit time. Reaction rates are found by measuring the rate at which the mass or concentration of a (a) reactant is decreasing; (b) product is increasing.
- The rate of a reaction is not constant but increases or decreases as the reaction proceeds.
- The point at which the rate curve becomes horizontal indicates the end point of the reaction when one of the reactants is completely used up.
- The gradient of the tangent at any particular point on the rate curve represents the reaction rate at that given instant or time.
- The *Collision Theory* assumes that reactant particles must collide for a chemical reaction to occur. Effective collisions only occur between reactant particles which possess a certain minimum amount of energy called *activation energy*.
- Factors which change (a) energy content of the reactant particles, (b) activation energy of the reaction, (c) frequency of effective collisions will also change the rate of reaction.
- Factors which affect the rate of reaction are given below.

Factors affecting the rate of a reaction	Effect	Rate curve
(a) Concentration of reactants, i.e. molarities for solutions and pressures for gases.	Changes the frequency of collisions.	
(b) Surface area or contact for solids and immiscible liquids.	Changes the frequency of collisions.	
(c) Increase or decrease in temperature.	Changes the energy content of the reactant particles and the frequency of collisions.	
(d) Catalyst.	Changes the energy of activation.	

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EXERCISES

1. Rate of chemical reaction depends on the following factors except
   A rate at which gas is evolved.
   B rate at which products are formed.
   C rate at which the colour of reactions change.
   D rate at which the reactants diminish.

2. The unit of rate of chemical reaction is
   A Mol dm^{-3} S^{-1}
   B Mol^{-1} S^{-1}
   C Mol^{-1}
   D S Mol^{-1}

3. If 2 g of zinc granules was reacted with excess dilute HCl to evolve hydrogen gas which came to completion after 5 minutes. Calculate the rate of the chemical reaction in g hr^{-1}.
   A 48 g hr^{-1}
   B 12 g hr^{-1}
   C 24
   D 240 g hr^{-1}

4. For most irreversible reactions,
   A the reaction rate increases with time.
   B the reaction rate decreases with time.
   C the rate stabilizes with time.
   D the rate produces a curve with time.

5. Minimum or critical amount of energy required before a chemical reaction could occur is called
   A reaction energy.
   B effective collision.
   C activation energy.
   D activated complex.

6. Reaction occurs when the colliding reactant particles
   A have energy less than the energy barrier.
   B have energy equal or greater than the energy barrier.
   C have energy less than effective collision.
   D have energy greater than that of the products.

7. These are factors affecting chemical reaction except
   A surface area.
   B catalyst.
   C nature of reactants.
   D activation energy.

8. What do we do to increase the surface area the reactants
   A breaking them into chips.
   B subjecting the reactants to high pressure
   C altering the direction of the reaction.
   D using reactants to of different densities.

9. In the reaction;

$$N_2(g) + H_2(g) \xrightleftharpoons[\text{iron}]{\text{Finely divided}} NH_3(g)$$

   Why was finely divided iron used as catalys
   A To increase the forward reaction.
   B To reduce the energy barrier.
   C To increase the surface area of reactants.
   D None of the above.

10. Temperature affects rate of reaction except
    A it increases the frequency of collision.
    B it burns the reactants with reckless heating
    C it increases the kinetic energies of the reactant.
    D the number of effective collisions of the reactants.

11. What factor is responsible for the following reactions:
    (i) decomposition of H_2O_2.
    (ii) reaction between methane and chlorine.
    (iii) conversion of silver halides to grey metallic silver.

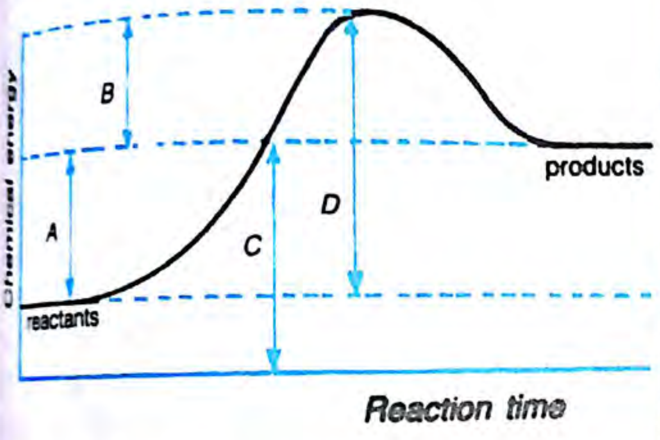
    A Decomposition
    B Light
    C Concentrators
    D Catalyst

12. Catalysts
    A increases the equilibrium constants of reactants.
    B brings about the energy barrier of reaction
    C lowers the activation energy of reaction.
    D summonts the energy barrier of reaction

13. Which of the following factors does not affect the rate of a chemical reaction between non-gaseous reactants?

A Concentration of reactants
B Pressure
C Temperature
D Presence of a catalyst
E Surface area of contact

14. The graph below gives the energy profile of a reacting system. Which of the energies represents the activation energy of the reaction?



A A C C E None
B B D D

15. Two identical samples of calcium trioxocarbonate(IV) are placed in two beakers. 100 cm^3 of 1.0 M hydrochloric acid are added to one, and 100 cm^3 of 0.5 M hydrochloric acid are added to the other. All other conditions are the same. Which of these is the same for the two cases?

A Average rate of evolution of gas.
B Mass lost from the beakers on completion of reaction.
C Time taken for the reaction to complete.
D Initial reaction rate.
E Molarity of chloride ions at any instant.

16. The volume of hydrogen produced from magnesium ribbon and excess dilute hydrochloric acid was measured at selected intervals until two successive readings agree. The readings recorded by one student were as follows:

Time(s)	5	10	15	20	25	30	40	60	100	150
Volume of H_2 collected (cm^3)	30	50	65	75	83	89	94	100	101	101

(a) Sketch the experimental set-up.
(b) Plot the volume of hydrogen gas collected against the time taken.
(c) State the time taken for the reaction to reach completion.
(d) Explain the gradual decrease of the reaction rate with time.
(e) Why did the student stop taking readings at 5-second intervals after 30 seconds?
(f) Explain the importance of taking readings until two successive readings agree.
(g) On the same axes, sketch and explain the curve that would be obtained at
  (i) a higher temperature,
  (ii) a lower acid concentration.

17. Equal lengths of magnesium ribbon were put in separate test-tubes containing equal amounts of different acids of the same concentration. The test-tubes were put in a water bath, and the duration of effervescence was noted in each case. The results were as shown:

Acid	A	B	C
Time(s)	30	70	100

(a) Why were the tubes put in a water-bath?
(b) Explain why the duration of effervescence in the three cases differ even though all the acids have the same concentration.
(c) What can you conclude about the strength of the three acids?
(d) What further test could you carry out to justify the conclusion you have drawn?

18. Two gaseous reactants A and B were placed in a reaction vessel in a dim room. The reactions were known to be photocatalytic. They react as shown

$$A(g) + B(g) \rightarrow C(s) + D(g) \quad \Delta H = -210 \text{ kJ mol}^{-1}$$

Describe the effect on the rate of reaction when the conditions are changed as follows:

(a) The pressure is halved.
(b) The temperature is increased.
(c) The reaction is conducted in a bright room.
(d) The concentration of A is doubled.

14

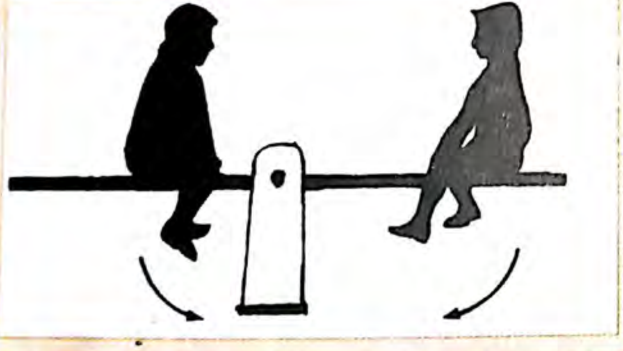
CHEMICAL EQUILIBRIUM

EQUILIBRIUM SYSTEMS

When two boys balance each other on a see-saw we say that the balanced see-saw is a system that is in equilibrium. The weight of one boy tends to move the see-saw in a clockwise direction, while that of the other tends to move it in an anticlockwise direction. Since these two opposing processes are equal, there is no change in the position of the see-saw.

In a broad sense, we can define *equilibrium as a state of a system where there is no observable change in the 'properties' of the system with respect to time.*

Fig. 14.1 A balanced see-saw is in a state of equilibrium.



Another example of a system in equilibrium is a saturated solution. To make a saturated sodium chloride solution, we dissolve the salt in water until some salt is left undissolved in the solution. In this system, at any given moment, undissolved sodium chloride particles are dissolving while the same number of dissolved sodium chloride particles are left undissolved. Here two opposing processes, dissolution and deposition, are taking place at the same rate. As a result, the net number of dissolved particles in the solution remains the same, i.e. there is no observable change in the 'properties' of the system.

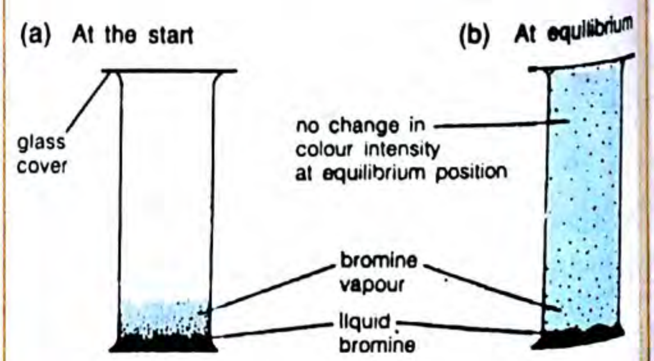
$$NaCl(s) \underset{\text{deposition}}{\overset{\text{dissolution}}{\rightleftharpoons}} NaCl(aq)$$

The balanced see-saw is an example of static equilibrium, since the see-saw is at rest or stationary. The saturated solution is an example of dynamic equilibrium since the salt particles are dissolving and depositing at the same rate, i.e. there is constant motion in the system.

A volatile liquid in an air-tight container is also an example of a system that can exist in a state of dynamic equilibrium (see fig. 14.2).

In general, dynamic equilibrium can occur during a physical change or a chemical change that is reversible. Dynamic equilibrium involving a physical change is referred to as *physical equilibrium* while that involving a chemical change is known as *chemical equilibrium*. In a physical equilibrium, there is no change in the composition of the substances involved. In a chemical equilibrium, the reactants undergo a change in composition to form the products, which in turn are reconverted to the original reactants at the same rate.

Fig. 14.2 In an air-tight jar, the liquid and vapour phases of bromine are in dynamic equilibrium.



$$Br_2(l) \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} Br_2(g)$$

EQUILIBRIUM IN REVERSIBLE REACTIONS

We shall now study dynamic equilibrium in reversible chemical reactions since it has many industrial applications.

Some reactions can be made to go either way, i.e. forward or backward. Such reactions are said to be reversible, and they are easily identified by the sign $\rightleftharpoons$ written between the reactants and products. When the reactants are written on the left and the products on the right, the *forward reaction* is represented by this arrow $\longrightarrow$ and the *reverse* or *backward reaction* is represented by $\longleftarrow$. All reversible reactions can proceed in either direction, depending on the conditions of the reactions. In some cases, both forward and backward reactions operate under the same conditions while in others they operate under different conditions.

A reversible reaction is one that proceeds in both directions under suitable conditions.

For a reaction which is reversible under the same conditions, both the forward and the reverse reactions can occur at the same time if all the reactants and products are present in one container.

Let us consider the following reaction:

$$\underbrace{A + B}_{\text{reactants}} \underset{\text{backward}}{\overset{\text{forward}}{\rightleftharpoons}} \underbrace{C + D}_{\text{products}}$$

When A and B are mixed together, the products C and D will begin to form almost immediately and at a very fast rate. This is because the initial concentrations (or numbers of reactant particles) of A and B are high, which result in a proportionately high rate of collision of the particles (this leads to the formation of the products). Gradually, A and B become used up and the rate of formation of C and D slows down. Meanwhile, products C and D, which have been forming in ever increasing amounts, will also begin to react. This backward reaction, where C and D react to form A and B, starts slowly but becomes rapid progressively as more and more of C and D accumulate.

Eventually, the forward and the backward reactions will go on at the same rate, i.e. the number of A and B combining to form C and D will be balanced by the number of C and D breaking up to form A and B again. The concentrations of A, B, C and D remain constant, i.e. there is no observable change in the 'properties' of the system with respect to time. At this position, the reversible reaction, $A + B \rightleftharpoons C + D$, is in dynamic equilibrium.

NOTE In a chemical system, 'properties' include concentrations and factors such as density, colour and pressure (for gases) which depend on concentration.

A reversible reaction is in dynamic equilibrium when both the forward and backward reactions are occurring at the same rate, thereby producing no net change in the concentrations of the reactants or products.

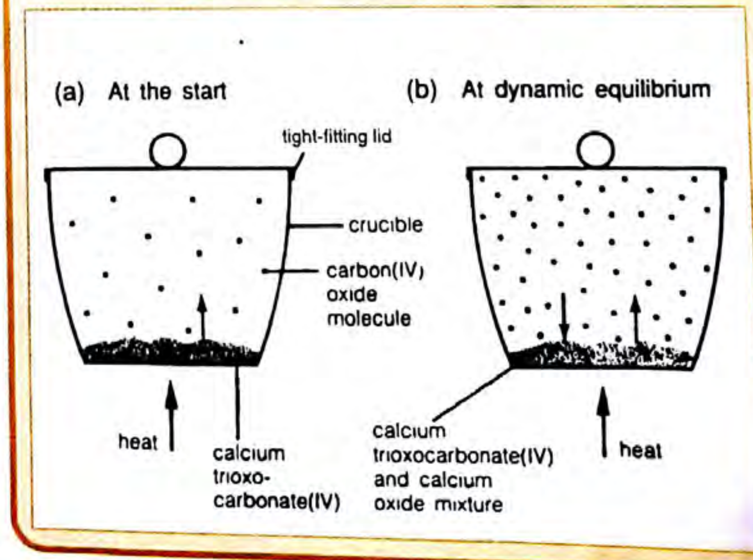
Closed system The reversible reaction just described can only reach dynamic equilibrium in a closed system. This means that the reaction must take place in a closed container or vessel, where during the process of the reaction, all reacting species (reactants and products) are present. In an *open system,* i.e. one in which one or more of the substances are being removed, the reaction cannot attain equilibrium even if it is a reversible one.

Let us look at the following reversible reaction.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

One of the reacting species is a gas. In an open system, the carbon(IV) oxide which is liberated escapes into the atmosphere. More calcium trioxocarbonate(IV) will decompose to replace the carbon(IV) oxide that has been lost. Hence, the reaction proceeds forward.

Fig. 14.3 Thermal decomposition of calcium trioxocarbonate(IV) in a closed system.



Eventually, all the trioxocarbonate(IV) will decompose. Thus, a reversible reaction in an open system behaves like an irreversible one and is represented as follows:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

If the reaction occurs in a closed system, e.g. heating calcium trioxocarbonate(IV) in a crucible with a tight-fitting lid at a constant temperature, the carbon(IV) oxide cannot escape. After a short while, some carbon(IV) oxide starts to react with calcium oxide to reform calcium trioxocarbonate(IV). Gradually, a stage is reached where the rate of the forward reaction just equals that of the reverse reaction. Calcium trioxocarbonate(IV) is in dynamic equilibrium with calcium oxide and carbon(IV) oxide. In a closed system, the calcium trioxocarbonate(IV) could never decompose completely as it does when it is heated in an open system.

Attaining equilibrium position from any starting point The dynamic equilibrium position can be attained irrespective of the starting point of the reaction. This means that if we heat some calcium oxide and carbon(IV) oxide in a closed vessel at a constant temperature, these reactants will combine form calcium trioxocarbonate(IV), i.e.

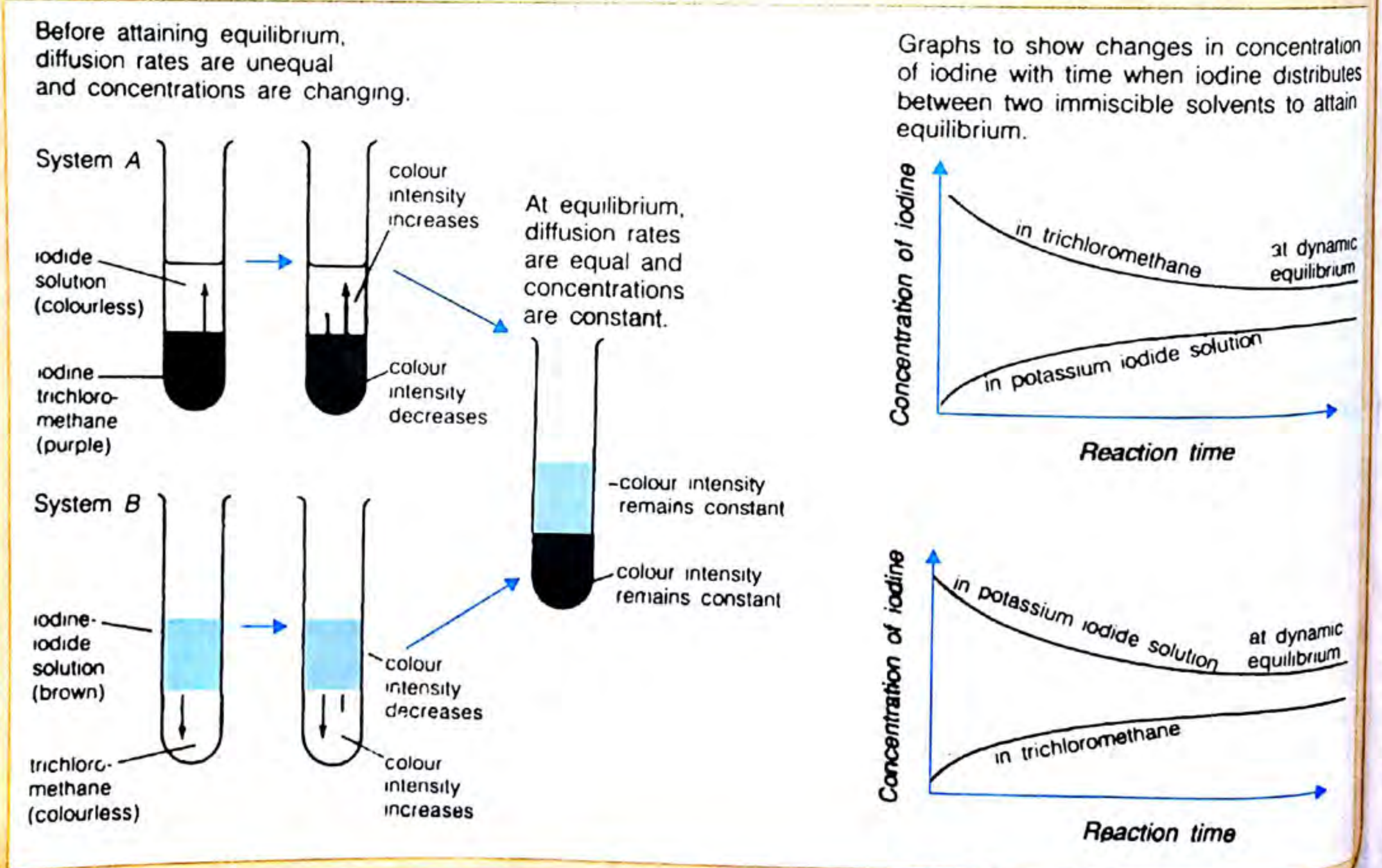
$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

and attain equilibrium eventually.

To illustrate this concept, we can use the iodine-iodide-trichloromethane system. Iodine (I_2) dissolves in aqueous potassium iodide (aq KI) to give a brown solution and in trichloromethane ($CHCl_3$) to give a purple solution. The solvents, water (in the case of aq KI) and trichloromethane, are immiscible. Using these solvents, we can set up Systems A and B and observe the colour changes that occur to study the attainment of the equilibrium position from different starting points.

System A	Dissolve a crystal of iodine in 10 cm³ of trichloromethane. To it, add 10 cm³ of 1 M potassium iodide.
System B	Dissolve a crystal of iodine in 10 cm³ of 1 M aqueous potassium iodide. To it, add 10 cm³ of trichloromethane.

Fig. 14.4 Distribution of iodine between aqueous potassium iodide and trichloromethane.



NOTE Trichloromethane, being denser than water, forms the lower layer in these systems.

System A At first the lower layer ($CHCl_3 + I_2$) is purple while the upper layer (aq KI) is colourless. Gradually the upper layer acquires a brownish colouration as iodine molecules diffuse into it from the lower layer. At the same time, the purple colour of the lower layer becomes much lighter. This is due to the loss of iodine molecules as they diffuse into the upper layer. Iodine molecules also diffuse from the upper layer to the lower layer. Thus, we have iodine molecules moving back and forth between the two solvent layers.

$$I_2\ (CHCl_3) \rightleftharpoons I_2\ (aq\ KI)$$

The forward diffusion rate of iodine molecules, i.e. $I_2(CHCl_3) \rightarrow I_2(aq\ KI)$, is fast at first but decreases progressively. This is indicated very clearly by the decreasing intensity of the purple colour in the lower layer. The reverse diffusion rate, i.e. $I_2(aq\ KI) \rightarrow I_2(CHCl_3)$, is slow at the beginning but increases gradually. This is reflected by the increasing intensity of the brown colour in the upper layer. Eventually, these two diffusion rates become equal. This is the position of equilibrium, and at this stage the colour intensities (which reflect the concentrations of iodine) of both the upper and lower layers remain constant.

System B Initially, the lower layer ($CHCl_3$) is colourless while the upper layer (aq KI + I_2) is brown. Gradually the lower layer acquires a purplish colouration as the iodine molecules diffuse into it from the upper layer. At the same time, the upper layer becomes lighter brown in colour. Again, the iodine molecules move back and forth between the two solvent layers. Equilibrium is eventually attained. The colour intensities of both layers at equilibrium position are similar to those obtained in System A.

Systems A and B show that the same equilibrium position can be reached irrespective of whether we dissolve the iodine in trichloromethane or aqueous potassium iodide.

Equilibrium Constant

The effect of concentration on the reaction rate was stated by Guldberg and Waage. This law, known as the *Law of Mass Action*, states that *at constant temperature, the rate of reaction is proportional to the active masses of each of the reactants.*

For our purposes, we shall interpret the active mass as the concentration of the substance raised to the appropriate power, which corresponds to the numerical coefficient of that substance in the equation of the reaction under study. The concentration is written in moles per dm^3 or mol dm^{-3}. If the substance is a gas, its partial pressure may be used instead of its concentration.

NOTE The active mass of the reactant is its molecular concentration multiplied by an activity coefficient. In most reactions, however, the active masses of the reactants may be taken as their molecular concentrations.

Let us consider a reaction in which n moles of substance A reacts with m moles of substance B. Let the rate of the reaction at a given temperature be r. Then

$$mA + nB \xrightarrow{r} \text{Products}$$

$$r \propto (\text{concentration of } A)^m$$

$$\text{and } \quad r \propto (\text{concentration of } B)^n$$

$$\therefore \quad r \propto \begin{pmatrix}\text{Concentration}\\ \text{of } A\end{pmatrix}^m \times \begin{pmatrix}\text{Concentration}\\ \text{of } B\end{pmatrix}^n$$

i.e. $r \propto [A]^m \,.\, [B]^n$,

where [X] represents the concentration in moles per dm^3 of the substance X.

$r = k \,.\, [A]^m\ [B]^n$,

where k is a constant, called the *velocity constant* of that reaction at that temperature.

Now, let us apply the Law of Mass Action to the reversible reaction represented by the following equation.

$$mA + nB \underset{r_2}{\overset{r_1}{\rightleftharpoons}} pC + qD$$

Rate of left-to-right reaction, $r_1 = k_1.\ [A]^m.\ [B]^n$

Rate of right-to-left reaction, $r_2 = k_2\ [C]^p.\ [D]^q$

where k_1 and k_2 are the velocity constants of the forward and backward reactions respectively. At equilibrium,

$$r_1 = r_2$$

$$k_1.[A]^m.\ [B]^n = k_2.\ [C]^p.\ [D]^q$$

$$\therefore \quad \frac{k_1}{k_2} = \frac{[C]^p.[D]^q}{[A]^m.[B]^n} = K$$

where K is the equilibrium constant of that reaction, at that temperature.

It is important to note that K is the ratio of the two velocity constants k_1 and k_2. Since the velocity constants usually vary with the temperature, it follows that K will vary with temperature. The addition of a catalyst, however, will not cause any change in the value of K. Varying the concentrations of any one of the substances (A, B, C or D) will also not affect the value of K. This is because the reaction will automatically adjust itself to attain equilibrium again to give the same value of K. For example, if the relative concentration of A is increased, the concentrations of C and D must increase too in order to maintain K at the same value. To do this, the position of equilibrium shifts to the right favouring the formation of C and D, thereby increasing their concentrations. This is how the reaction adjusts itself to attain equilibrium and maintain K constant in this case.

Le Chatelier's Principle

Every reversible reaction reaches its own specific equilibrium under a given set of conditions. This equilibrium state is dependent on

- temperature of the reacting system;
- pressure of the reacting system (for gases);
- concentration of the reacting system.

A change in any one of these factors will upset the balance of the system and result in a shift in the position of the equilibrium. These factors and their effects on chemical systems in equilibrium were studied by Le Chatelier (1850–1936) who formulated the Le Chatelier's Principle.

> *Le Chatelier's Principle states that if an external constraint such as a change in temperature, pressure or concentration, is imposed on a chemical system in equilibrium, the equilibrium will shift so as to annul or neutralize the constraint.*

This principle is of great importance in chemical industry because it can help to

- define the optimum conditions for the chemical processes employed in industry;
- reduce undesirable reversibility;
- predict the effect of an altered factor on the equilibrium position of an untried reaction.

Effect of a change in temperature

In the following thermochemical equations,

$$A + B \rightleftharpoons C \quad \Delta H = +\text{ve}$$
$$X + Y \rightleftharpoons Z \quad \Delta H = -\text{ve}$$

- if ΔH is positive, the forward reaction is endothermic, and the backward reaction is exothermic;
- if ΔH is negative, the forward reaction is exothermic, and the backward reaction is endothermic.

If a chemical system is in equilibrium and the temperature is lowered, then according to Le Chatelier's Principle, the equilibrium position will shift so as to annul the cooling effect by releasing more heat. Conversely, if the temperature is raised, then the equilibrium position will shift so as to annul the heating effect by absorbing more heat. In the following reversible reaction, the forward reaction is *endothermic.*

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad \Delta H = +90.4 \text{ kJ mol}^{-1}$$

- Increasing the temperature of the system will shift the equilibrium position to the right, favouring the forward reaction, i.e. product formation. Hence, the value of the equilibrium constant K also increases. So, for a given reversible reaction, a higher value of K would mean a greater yield of product(s).
- Lowering the temperature of the system will shift the equilibrium position to the left, favouring the backward reaction, i.e. reactant formation. This results in a lowering of the K value. So, for a given reversible reaction a lower value of K would mean a greater yield of reactant(s).

In the following reaction, the forward reaction is *exothermic*

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -395.7 \text{kJ mol}^{-1}$$

In this case, an increase in temperature will cause the equilibrium position to shift to the left, i.e. it th favours reactant formation. Conversely, a decrease in temperature will cause the equilibrium position to shift to the right, i.e. it favours product formation.

Generally, according to Le Chatelier's Principle, the forward reaction in an exothermic system is favoured by lowering the temperature, while the forward reaction of an endothermic system is favoured by raising the temperature.

ble 14.1 *Effect of changes in temperature on the equilibrium of some reversible reactions.*

Reversible reactions where forward reaction:	**When temperature of equilibrium system:**	
s endothermic	***increases***	***decreases***
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $Cl_5(l) \rightleftharpoons PCl_3(l) + Cl_2(g)$ $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	Equilibriu position shifts to right; K increases.	Equilibrium position shifts to left; K decreases.
s exothermic		
$H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	Equilibrium position shifts to left; K decreases.	Equilibrium position shifts to right; K increases.

We can illustrate the effect of temperature changes n equilibrium position with the nitrogen(IV) oxide N_2O_4) nitrogen(IV) oxide (NO_2) chemical system see experiment 14.1).

Dinitrogen(IV) oxide molecules are pale yellow, whereas nitrogen(IV) oxide molecules are reddish-brown in colour. At low temperatures, dinitrogen(IV) oxide predominates while at higher temperatures, it dissociates to give the monomer, NO_2. If a sealed glass vessel containing an equilibrium mixture of the two is warmed or cooled, the colour changes give a visual demonstration of the effect of temperature on the equilibrium position of the reaction.

$$\underset{\text{pale yellow}}{N_2O_4(g)} \underset{\text{cold}}{\overset{\text{heat}}{\rightleftharpoons}} \underset{\text{reddish-brown}}{2NO_2(g)}$$

Effect of a change in pressure

For a change in pressure to affect a chemical system in equilibrium,

- one of the reactants or products in the reversible reaction must be gaseous;
- the total number of moles of gaseous molecules on the left side of the equation must be different from the total number of moles of gaseous molecules on the right side.

An example of such a reaction is the formation of ammonia from nitrogen and hydrogen. Here, 4 moles (or volumes) of reactants give only 2 moles (or volumes) of products. The forward reaction results in a decrease in the number of moles and hence a decrease in the pressure of the system. The backward reaction results in an increase in the number of moles and hence an increase in the pressure of the system.

$$\underbrace{N_2(g) + 3H_2(g)}_{\text{4 moles or volumes}} \rightleftharpoons \underset{\text{2 moles or volumes}}{2NH_3(g)}$$

According to Le Chatelier's Principle, if a high pressure is applied to an equilibrium system, the reaction which involves a reduction in pressure will be favoured. Conversely, if low pressure is imposed on an equilibrium system, then the reaction which results in an increase in pressure will be favoured.

In the formation of ammonia, a high pressure will favour the forward reaction where a reduction in volume occurs, causing the equilibrium position to shift to the right. This is because the forward reaction will counteract the high pressure imposed on the system by lowering the pressure, thus keeping the equilibrium constant, K, unchanged. In the process, a high percentage yield of the product is obtained.

On the other hand, a low pressure will cause the equilibrium position of this system to shift to the left, favouring the backward reaction. This will cause an increase in the pressure of the system and, thus, keep the equilibrium constant unchanged. It will also result in high yields of the rectants.

In the following endothermic reaction, the forward reaction results in an increase in volume.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

In this case, a low pressure will favour the forward reaction and product formation, while a high pressure will favour the backward reaction.

In reversible reactions involving the same numb

Experiment 14.1 To see the effect of temperature changes on an equilibrium mixture of nitrogen(IV) oxide and dinitrogen(IV) oxide.

Method **(a)**Place some lead(II) trioxonitrate(V) crystals in a test-tube and heat strongly. When reddish-brown fumes start to evolve, connect a gas syringe with a rubber tubing to the test-tube as shown in fig 14.5. Slowly withdraw the plunger to collect about 50 cm^3 of the gas. Allow the gas in the syringe to cool down to room temperature. Note its colour.

(b) Set up beakers, one containing ice-water at 0 °C and another containing hot water at 100 °C. Immerse the syringe containing the gas collected in **(a)** into the ice-water for a few minutes. Note the rapid change in colour. Next, plunge the syringe into the hot water and observe what happens.

Fig. 14.5 Preparation of nitrogen(IV) oxide.

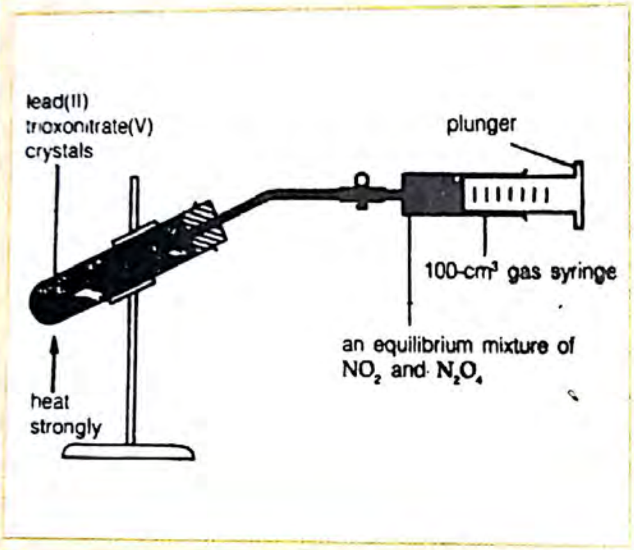
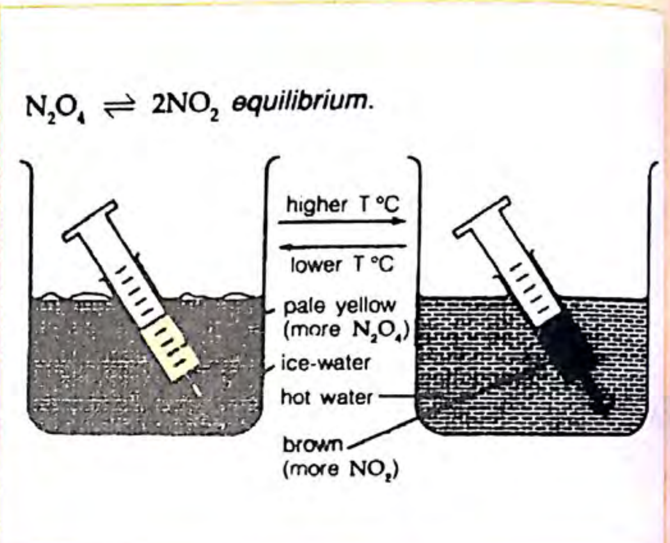


Fig. 14.6 Effect of temperature change on the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium



Result At room temperature, the gaseous mixture is light brown in colour as both nitrogen(IV) oxide and dinitrogen(IV) oxide molecules present in appreciable amounts. At 0 °C, the mixture is pale yellow as dinitrogen(IV) oxide predominates. At 100 °C, the mixture turns dark brown as most of the dinitrogen(IV) oxide molecules dissociate to nitrogen(IV) oxide molecules

Conclusion The equilibrium position of a reaction shifts when the temperature changes.

of moles of gaseous molecules on the right and left sides of the equation as shown in the reaction below, a change in pressure has no effect on the position of equilibrium. However, the rate at which equilibrium is attained is faster at higher pressures.

$$3Fe(s) + 4H_2O(g) \xrightleftharpoons{\text{red heat}} Fe_3O_4(s) + 4H_2(g)$$

Effect of a change in concentration

In an equilibrium mixture, there is a balance between the concentrations of the reactants and the products, i.e. these concentrations are in a definite ratio which depends on the conditions of the reaction. If more reactants are introduced into the equilibrium system, the balance will be upset. In order to relieve this constraint (i.e. the increase in the concentration of reactants), the equilibrium position will shift to the right, favouring the forward reaction. This results in a proportional increase in the concentration of the products, and so the equilibrium constant remains unchanged. Another way of increasing the amount of products formed is by continually removing the products from the system. Again, in order to relieve the constraint, the equilibrium will shift to the right, favouring the forward reaction.

In the reversible reaction of iron with steam,

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

the hydrogen is constantly being removed by a current of steam that passes over the heated iron, until all the iron is converted to iron(II) diiron(III) oxide. The reverse process occurs if water vapour is removed.

The preparation of many important chemicals from reversible systems depends upon the principle of removing one of the products from the reaction vessel. In the manufacture of calcium oxide by the heating of limestone in a limekiln, the carbon(IV) oxide produced is removed by an air current.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

We can illustrate the effect of concentration on the position of equilibrium by using the following chemical systems.

Iron (III) thiocyanate system When we add some iron(III) trioxonitrate(V) solution to an equal volume of potassium thiocyanate solution, a blood-red colouration of a certain intensity results when equilibrium is reached. The reaction is represented as follows:

Experiment 14.2 To observe the effect of pressure changes on an equilibrium mixture of nitrogen(IV) oxide and dinitrogen(IV) oxide.

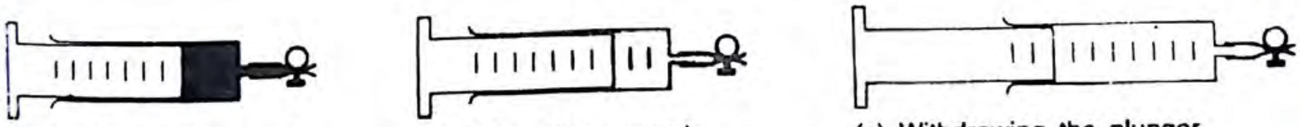
Theory An equilibrium mixture of nitrogen(IV) oxide and dinitrogen(IV) oxide can be represented as follows:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Here the forward reaction results in an increase in volume.

Method Collect about 80 cm³ of gas in a syringe as described in experiment 14.1. Note its colour at normal pressure. To increase the pressure of the system, push the plunger down quickly to compress the gas to 30 cm³. Note the colour immediately. After a few seconds, note its colour again. Then, withdraw the plunger to the 80 cm³ mark and observe the colour changes.

Fig. 14.7 The effect of high pressure on the $N_2O_4 \rightleftharpoons 2NO_2$.



(a) Immediately on plunging.

(b) After a few seconds.

(c) Withdrawing the plunger.

Result At normal pressure, the gaseous mixture is a light brown colour. When the pressure of the system is increased by compressing the mixture, at the very instant after pushing in the plunger, a darker brown colour results. This is due to a sudden concentration of the nitrogen(IV) oxide molecules as a result of decreased volume. After a few seconds, the colour becomes lighter as more nitrogen(IV) oxide molecules combine to give pale yellow nitrogen(IV) oxide. This shows that the equilibrium of the reaction, $N_2O_4 \rightleftharpoons 2NO_2$, is shifting to the left.

When the pressure of the system is released, instantaneously it becomes lighter, then slightly darker again. This shows that the equilibrium of the reaction, $N_2O_4 \rightleftharpoons 2NO_2$, is shifting to the right, and more of the pale yellow dinitrogen(IV) oxide molecules are breaking down to form the dark brown nitrogen(IV) oxide molecules.

Conclusion Pressure changes affect the equilibrium position of the gaseous reaction, $N_2O_4 \rightleftharpoons 2NO_2$.

Table 14.2 The effect of a change in pressure on the

Reversible reaction	Shift in equilibrium position when pressure:		Effect on equilib constant
	increases	*decreases*	
Forward reaction: decrease in volume			
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$	right	left	K constant
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	right	left	K constant
$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$	right	left	K constant
Forward reaction: increase in volume			
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	left	right	K constant
No volume change			
$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$	—	—	K constant
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	—	—	K constant

$$\underset{\text{yellow}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^-(aq)} \rightleftharpoons \underset{\text{blood-red colouration}}{[Fe(SCN)]^{2+}(aq)}$$

The intensity of the red colour in the reaction mixture remains the same as long as the equilibrium is not disturbed. If the concentration of a reactant or product is changed, the equilibrium position shifts to annul the change. This is seen by a change in the colour intensity of the reaction mixture.

Potassium heptaoxochromate(VI) system

Potassium heptaoxochromate(VI) is an orange coloured solid which when dissolved in water, dissociates into hydrogen ions and yellow tetraoxochromate(VI) ions as shown.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + H_2O(l) \rightarrow \underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq)$$

At neutral pH, there are more tetraoxochromate(VI) ions than heptaoxochromate(VI) ions. The yellow colour of the tetraoxochromate(VI) ions masks the orange colour of the heptaoxochromate(VI) ions. Thus, a neutral solution of potassium heptaoxochromate(VI) looks yellow.

When the hydrogen ion concentration is increased (by adding an acid), the equilibrium position shifts to the left. This is reflected by the colour of the solution changing from yellow to orange. When the hydrogen ion concentration is decreased (by adding an alkali), the equilibrium position shifts to the right as indicated by an increase in the intensity of the yellow colour.

Effect of a catalyst

We have learnt that a catalyst does not change the position of equilibrium. Thus, it cannot be used to increase product formation. However, catalysts are extremely important in chemical industry because they affect the time taken for a reaction to reach equilibrium. A positive catalyst increases the rates of both the forward and backward reactions to the same extent by lowering the activation energy of the reaction. As a result, equilibrium is reached in a shorter time than in an uncatalyzed reaction.

Table 14.3 The effect of a change in concentration on the position of equilibrium.

Reversible reactions	When reactants are added and/or products are removed	When reactants are removed and/or products are added	Effect on equilibrium constant
$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$ $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	Equilibrium position shifts to right	Equilibrium position shifts to left	K remains constant

nt 14.3 **To investigate the effect of concentration of the position of equilibrium using iron(III) thiocyanate solution.**

Method Weigh out 13 g of iron(III) trioxonitrate(V) and 8 g of potassium thiocyanate. Dissolve each in 50 cm^3 of water. Add equal volumes of these two solutions to obtain the blood-red iron(III) thiocyanate solution. Take 4 test-tubes, label them A, B, C and D. Add 5 cm^3 of the iron(III) thiocyanate solution to each. To test-tube A add a few crystals of potassium thiocyanate; test-tube B, a few crystals of iron(III) trioxonitrate(V); and test-tube C, a few drops of silver trioxonitrate(V) solution. Let test-tube D serve as a control for colour comparison. Note the colour changes on shaking the solution in each test-tube.

Result

Test-tube	Intensity of red colour	Concentration of iron(III) thiocyanate ions
A	Increases	Increases
B	Increases	Increases
C	Decreases	Decreases

In test-tubes A and B, the concentration of one of the reactants (thiocyanate ions in A and iron(III) ions in B) is increased, thus disturbing the equilibrium of the system. To counteract the increased concentration of the reactants, the equilibrium position shifts to the right, resulting in greater formation of iron(III) thiocyanate ions, $[Fe(SCN)]^{2+}$. This accounts for the deepening red colour.

$$\underset{\text{yellow}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^{-}(aq)} \rightleftharpoons \underset{\text{blood-red colouration}}{[Fe(SCN)]^{2+}(aq)}$$

In the test-tube C, the silver trioxonitrate(V) solution reacts with the thiocyanate ions to form an insoluble precipitate of silver thiocyanate, AgSCN. This removes some of the thiocyanate ions from the reaction mixture. To counteract the decreased concentration of the reactants, the equilibrium position shifts to the left. This accounts for the decrease in the intensity of the red colour.

$$\underset{\text{yellow}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^{-}(aq)} \rightleftharpoons \underset{\text{blood-red colouration}}{[Fe(SCN)]^{2+}(aq)}$$

Conclusion The addition or removal of any one of the reactants by a change in concentration will cause the equilibrium position to shift to a new stable one.

A negative catalyst slows down the rate of reaction that a longer time is needed to reach equilibrium.

QUILIBRIUM CONSTANT, FREE NERGY AND ELECTRODE OTENTIALS

explained in Le Chatelier's Principle, if the ilibrium of a chemical system is disturbed by nges in conditions like temperature, pressure or centration, the system would adjust itself to attain ilibrium again. This is because at equilibrium, the energy change of a closed system at constant perature and pressure is at a minimum, i.e. the em is most stable at equilibrium. No net flow of or species occurs and no work can be done by the system. The following simple relationship exists between the change in free energy, ΔG, of a reaction and the equilibrium constant, K:

$$\Delta G^{\ominus} = -RT \ln K$$

where $\Delta G^{\ominus}$ is the standard free energy change of the system,

K is the equilibrium constant,
R is the gas constant, and
T is the temperature of the system in kelvin.

In an electrochemical cell, oxidation occurs at one electrode and reduction at the other. If such a reaction (as the one below) is at equilibrium,

$$Zn(s) + Pb^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Pb(s)$$

then the relationship between $E^\ominus$ and K is given by

$$E^\ominus = \frac{RT \ln K}{nF}$$

where $E^\ominus$ is the standard electrode potential of the reaction,

R is the gas constant,
T is the temperature in kelvin,
F is the Faraday's constant,
K is the equilibrium constant, and
n is the number of moles of electrons.

The value of K is important, especially in the electroplating industry. For example, if a coating of lead is to be deposited onto an object, a higher value of K would mean that the forward reaction is favoured, resulting in a thicker coating of lead.

$$Zn(s) + Pb^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Pb(s)$$

The relationship between electrode potential and free energy change of an electrochemical cell can be expressed by the following equation.

$$\Delta G^\ominus = -nFE^\ominus$$

where $\Delta G^\ominus$ is the standard free energy change,

n is the number of moles of electrons,
$E^\ominus$ is the standard electrode potential, and
F is the Faraday's constant.

A negative value of $\Delta G^\ominus$ in this equation means that work is obtained from the electro-chemical cell.

Equilibrium in Practice

In industrial processes involving reversible reactions, the concept of chemical equilibrium and Le Chatelier's Principle are applied to decide on the optimum conditions of operation. These conditions (temperature, pressure, concentration) are chosen by industrial chemists with the aim of

- minimizing cost of production by ensuring
  - (a) the capital cost of the plant is not too high;
  - (b) the starting materials are cheap;
- maximizing yield of products by
  - (a) shifting the equilibrium position in the desired direction;
  - (b) increasing the value of the equilibrium constant, K, for the process concerned;
- ensuring that the shortest possible time is taken to reach equilibrium.

Two important industrial processes, the Haber Process and the Contact Process, will be discussed to illustrate how Le Chatelier's Principle is used to determine their optimum operating conditions.

The Haber Process

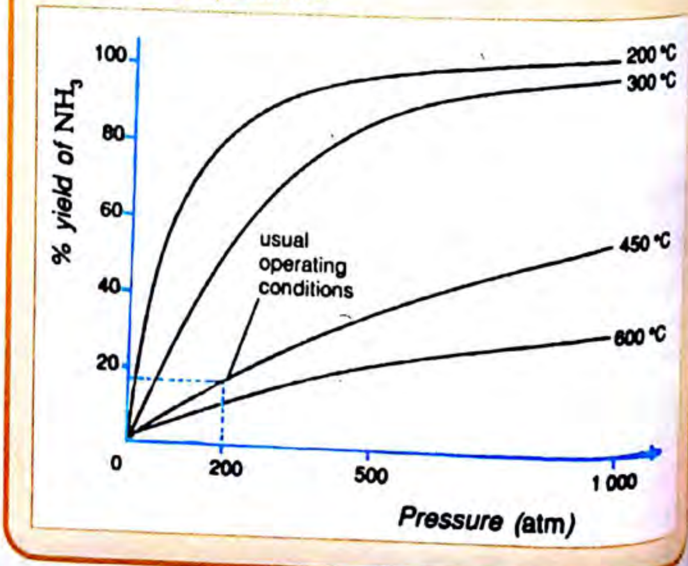
In the Haber Process, every 3 moles of hydrogen gas will react with 1 mole of nitrogen gas to yield 2 moles of ammonia. The forward reaction is exothermic, while the reverse reaction is endothermic.

$$\underset{\text{3 moles}}{3H_2(g)} + \underset{\text{1 mole}}{N_2(g)} \rightleftharpoons \underset{\text{2 moles}}{2NH_3(g)} \quad \Delta H = -46.1 \text{ kJ mol}^{-1}$$

Since the forward reaction is exothermic, decreasing the temperature will give a high yield of ammonia. Thus, the temperature of the system is kept as low as 450 °C. Lower temperatures of 200 °C and 300 °C give better yields of ammonia, but are not economically feasible as it will take too long for the reaction system to attain equilibrium. This is because the rate of reaction decreases as temperature decreases.

In the Haber Process, the forward reaction results in a decrease in the pressure of the system. According to Le Chatelier's Principle, if the pressure of the system is increased by supplying more of the gaseous reactants

Fig. 14.8 Percentage yield of ammonia in the Haber Process at various pressures and temperatures.



(in the correct ratio), the equilibrium position will shift to favour the forward reaction. The Haber Process is always operated at very high pressures of about 200 atm in order to get high yields of ammonia. A higher pressure, such as 1 000 atm, would give a higher yield. However, it would be extremely costly to build production plants that would be strong enough to withstand such a high pressure.

To further increase the yield of ammonia, the raw materials, i.e. hydrogen and nitrogen gases, are supplied continuously while the ammonia produced is removed continuously by liquefaction.

In addition, the production time of the process is shortened by using small pellets of iron to act as a catalyst. The catalyst speeds up the reaction rates, enabling equilibrium to be attained in a shorter time.

Table 14.4 *Haber Process: operating conditions.*

Temperature	450 °C
Pressure	200 atm
Catalyst	Small pellets of iron
Yield	15%

Table 14.4 sums up the usual operating conditions and yield of the Haber Process. In an effort to minimize cost and time, the operating conditions only give a yield of 15%. However, there is no wastage of material as the unreacted gases are recycled.

The Contact Process

In the Contact Process, sulphur(VI) oxide is manufactured from sulphur(IV) oxide and atmospheric oxygen.

$$\underset{\text{2 moles}}{2SO_2(g)} + \underset{\text{1 mole}}{O_2(g)} \rightleftharpoons \underset{\text{2 moles}}{2SO_3(g)} \quad \Delta H = -395.7 \text{ kJ mol}^{-1}$$

Since the reaction is exothermic, a low temperature will favour the forward reaction. In practice, however, a temperature of 450–500 °C and a catalyst are used. These conditions increase the reaction rates and enable equilibrium to be reached in a shorter time, thus making the process economically feasible.

The production of sulphur(VI) oxide is accompanied by a reduction in pressure. According to Le Chatelier's Principle, imposing high pressure on the system will favour the forward reaction. In practice, atmospheric pressure is sufficient to give a high yield of 98%.

In addition, an excess of air, i.e. an increase in the concentration of one of the reactants, is used to shift the position of equilibrium to the right and favour product formation.

Table 14.5 *Contact Process: operating conditions.*

Temperature	450–500 °C
Pressure	1 atm
Catalyst	Vanadium(V) oxide
Yield	98%

ACID-BASE EQUILIBRIUM

We know that an acid dissociates to form hydrogen ions or protons, and a base reacts with an acid to form a salt and water only. We shall now study the chemical equilibrium that exists between acids and their associated bases.

Theories on Acids and Bases

Arrhenius' Theory The earliest theory of acid-base action that is still useful was put forward by the Swedish chemist, Arrhenius, in the nineteenth century. He defined *an acid as a substance which dissociates in water to produce hydrogen ions, H^+*;

$$HCl \rightarrow H^+ + Cl^-$$

and *a base as a substance which gives hydroxide ions, OH^-, in water.*

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

However, chemists realized that the hydrogen ion which is simply a proton (with a diameter of 3×10^{-15} m) could not exist independently in aqueous solution. Studies showed that each proton associates with a water molecule to form the hydroxonium (or oxonium) ion, H_3O^+. The dissociation of an acid in water is now represented more accurately as follows:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

NOTE Although hydrogen ions exist in aqueous solution as hydroxonium ions, we shall, for convenience, use H^+ or $H^+(aq)$ in equations — using $H_3O^+(aq)$ only when it is more appropriate.

With these refinements, the Arrhenius' Theory recognized the role of the 'solvent' water molecules in the dissociation of acids. It was able to explain why substances such as hydrogen chloride and ethanoic acid exhibit acidic properties only in the presence of water. Pure dry ethanoic acid and pure dry hydrogen chloride dissolved in dry methylbenzene do not affect litmus paper or react with metals to liberate hydrogen.

Brønsted-Lowry Theory Arrhenius' Theory can only be applied to reactions which occur in aqueous solution. By now chemists knew that acidity is not an inherent property of a substance but rather a mode of behaviour of a substance under certain conditions. The first theory that had this view was put forward by Brønsted and Lowry. According to their theory, *an acid is a substance which donates a proton, while a base is a molecule or ion which accepts the proton.* These definitions of an acid and a base could be extended to include acid-base reactions in non-aqueous solutions.

An example of a Brønsted-Lowry acid-base reaction is that between ethanoic acid and the hydroxide ion.

$$\underset{\text{acid}}{CH_3COOH(aq)} + \underset{\text{base}}{OH^-(aq)} \rightleftharpoons \underset{\text{base}}{CH_3COO^-(aq)} + \underset{\text{acid}}{H_2O(l)}$$

In the forward reaction, an ethanoic acid molecule donates a proton to a hydroxide ion which accepts it. The ethanoic acid behaves as an acid while the hydroxide ion behaves as a base. In the reverse reaction, the ethanoate ion accepts a proton from a water molecule, i.e. the ethanoate ion acts as a base (proton acceptor) while the water molecule acts as an acid (proton donor).

In the above reaction, the ethanoic acid and the ethanoate ion are a conjugate acid-base pair. Similarly, the water molecule and the hydroxide ion are also a conjugate acid-base pair. Thus, a conjugate acid-base pair is an acid-base combination in which one is related to the other by a gain or loss of a proton.

Other examples of Brønsted-Lowry acid-base reactions are as follows:

- When ammonia reacts with hydrogen chloride, ammonia acts as a base by accepting the proton from hydrogen chloride, which in turn acts as an acid by donating the proton. The equilibrium this reaction lies to the far right (indicated by longer arrow of the forward reaction) becau hydrogen chloride is a stronger acid than ammonium ion.

$$\underset{\text{acid}}{HCl(g)} + \underset{\text{base}}{NH_3(g)} \rightleftharpoons \underset{\text{acid}}{NH_4^+}\underset{\text{base}}{Cl^-}(s)$$

- In the dissociation of hydrogen chloride in wate the hydrogen chloride molecule donates a proto to the water molecule which accepts it. Thu hydrogen chloride is acting as an acid and wate as a base. The equilibrium of this reaction is al to the far right because hydrogen chloride is stronger acid than the hydroxonium ion.

$$\underset{\text{acid}}{HCl(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{base}}{Cl^-(aq)} + \underset{\text{acid}}{H_3O^+(aq)}$$

- When water dissociates, it serves as both the aci and the base. Thus, one water molecule donates a proton, which the other accepts to form hydroxonium ion.

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{base}}{H_3O^+(aq)} + \underset{\text{acid}}{OH^-(aq)}$$

Hydrogen Ion Concentration

Dissociation of water

Pure water is neutral and it ionizes very slightly to yield an equal number of hydrogen ions and hydroxide ions. This is confirmed by conductivity measurements which show that at 25 °C, the concentration of hydrogen ions, $[H^+]$, and the concentration of hydroxide ions $[OH^-]$, are both equal to 10^{-7} mol dm^{-3}, i.e.

$$[H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol dm}^{-3} \text{ (at 25 °C)}$$

The product of these two ionic concentrations is the *ionic product of water.* It is represented by

$$K_w = [H^+][OH^-] = (10^{-7} \times 10^{-7}) \text{ (mol dm}^{-3})^2$$
$$= 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ (at 25 °C)}$$

K_w is kept constant under all circumstances at 25 °C. Thus, in all neutral aqueous solutions, the

Table 14.6 *Hydrogen ion concentrations of solutions.*

Aqueous liquid	H^+ concentration ($mol\ dm^{-3}$)	OH^- concentration ($mol\ dm^{-3}$)
Neutral	10^{-7}	10^{-7}
Acidic	More than 10^{-7}	Less than 10^{-7}
Alkaline	Less than 10^{-7}	More than 10^{-7}

concentrations of both hydrogen and hydroxide ions would be 10^{-7} mol dm^{-3}. When acids, which yield hydrogen ions, are added, the hydrogen ion concentration in the aqueous solution would increase to above 10^{-7} mol dm^{-3}. At the same time, the hydroxide ion concentration would decrease correspondingly to below 10^{-7} mol dm^{-3} in order to maintain K_w at 10^{-14} $mol^2\ dm^{-6}$. If the solution is made alkaline, then $[OH^-]$ would increase to above 10^{-7} mol dm^{-3} while $[H^+]$ would decrease proportionally to below 10^{-7} mol dm^{-3}.

pH scale

In order to avoid

- the inconvenience of using negative indices, and
- to accommodate the wide range of $H^+(aq)$ and $OH^-(aq)$ concentrations which are commonly encountered in acid-base reactions,

Sorensen devised the logarithmic pH scale in 1909. He defined the pH of a solution as *the negative logarithm of the hydrogen ion concentration to the base 10.* For example, if the hydrogen ion concentration of a given aqueous medium is 10^{-5} mol dm^{-3}, the acidity of the solution could be written in terms of its pH as follows:

$$\begin{aligned} [H^+] &= 10^{-5} \\ \log\,[H^+] &= \log 10^{-5} = -5 \\ pH &= -\log\,[H^+] = -(-5) = 5 \end{aligned}$$

Thus, if $[H^+] = 10^{-x}$, then $pH = x$.

Since the concentration of the hydroxide ions is always inversely proportional to the hydrogen ion concentration, the pH value would indicate both the acidity and the alkalinity of a solution.

$$\begin{aligned} [H^+][OH^-] &= 10^{-14} \\ \therefore pH + pOH &= 14, \text{ where pOH is the hydroxide ion index.} \\ pOH &= 14 - pH \end{aligned}$$

A high pH value would indicate a low hydrogen ion concentration, i.e. a weak acidity, and a correspondingly high hydroxide ion concentration, i.e. a strong alkalinity. Since

$$[H^+] = [OH^-] = 10^{-7}$$

at neutrality, the neutral pH value is 7. A pH value which is less than 7 would indicate an acidic medium while a pH value which is more than 7 would indicate an alkaline medium. The full pH range is given in fig. 14.9.

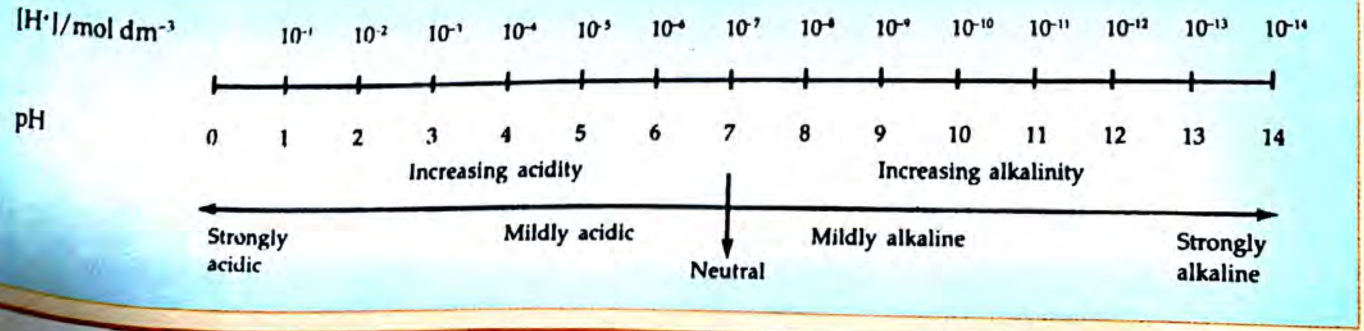
EXAMPLES

1 *Find the hydrogen and hydroxide ion concentrations in*

(a) 0.01 M tetraoxosulphate(VI) acid solution,
(b) 0.001 M potassium hydroxide solution.

(a) Tetraoxosulphate(VI) acid ionizes completely in solution. Being dibasic, every mole of the acid would ionize to give two moles of hydrogen ions.

Fig. 14.9 The pH scale.



$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

In a 0.01 M (i.e 0.01 mol dm^{-3}) solution,

$$[H^+] = 2 \times 0.01 = 2 \times 10^{-2} \text{ mol dm}^{-3}$$
$$\therefore (2 \times 10^{-2}) \times [OH^-] = 10^{-14}$$
$$[OH^-] = 0.5 \times 10^{-12} \text{ mol dm}^{-3}$$

(b) Potassium hydroxide also ionizes completely, with one mole of the alkali giving one mole of hydroxide ions

$$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$$

In a 0.001 M (i.e. 0.001 mol dm^{-3}) solution,

$$[OH^-] = 10^{-3} \text{ mol dm}^{-3}$$
$$\therefore [H^+] \times 10^{-3} = 10^{-14}$$
$$[H^+] = 10^{-11} \text{ mol dm}^{-3}$$

2 The concentration of H$^+$ in two solutions 1 × 10^{-14} mol dm^{-3}, and **(b)** 5 × 10^{-9} mol dm What is the pH of each solution?

$$\textbf{(a)}[H^+] = 10^{-14} \text{ mol dm}^{-3}$$
$$\therefore pH = -\log_{10}(10^{-14}) = -(-14) = 14$$

$$\textbf{(b)}[H^+] = 5 \times 10^{-9} \text{ mol dm}^{-3}$$
$$\therefore pH = -\log_{10}(5 \times 10^{-9})$$
$$= -\log_{10}(10^{0.70} \times 10^{-9})$$
$$= -\log_{10}(10^{-8.30})$$
$$= -(-8.30) = 8.30$$

The solutions have pH of 14 and 8.3 respective

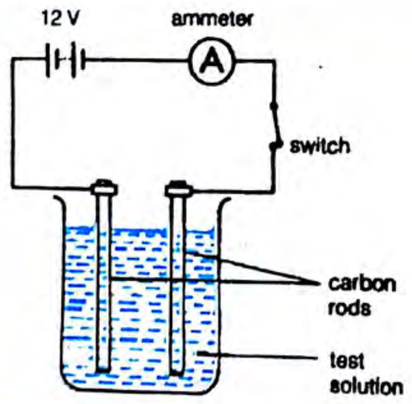
Experiment 14.4 To determine the relative strengths of some acids and bases.

Method (a)Place 25 cm^3 of 1 M hydrochloric acid in a clean test-tube. Put three drops of universal-indicator solution into the test-tube and note the colour of the solution. Work out the pH of the solution from the colour chart provided with the indicator.

Repeat the experiment with 25 cm^3 of 1 M solutions of ethanoic acid, potassium hydroxide and aqueous ammonia.

(b)Place 25 cm^3 of 1 M hydrochloric acid in a clean test-tube. Put a 5-cm strip of clean magnesium ribbon into the test tube and note the time taken for the magnesium to be used up. Repeat the experiment with 25 cm^3 of 1 M ethanoic acid. Note down the observations.
(c)Place 100 cm^3 of 1 M hydrochloric acid in a beaker. Set up the apparatus as shown in fig. 14.10. Switch on the circuit and note the ammeter reading. Repeat the experiment with the same volume of 1 M ethanoic acid, potassium hydroxide and aqueous ammonia. Record your readings in a table form.

Fig. 14.10 Testing the conductances of electrolytes.



Acid/Base	Ammeter reading (conductance)
Hydrochloric acid	
Ethanoic acid	
Potassium hydroxide	
Aqueous ammonia	

Result From these experiments, we see that different acids and bases have different strengths. Hydrochloric acid is a strong acid, while ethanoic acid is a weak one. Potassium hydroxide is a strong base, while aqueous ammonia is a weak one.

Note A stronger acid or base would show a higher current flowing in the circuit.

Conclusion The relative strength of an acid or a base can be determined by using the universal indicator as well as from their conductivities as an electrolyte.

3 A solution has a pH of 3. 4. What is its hydrogen ion concentration?

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

we have, $3.4 = -\log_{10}[H^+]$,

$\therefore \log_{10}[H^+] = -3.4 = -4.0 + 0.6 = \bar{4}.6$

$\therefore [H^+] = \text{antilog } \bar{4}.6$

$= 4 \times 10^{-4}$ mol dm^{-3}

Strengths of acids and bases

When an acid HA dissolves in water, the following equilibrium is established.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The position of equilibrium indicates the strength of an acid. In a strong acid, the reaction goes virtually to completion. For example,

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

In a weak acid, like ethanoic acid, most of the acid molecules are undissociated.

$$CH_3COOH(aq) + H_2O(l) \leftrightharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Hydrolysis of Salts

When salts, which are strong electrolytes, are dissolved in water, it might be expected that the resulting solution would be neutral, i.e. with a pH of 7. Some salts, however, dissolve in water to produce solutions having a pH different from 7. It was found that such salts were derived from weak acids, or weak bases, or both.

Salt of a weak acid and a strong base

Potassium ethanoate is a good example of a salt from a weak acid (ethanoic acid) and a strong base (potassium hydroxide). When this salt is dissolved in water, it will dissociate completely.

$$CH_3COOK(aq) \rightarrow CH_3COO^-(aq) + K^+(aq)$$

The solution also contains hydrogen and hydroxide ions from the dissociation of water.

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

Note: When the symbol for reversible reaction is represented by arrows of unequal lengths, the longer arrow indicates the favoured reaction, i.e. if the longer arrow is pointing from left to right, it means that the forward reaction is favoured.

Nothing happens to the potassium ion but the ethanoate ion, being a stronger base than water, reacts with the hydrogen ions from the water to form ethanoic acid, which being a weak acid is not completely ionized. Hydrogen ions are removed from the solution, causing more water molecules to dissociate (Le Chatelier's Principle). Hydroxide ions are not removed because potassium hydroxide is a strong base and is completely ionized. There is an excess of hydroxide ions causing the solution to be alkaline, i.e. the solution has a pH greater than 7.

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(l)$$

Salt of a strong acid and a weak base

A good example of a salt formed from a weak base and a strong acid is ammonium chloride. It completely dissociates in water to give ammonium and chloride ions. There are also hydrogen and hydroxide ions in the solution.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$
$$H_2O(l) \leftrightharpoons H^+(aq) + OH^-(aq)$$

Ammonium ions react with hydroxide ions to give aqueous ammonia. Since aqueous ammonia is a weak base, hydroxide ions are removed from the solution. This causes water to ionize further to produce more hydrogen and hydroxide ions. The hydroxide ions continue to be removed as long as there are ammonium ions. The hydrogen ions are not removed because hydrochloric acid is a strong acid and is completely ionized in solution. There is an excess of hydrogen ions, causing the solution to be acidic, i.e. the solution has a pH less than 7.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3.H_2O(aq)$$

Salt of a weak base and a weak acid

Ammonium ethanoate is a good example of a salt formed from a weak base (aqueous ammonia) and a weak acid (ethanoic acid). The salt is fully ionized in solution to give ammonium and ethanoate ions. The solution also contains hydrogen and hydroxide ions from the dissociation of water.

$$CH_3COONH_4(aq) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ammonium and ethanoate ions react with hydroxide and hydrogen ions respectively to give aqueous ammonia and ethanoic acid.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3.H_2O(aq)$$
$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(l)$$

Since both aqueous ammonia and ethanoic acid are weakly ionized molecules, the ionic equilibrium of water is upset. So more water molecules dissociate. This process continues until all the ammonium and ethanoate ions are converted into undissociated molecules. The solution remains almost neutral, even though the salt is strongly hydrolyzed in solution.

Salt of a strong acid and a strong base

A good example of a salt of a strong acid and a strong base is sodium chloride.

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Since the acid (hydrochloric acid) and the base (sodium hydroxide) are both strong, they ionized completely. There is no tendency for reaction betwe sodium and hydroxide ions, or between hydrogen a chloride ions. The sodium and chloride ions remaine unchanged. The only chemical reaction is betwee the hydrogen and hydroxide ions.

$$OH^- + H^+ \rightleftharpoons H_2O$$

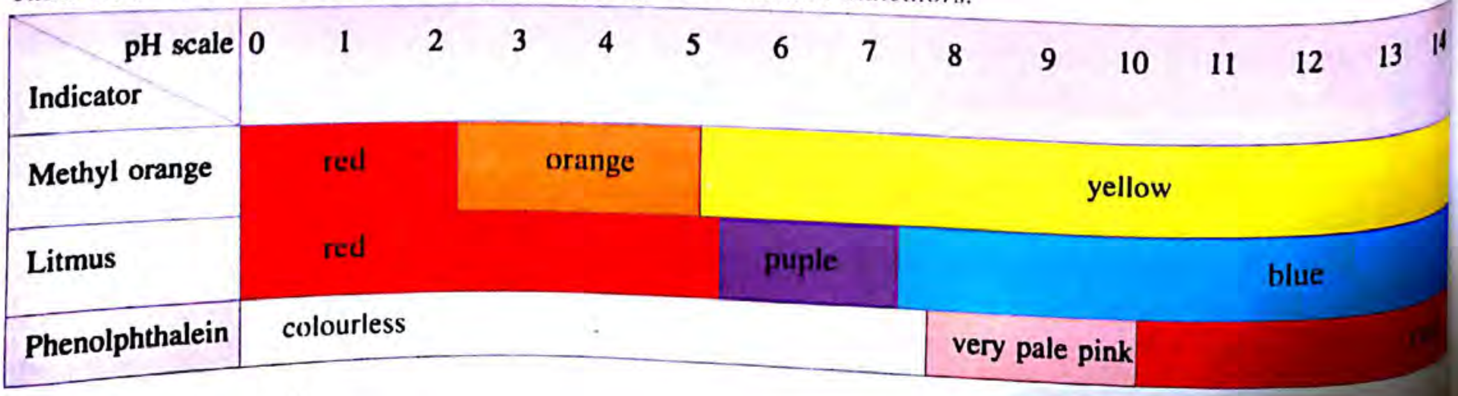
The ionic equilibrium of water is not disturbed a there is no hydrolysis. So the salt solution remain neutral.

Indicators

Indicators are weak organic acids or bases which wi produce different colours in solution according to the hydrogen ion, H^+, concentration in that solution.

Since indicators are usually weak organic acids or bases, they ionize slightly in solution. The colours of the ions produced are different from that of the undissociated molecules. Thus, the colour of the indicator is dependent on the relative proportion of the ions and the molecules. This is determined by the degree of dissociation of the indicator, which in turn is dependent on the hydrogen ion concentration or pH of the medium. Generally, the complete change from one colour to another occurs gradually over two pH units. An indicator will indicate neutrality when the numbers of undissociated molecules and free ions present in solution are the same, for then the two colours of the indicator will show to an equal extent. This half-way colour of an indicator, which indicates neutrality, occurs over a different pH range for different indicators.

Table 14.7 The colour changes and pH ranges of some common indicators.



pH scale / Indicator	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Methyl orange	red		orange			yellow									
Litmus	red					puple		blue							
Phenolphthalein	colourless								very pale pink		🟥				

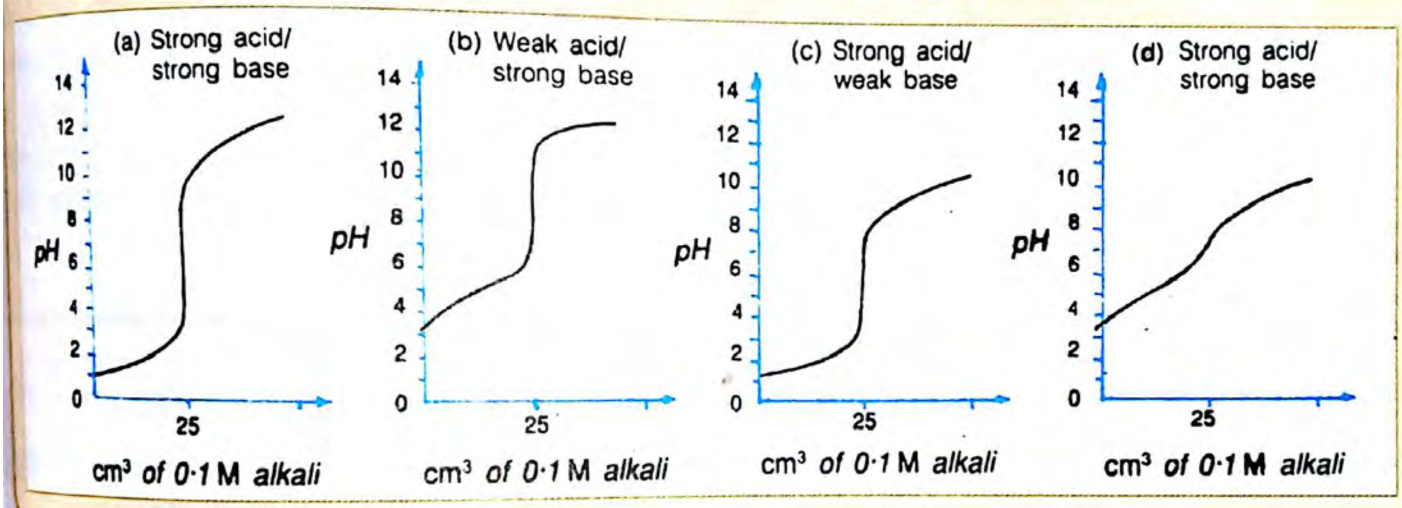
periment 14.5 To study the variation of pH of various acid-base titrations.

Method Pipette 25 cm^3 of 0.1 M hydrochloric acid into a conical flask. Add three drops of universal indicator solution. Note the colour of the solution and read off the pH from the colour chart. Place 0.1 M sodium hydroxide in a burette. Add the base into the flask, 1 cm^3 at a time. After each addition, shake the flask and note the colour of the solution, and then record the pH of the solution. Continue this process until you have added 40 cm^3 of the alkali. Plot the curve of the pH values against the volume of alkali used.

Repeat the experiment with the following acid-base pairs.

- Sodium hydroxide and ethanoic acid
- Aqueous ammonia and hydrochloric acid
- Aqueous ammonia and ethanoic acid

Fig. 14.11 The titration curves showing pH changes that occur when alkali is added to acid.



Result Fig. 14.11 shows the variation of pH when the alkali is added to the acid. These graphs indicate that the pH changes slowly at first, then rapidly at the equivalence point, and finally gradually once more.

Conclusion The results may be summarized in the following table.

Titration	Example	Rapid change of pH	Indicator
Strong acid Strong base	Hydrochloric acid Sodium hydroxide	3.5 to 9.5	Any indicator
Weak acid Strong base	Ethanoic acid Sodium hydroxide	7.0 to 9.5	Phenolphthalein
Strong acid Weak base	Hydrochloric acid Aqueous ammonia	3.5 to 7.0	Methyl orange
Weak acid Weak base	Ethanoic acid Aqueous ammonia	No sharp change	No suitable indicator

An indicator such as phenolphthalein will ionize to produce hydrogen ions together with negatively charged indicator ions. The undissociated phenolphthalein molecule is colourless but the phenolphthalein anion is red. If we represent the phenolphthalein molecule as HIn and the phenolphthalein anion as In, then the ionization process can be represented as follows:

$$\underset{\text{colourless}}{HIn} \rightleftharpoons H^+ + \underset{\text{red}}{In^-}$$

In an alkaline solution, the hydrogen ions formed from the ionization of phenolphthalein will become associated with the hydroxide ions (from the ionization of the alkali) to form stable water molecules. This removes the hydrogen ions from the system and leads to the ionization of more phenolphthalein molecules (Le Chatelier's Principle). As a result, the relative proportion of the red phenolphthalein ions is higher than that of the colourless molecules. Thus, the indicator appears red in an alkaline medium.

$$\underset{\substack{\text{from}\\\text{indicator}}}{H^+(aq)} + \underset{\substack{\text{from}\\\text{alkali}}}{OH^-(aq)} \rightleftharpoons H_2O(l)$$

$$\underset{\text{colourless}}{HIn} \rightleftharpoons H^+ + \underset{\text{red}}{In^-}$$

In an acidic solution, the presence of excess hydrogen ions (from the ionization of the acid) will favour the formation of undissociated phenolphthalein molecules (Le Chatelier's Principle). As a result, the relative proportion of the colourless undissociated molecules becomes higher and the indicator appears colourless in an acidic medium.

$$\underset{\text{red}}{In^-} + H^+ \rightleftharpoons \underset{\text{colourless}}{HIn}$$

In the case of methyl orange, which is a weak organic base, the undissociated form is red while the dissociated form is yellow in colour. This indicator also behaves like phenolphthalein in the presence of acids and alkalis.

Acid-Base Titrations

During a titration, there is a change in pH as the acid is added to the alkali. This change in pH may be stud using a pH meter or by using an indicator — the b indicator being the universal indicator. The change pH during the course of the titration depends on th strength of the acid and alkali used.

Buffer Solutions

The progress of many chemical reactions is dependen on the pH of the solution in which they take place. I is, therefore, necessary to control the pH of the aqueou reaction medium.

The pH of aqueous solutions is extremely sensitiv to the addition of small amounts of acids or alkali For example, when 0.1 cm^3 of 1.0 M hydrochlori acid is added to 1 dm^3 of distilled water or sodium chloride solution, the pH changes from 7.0 to 4.0 Such a change of pH would prove fatal to living organisms. Fortunately, animals and plants are protected against any sharp changes in pH, resulting from the addition of small amounts of acids or alkalis, by the presence of buffers.

A buffer solution is one which resists changes in pH on dilution or on addition of small amounts of acids or alkalis.

They usually consist of a weak acid or weak base in the presence of one of its salts. Examples of buffers are

- ethanoic acid and sodium ethanoate;
- aqueous ammonia and ammonium chloride;
- trioxocarbonate(IV) acid and sodium hydrogentrioxocarbonate(IV).

Buffer solutions are of great importance in medicine and biochemistry, where pH values are often critical and have to be maintained at a steady value. For example, blood has a pH of about 7.4 and a change of +0.5 would probably be fatal. Injections into the bloodstream must be buffered so as not to upset this delicate balance. Similarly, many fermentation processes and enzyme reactions depend on the pH, which can only vary within very narrow limits. Buffer solutions are widely used in processed foods and drinks to prevent excess acidity.

SUMMARY

- Dynamic equilibrium can be defined as an intermediate stage of a reversible reaction when both the forward and backward reactions are occurring at the same rate, thereby producing no net change in the concentrations of the reactants and products. Such dynamic equilibrium can only occur in a closed system.

- The equilibrium constant in a given stoichiometric equation such as $mA + nB \rightleftharpoons pC + qD$ is given by $K = \frac{[C]^p[D]^q}{[A]^m[B]^n}$ where [A], [B], [C], [D] are the concentrations of A, B, C and D respectively (in mol dm^{-3} or in atm for gases). The letters m, n, p and q represent the numbers of moles of the reactants and products respectively.

- The equilibrium constant is not affected by changes in concentration, pressure and catalyst but varies with temperature. A higher temperature will lead to an increase in the value of K and consequently the yield of the products of that particular reaction.

- The position of equilibrium will shift under the effects of changes in temperature, pressure and concentration. The use of a catalyst only increases the rate at which equilibrium can be attained.

- Le Chatelier's Principle states that if an external constraint, such as a change in temperature, pressure or concentration, is imposed on a chemical system in equilibrium, the equilibrium will shift so as to eliminate this constraint. This principle is used to determine the optimum operating conditions for chemical processes in industry. The effects of these conditions are summarized in the following table.

Factor	Changes in factor	Effects on the forward/backward rates	Predominant species	Shift in positions of equilibrium	Effect on equilibrium constant
Temperature		For exothermic reactions:			
	Increase	$A + B \underset{\longleftarrow}{\rightharpoonup} C + D$	$A + B$	Left	Decrease
	Decrease	$A + B \overset{\longrightarrow}{\leftharpoondown} C + D$	$C + D$	Right	Increase
		For endothermic reactions			
	Increase	$A + B \overset{\longrightarrow}{\leftharpoondown} C + D$	$C + D$	Right	Increase
	Decrease	$A + B \underset{\longleftarrow}{\rightharpoonup} C + D$	$A + B$	Left	Decrease
Pressure (for gases)	Increase	$nA(g) \underset{\longleftarrow}{\rightharpoonup} mB(g)$ $n < m$	A	Left	Constant
	Decrease	$nA(g) \overset{\longrightarrow}{\leftharpoondown} mB(g)$	B	Right	Constant
Concentration	Increasing A + B	$A + B \overset{\longrightarrow}{\leftharpoondown} C + D$	$C + D$	Right	Constant
	Decreasing A + B	$A + B \underset{\longleftarrow}{\rightharpoonup} C + D$	$A + B$	Left	Constant
Catalyst		$A + B \rightleftharpoons C + D$ Equilibrium is attained quickly but equilibrium position is unchanged.		No change	Constant

- At chemical equilibrium, the free energy change of a closed system at constant temperature and pressure is at a minimum.
- An acid-base reaction is a dynamic equilibrium between two conjugate acid-base pairs.

$$\underset{\text{acid 1}}{HCl(aq)} + \underset{\text{base 2}}{H_2O(l)} \rightleftharpoons \underset{\text{base 1}}{Cl^-(aq)} + \underset{\text{acid 2}}{H_3O^+(aq)}$$

- Ionic product of water, $K_w = [H^+][OH^-]$

$$= (10^{-7} \times 10^{-7})\ (\text{mol dm}^{-3})^2$$
$$= 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

- The pH of a solution is the value of the negative logarithm (to the base 10) of the hydrogen ion concentration.
- Salts may hydrolyze in water to produce solutions which are acidic, alkaline or neutral.

Salt of	Does it hydrolyze?	pH of solution
Weak acid + strong base	Yes	Alkaline
Strong acid + weak base	Yes	Acidic
Weak acid + weak base	Yes	Neutral
Strong acid + strong base	No	Neutral

- Indicators are weak organic acids and bases which will produce different colours in solution according to the hydrogen ion concentration in that solution.
- A buffer solution resists changes in pH on dilution or on addition of small amounts of acids or alkalis.

EXERCISES

1. Two boys balanced steady in a sea-saw game is an example of

A static equilibrium.
B dynamic equilibrium.
C homogenous equilibrium.
D mutual equilibrium.

2. In the reaction; $SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_5} SO_3(g)$
The use of double arrows shows

A the reaction is in physical equilibrium.
B contact process.
C the reaction involves both forward and backward reactions.
D the reaction is the rate determining step.

3. In the decomposition of
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
The reaction will attain dynamic equilibrium only

A when the reaction is in open system.
B when the reaction is heated strongly.
C when the reaction is in a closed sytem.
D when the reaction is catalysed.

4. The equilibrium constant, K, of this reaction is
${}_xZ + {}_bQ \rightleftharpoons {}_tM + {}_nR$

A $K = \dfrac{[Z]^x[Q]^b}{[M]^t[R]^n}$ B $K = \dfrac{[M]^t[R]^n}{[Z]^x[Q]^b}$

C $K' = \dfrac{[Q]^b[M]^t}{[Z]^x[R]^n}$ D $K = \dfrac{[t]^M[n]^D}{[x]^Z[Q]^b}$

5. Factors affecting equilibrium reactions include the following except
A pressure (for solid systems).
B concentration.
C temperature.
D pressure (for gaseous systems).

What happens if the temperature of this system is decreased?
$SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, $\Delta H = -xKJ\ mol^{-1}$

A The reaction favours backward reaction.
B The reaction attains equilibrium fast.
C The reaction favours forward reaction.
D The reaction favours both forward and backward reactions.

In most equilibrium reactions, catalyst is not required because
A catalyst reduces the energy barrier.
B most catalyst are easily poisoned when wrongly chosen.
C catalyst favours both forward and backward reactions.
D catalyst could be positive or negative.

All except one is not a condition for considering pressure in an equilibrium system.
A There must be concentration gradient between the reactants and the products.
B The reactants could be gases while the products may be solids.
C Both products and reactants must be gaseous.
D The reaction takes place in a closed system.

In the reaction, what effect has conc. H_2SO_4 on the equilibrium?

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{\text{conc. } H_2SO4} CH_3COOC_2H_5 + H_2O$$

A To acidify the system.
B To encourage backward reaction.
C To encourage forward reaction.
D To produce more CH_3OOH.

In the reaction; $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
The effect of pressure on this system is
A to encourage forward reaction.
B to encourage backward reaction.
C to remove the energy barrier.
D pressure may not have any effect.

11. Catalysts are important in chemical industry in that
A it affects the purity of the products.
B it affects the quantity of the products.
C it increases the time for reacting equilibrium.
D bond breaking is slowed down.

12. From $E^\theta = \frac{RT \ln K}{nF}$ where E^θ is standard electrode potential of a reaction, increasing the value of K will
A increase the forward reaction.
B increase the backward reaction.
C decrease the forward reaction.
D decrease the backward reaction.

13. Give the name of the scientist who defined acid as: acid is a proton donor while base is a proton acceptor.
A Lewis
B Le-chatelier
C Arrhenius
D Brønsted-Lowry

14. Calculate the pH of a 0.001 m acid solution.
A 5
B 3
C 4
D 2

15. Calculate the hydrogen ion concentration of a solution whose pH is 2.4
A 3.6×10^{-2}
B 2.5×10^{-4}
C 2.5×10^{-2}
D 7.0×10^{-2}

16. In which of the following cases will a decrease in pressure and an increase in temperature shift the equilibrium position to the right?
A $X_2(g) + Y_2(g) \rightleftharpoons 3Z_2(l)$ ΔH is positive
B $X_2(g) + Y_2(g) \rightleftharpoons 2Z_2(g)$ ΔH is negative
C $X_2(g) + Y_2(g) \rightleftharpoons 3Z_2(g)$ ΔH is positive
D $X_2(g) + Y_2(g) \rightleftharpoons 3Z_2(g)$ ΔH is negative
E $X_2(g) + Y_2(g) \rightleftharpoons Z_2(g)$ ΔH is negative

17. The following equilibrium is established in a closed vessel.

$$A(g) + B(g) \rightleftharpoons 3C(s) + D(g) \quad \Delta H \text{ is negative}$$

Which would increase the yield of C?
A Increasing the temperature.
B Adding a positive catalyst.
C Using a larger closed vessel.
D Decreasing the pressure on the reacting mixture.
E Removing some D.

18. A solution of potassium chloride is
A unionized. D neutral.
B acidic. E alkaline.
C neutral but strongly hydrolyzed.

19. Steam reacts reversibly with iron at red-heat in the following way.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Describe and explain what happens when the conditions of the reaction are varied as follows:

(a) Increasing the partial pressure of the steam.
(b) Adding more of the iron(II) diiron(IV) oxide, Fe_3O_4.
(c) Removing the hydrogen gas formed.

20. How do the equilibrium positions of the following reactions change with pressure? What is the equilibrium constant and its unit in each case?

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

21. Bromine, a red-coloured liquid, dissolves in water to give a pale brown solution. The pale brown colour, caused by free bromine in solution, disappears when sufficient amount of sodium hydroxide solution is added but reappears as a deeper brown colour on acidification.

$$Br_2(l) + H_2O(l) \rightleftharpoons HBr(aq) + HOBr(aq)$$

Explain the above phenomenon using Le Chatelier's Principle and the concept of equilibrium constant.

22. The melting process represents an equilibrium. At the melting point, the solid and its liquid co-exist. For the water-ice system, it was found that a higher pressure causes ice to melt at a lower temperature. A higher temperature causes ice to melt more rapidly. Do these agree with Le Chatelier s Principle? (Given that at 0°C, ice has a lower density than water and the melting process is endothermic.)

23. Given the following equilibrium mixture of ga at 500 °C where ΔH is negative, what will be th effect of

$$2CO(g) + O_2 \rightleftharpoons 2CO_2(g)$$

(a) adding more O_2 at constant pressure?
(b) increasing the temperature?
(c) cooling below 100 °C?
(d) adding a catalyst?
(e) doubling the pressure at 200 °C?
(f) adding a base to absorb CO_2?

24. The concentration of H^+ in two solutions are
(a) 1×10^{-3} mol dm^{-3}, and
(b) 6×10^{-9} mol dm^{-3}.
What is the pH of each solution?

25. Describe two experiments which can be performed to determine the relative strengths of acids and bases.

26. Classify these salts according to the strengths of the acids and bases they are formed from. Briefly discuss whether hydrolysis occurs in each case.
(a) Sodium ethanoate
(b) Ammonium ethanoate
(c) Potassium chloride
(d) Ammonium chloride

27. Define buffer solution and give two uses of buffer solutions.

28. The pH values of three solutions are 4.0, 9.0 and 13.5. Predict the colours that these indicator would attain for the different solutions. Fill i the following table.

pH	Colours of indicators		
	Methyl orange	Litmus	Phenolphthalei
4.0			
9.0			
13.5			

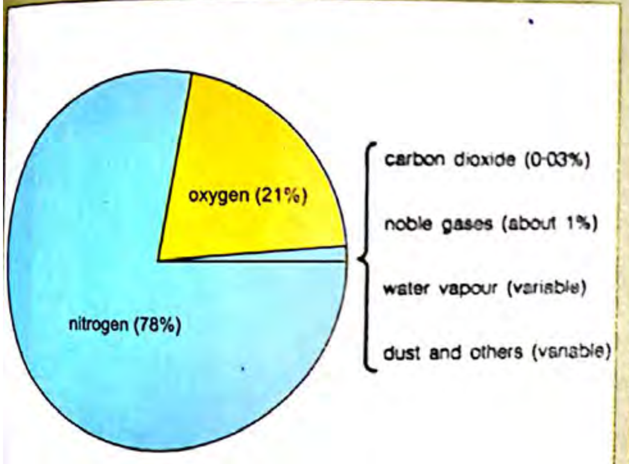
AIR • AIR POLLUTION

15

COMPOSITION OF AIR

The atmosphere surrounding the earth contains air. Air is a mixture of gases, composed mainly of nitrogen and oxygen with small amounts of carbon(IV) oxide, noble gases and water vapour.

Fig. 15.1 Percentage composition of air by volume.



idence that air is a mixture

The constituents of air can be separated easily by physical methods. For example, if highly compressed air is allowed to escape through a minute aperture, it expands suddenly and loses heat to the environment. If this process is continuously repeated, the air will liquefy. Pure nitrogen and oxygen can then be separated out at different temperatures by fractionally distilling the liquid air.

The constituents of air still retain their individual properties.

(a) The carbon(IV) oxide in air retains its affinity for caustic soda NaOH(aq) and lime water $Ca(OH)_2(aq)$. When a stream of air is passed through a solution of caustic soda, the carbon(IV) oxide in the air is absorbed by the caustic soda. Similarly, if air is passed through lime water, the carbon(IV) oxide is absorbed and the lime water turns chalky.

(b) The oxygen retains its oxidizing property. When a stream of air is passed over heated copper, the latter becomes oxidized by the oxygen in the air to form copper(II) oxide.

(c) The nitrogen and the rare gases retain their inertness.

3 If the appropriate proportions of each of the different constituents of air are mixed together under ordinary conditions, there will be no evidence of any chemical combination such as heat production or volume change. The mixture obtained, however, will resemble ordinary air in every way.

4 The composition of air cannot be represented by a chemical formula as in the case of a compound. The exact composition of air varies from place to place. For example, the composition of air in the countryside and that in an industrial town would differ slightly.

Atmospheric Oxygen

Although oxygen makes up only one-fifth by volume of air, it is the most active constituent. It is necessary for cellular respiration in all living organisms, and is needed for burning and rusting.

Combustion of substances in air

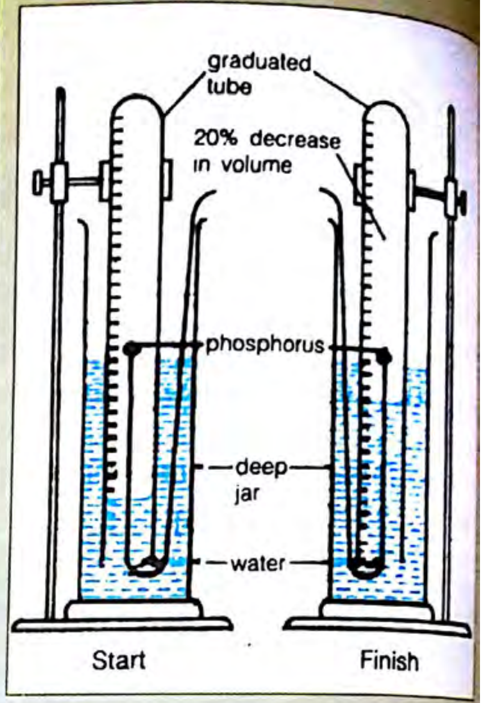
Most substances burn in air. Burning or combustion is a chemical reaction which is frequently accompanied by the production of light and heat. During this reaction, the combustible material usually combines with atmospheric oxygen to form oxides and other products. For example, when candle wax, a hydrocarbon, is ignited, it melts, vaporizes and decomposes into its constituent elements, namely

Experiment 15.1 To find the proportion by volume of oxygen in air.

Method Fill a graduated tube to a depth of about 5 cm with water. Close the open end of the tube with the thumb, invert it into a deep jar of water and clamp it in position. Leave the apparatus to stand for some time to allow the air inside the tube to become saturated with water vapour. Then adjust the tube so that the water levels inside and outside the tube are the same. Read off the volume of air in the tube and note the temperature and the pressure of the laboratory.

Push a flexible wire carrying a piece of yellow phosphorus up the tube. Note the temperature and pressure of the laboratory. After a while, the phosphorus begins to smoulder, uses up the oxygen and gives off white fumes which dissolve in water. Leave the apparatus aside until the phosphorus stops smouldering. Then remove the wire and any remaining phosphorus. Lower the tube so that the water levels inside and outside the tube are the same. Read off the volume of the air in the tube, and note the temperature and pressure of the laboratory.

Fig. 15.2 Composition of air.



Result and Calculation First correct the initial and final volumes of air to s.t.p.

Initial volume of air at s.t.p. = V cm^3

Final volume of air at s.t.p. = v cm^3

Volume of air used up = $(V - v)$ cm^3

Percentage of air used up = $\frac{V-v}{V} \times 100\%$

The percentage of air used up is found to be about 21%.

Conclusion The air used up is oxygen. It makes up about 21% by volume of air.

Note Instead of phosphorus, this experiment can also be done using alkaline pyrogallol, which absorbs oxygen. A few drops of the pyrogallol can be placed in an aluminium boat, which floats in the water inside the tube.

hydrogen and carbon. These then combine with atmospheric oxygen during the process of burning to produce water and carbon(IV) oxide respectively.

When the supply of air is very limited, there is incomplete combustion of the carbon, with the result that either carbon(II) oxide, CO, or black particles of carbon (soot) may be produced.

Flames

Flames are produced when substances burn. A flame can be described as a region where gases combine chemically, with the production of heat and light. In most cases, one of the gases involved is oxygen although combustion can occur without oxygen, for example, when hydrogen burns in chlorine.

Flames are not homogeneous, but are composed of several defined zones. The type of flame produced depends on the nature of the substance that is burning. A flame may be luminous or non-luminous. The luminosity of a flame is caused by the presence of solid particles in the flame. An increase in the temperature or pressure of the burning gases also increases the luminosity of a flame.

Hydrogen flame Hydrogen burns with a very faint non-luminous flame. The structure of the hydrogen flame is simple, consisting of only two regions: the unburnt gas zone and the zone of complete combustion.

Candle flame A candle burns with a luminous flame. Four zones can be identified in the flame:

- the zone of unburnt gas around the wick;

Experiment 15.2(a) To identify the products of the combustion of candle wax.

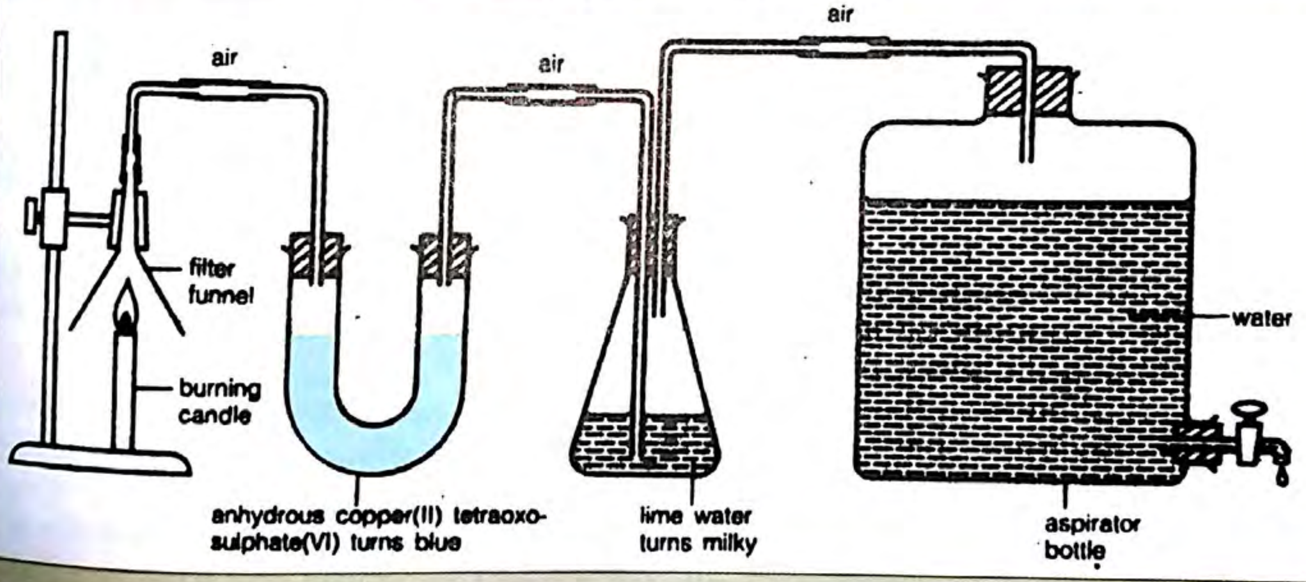
(b) To show that the products of the combustion of candle wax weigh more than the original candle wax.

Method **(a)** Set up the apparatus as shown. Turn on the aspirator tap. As the water in the bottle drains off, air is drawn in through the funnel, carrying the products formed by the burning of the candle into the system. Note any colour changes in the white anhydrous copper(II) tetraoxosulphate(VI) crystals in the U-tube and the lime water in the adjacent conical flask.

(b) Modify the apparatus by replacing the U-tube containing the white anhydrous copper(II) tetraoxosulphate(VI) with another containing fused anhydrous calcium chloride. Also, replace the conical flask containing the lime water with another one containing caustic soda solution.

Place the candle on a retort stand. Before you assemble the apparatus, find the total mass of the candle on the retort stand, the U-tube with its contents, and the conical flask containing the caustic soda. Then, ignite the candle and place it in position. Turn on the aspirator tap immediately so that the products from the burning candle are drawn through the systems as before. When all the water in the aspirator has been drained off, dismantle the U-tube and the conical flask, and re-weigh them together with the remainder of the candle on the stand.

Fig. 15.3 Products formed during the combustion of candle wax.

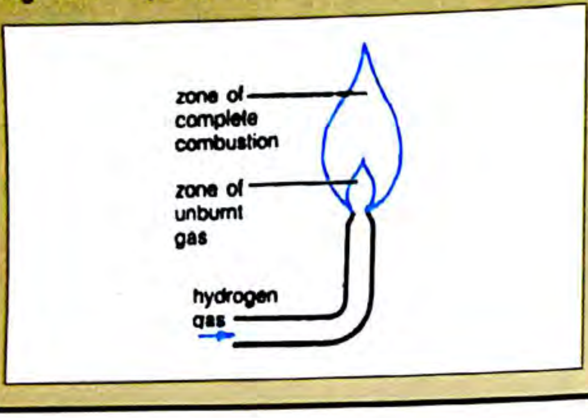


Result **(a)** The white anhydrous copper(II) tetraoxosulphate(VI) turns blue, showing the presence of moisture. At the same time, the lime water in the conical flask turns milky, indicating the presence of carbon(IV) oxide.

(b) The mass of the apparatus after the experiment is greater than that before the experiment. This gain in mass is due to the mass of the atmospheric oxygen, which has combined with the carbon and hydrogen of the candle wax during burning, to produce the carbon(IV) oxide and water which are absorbed by the caustic soda and fused calcium chloride respectively.

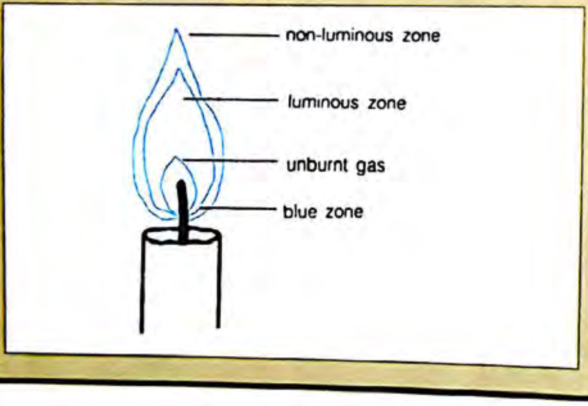
Conclusion When a candle burns, the products formed are water and carbon(IV) oxide. The mass of these products is greater than that of the candle wax which was burnt to form them.

Fig. 15.4 Hydrogen flame.



- the bright yellow luminous zone where there is incomplete burning of the hydrocarbon due to insufficient air supply—the luminosity is caused by the presence of unburnt carbon particles;
- the barely visible, non-luminous zone on the outside—where complete combustion of carbon particles takes place because of a plentiful supply of air from the atmosphere;
- the blue zone at the base of the flame which is also a region of complete combustion.

Fig. 15.5 Candle flame.



Bunsen flame A Bunsen burner is built with an air inlet at the base of the burner tube so that a stream of air can be supplied to the flame together with the fuel gas. This supplements the external supply of air, and allows a more complete combustion of the fuel. The air-hole can also be adjusted to give a flame with the required luminosity.

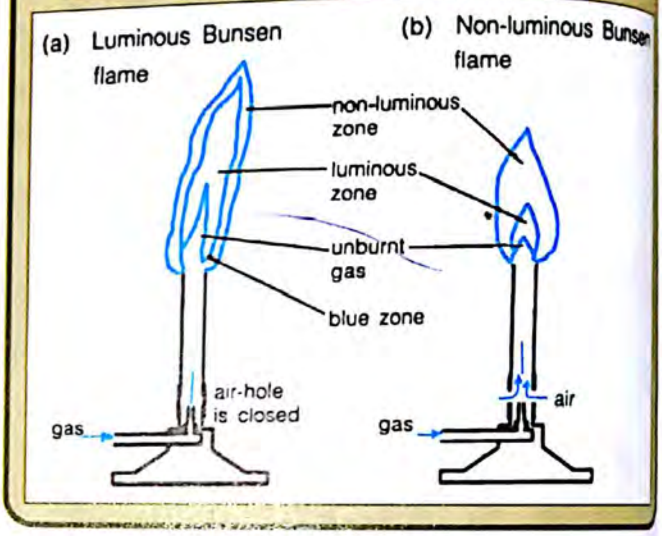
The fuel for the Bunsen burner is a mixture of hydrocarbon gases (methane and butane) and some hydrogen and carbon(II) oxide. The products of combustion are mainly water, carbon(IV) oxide, carbon(II) oxide and soot.

To produce a luminous Bunsen flame, the airhole at the base of the burner tube should be closed. The flame produced is high and wavy, with a large, bright yellow zone within it. It is not hot, and deposits soot on the surface of any object held in it. Like the candle flame, it has four zones.

To produce a non-luminous Bunsen flame, the air-hole should be kept open. The flame is non-luminous, much hotter, cleaner and more compact than the luminous Bunsen flame. Only three zones can be seen in the flame:

- the unburnt gas zone, much reduced in size when compared to that of the luminous Bunsen flame;
- the luminous zone, also much smaller;
- the outermost non-luminous zone which has increased in size because the flame has a sufficient supply of air.

Fig. 15.6 Bunsen flame.



If the air-hole of a Bunsen burner is opened too widely or the fuel supply is slowly turned down, the rate of combustion may exceed the rate of supply of the fuel mixture with the result that the flame enters the tube to consume any oncoming fuel. This phenomenon is known as striking-back. It can be corrected by making the air-hole smaller to reduce the air supply. To be safe, however, the burner should be turned off at once and then relit with the air-hole opened to a suitable extent.

Corrosion of metals

The corrosion of metals results from the combined action of atmospheric oxygen and water. It is accelerated by the presence of carbon(IV) oxide and gaseous pollutants like sulphur(IV) oxide in the air.

The most important example of metallic corrosion is that of iron. The corrosion of iron is commonly

periment 15.3 To show that air and moisture are necessary for the rusting of iron.

Method Take three test-tubes and label them *A*, *B* and *C*. Place an equal number of the same kind of new iron nails in each.

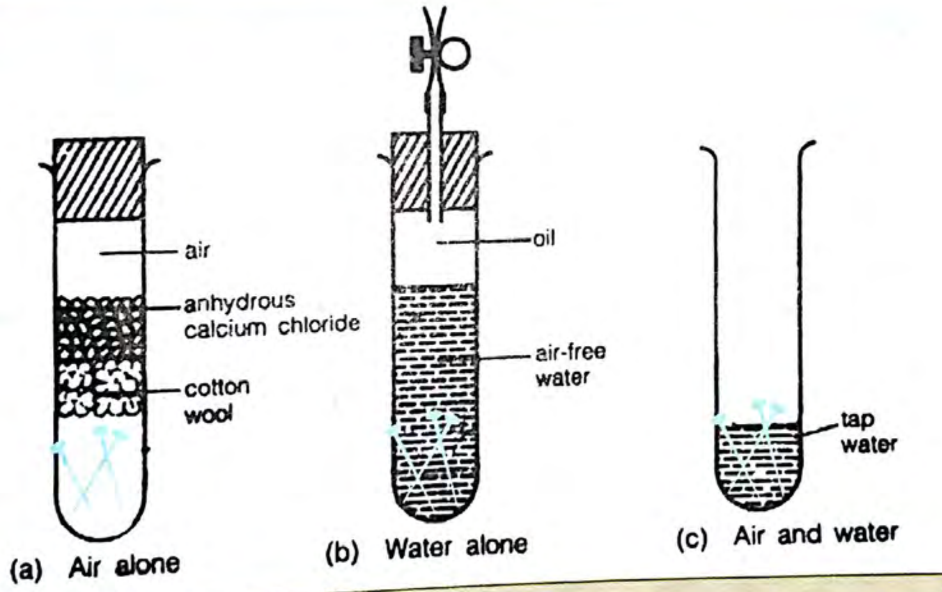
Tube A Into tube *A*, push in a pad of cotton wool and add some pieces of anhydrous calcium chloride before sealing the tube with a rubber stopper. The calcium chloride will absorb any moisture inside the tube. Tube *A* contains oxygen but no moisture.

Tube B Boil some tap water to drive out any dissolved air, rapidly cool it and pour it into tube *B*. Then add oil up to the brim of the tube. Seal the tube with a rubber stopper carrying a short glass tube with a rubber tubing at the end. Close the rubber tube by means of a small clip, thereby making the apparatus air-tight. Tube *B* contains moisture but no oxygen.

Tube C Add some tap water to tube *C* and leave it unstoppered. The nails in tube *C* are exposed to both oxygen and moisture.

Leave the tubes for about a week before examining the nails in each tube.

Fig. 15.7 Conditions for rusting.



(a) Air alone (b) Water alone (c) Air and water

Result Only the nails in tube C have become rusty. The rest remain unchanged.

Conclusion Both moisture and oxygen are necessary for the rusting of iron.

known as rusting. Iron rusts by combining with oxygen in the presence of water to form brown hydrated iron(III) oxide (commonly known as rust), $Fe_2O_3.xH_2O$. Rust is soft and breaks off easily. When this happens, the metal below begins to rust too. Therefore, if iron is exposed to moist air long enough, it will rust completely.

$$4Fe(s) + 3O_2(g) + 2xH_2O(l) \rightarrow 2Fe_2O_3.xH_2O(s)$$

The rusting of iron is of economic importance, since we use iron for many purposes. There are several ways of preventing the rusting of iron.

1 Iron parts installed in vehicles, machinery and buildings are often protected with paint. Tar, which is cheaper and lasts longer, is frequently used instead of paint on those parts which we do not see, such as the bottom of ships.
2 Exposed and moving iron parts of vehicles and machinery are periodically coated with grease and oil to prevent rusting.
3 Sometimes, iron is protected by a coating with zinc. This is known as *galvanized iron*. It is used

for making roofs, baths, buckets, and so on. It is made by dipping the piece of iron in molten zinc.

4 Iron may also be coated by other metals like copper, tin, chromium, gold and silver. This is brought about by electroplating.

5 Iron, used in making cooking utensils, is often coated with enamel. Enamel is hard, impervious to air and water and does not react with food.

In these methods, the aim is to prevent both air and moisture from coming in contact with iron. A lot of money is spent on such protective measures.

Comparing rusting and burning

1 Both rusting and burning are oxidation processes since they require oxygen. Water is necessary for rusting to take place whereas burning is difficult in the presence of water.

2 Burning is an active rapid process whereas rusting is a very slow process.

3 Both processes give out heat. The heat given out during burning is in large amounts within a short period of time and is easily detected. The heat given out during rusting is given out in small amounts over a long period of time and is not perceptible.

4. Rusting must involve iron while burning may not.

Atmospheric Carbon(IV) Oxide

The atmosphere contains about 0.03% by volume of carbon(IV) oxide. This proportion is kept fairly constant by a balance in nature between the processes which remove carbon(IV) oxide from the atmosphere and those which return it to the atmosphere (see page 130) under carbon cycle.

Respiration in living organisms

Respiration is the process whereby living things use oxygen from the air to oxidize food substances (mainly glucose) in their body cells to release energy. Carbon(IV) oxide is produced as a waste product and liberated into the surrounding air.

$$\underset{\text{glucose}}{C_6H_{12}O_6(s)} + \underset{\text{oxygen}}{6O_2(g)} \rightarrow \underset{\text{water}}{6H_2O(l)} + \underset{\text{carbon(IV) oxide}}{6CO_2(g)} + \text{energy}$$

In most higher animals, this gaseous exchange takes place in the lungs. The oxygen in the air that is breathed in (inspired air) diffuses into the blood in the lungs. At the same time, the carbon(IV) oxide in the blood diffuses out into the lungs and is expelled in the air that is breathed out (expired air). This means that expired air contains a higher percentage of carbon(IV) oxide than inspired air.

Photosynthesis in plants

Photosynthesis is a process whereby green plants manufacture carbohydrates (glucose) from atmospheric carbon(IV) oxide and water from the soil in the presence of sunlight which provides the necessary energy for the reaction. The process occurs in the chlorophyllous cells of the leaves and stems only. Oxygen is produced as a waste product and released into the atmosphere.

$$6H_2O(l) + 6CO_2(g) \xrightarrow[\text{chlorophyll}]{\text{light energy}} C_6H_{12}O_6(s) + 6O_2(g)$$

Photosynthesis is an *anabolic* (building up) *process* as opposed to respiration which is a *catabolic* (breaking down) *process.*

Atmospheric Nitrogen

The major constituent, making up 78% by volume, of air is nitrogen. Gaseous nitrogen is relatively inactive but it acts as an important diluent of air to slow down combustion and corrosion. If it were absent in air, we would be unable to light even a cigarette without it bursting into flames. At the same time, metals would corrode so rapidly that it would be impractical to use many of them.

The Noble Gases

The noble gases constitute about 1% by volume of air and are characterized by their chemical inertness. They consist of helium, neon, argon, krypton, xenon and radon. Of these, argon is the most abundant in the atmosphere.

Uses of the noble gases

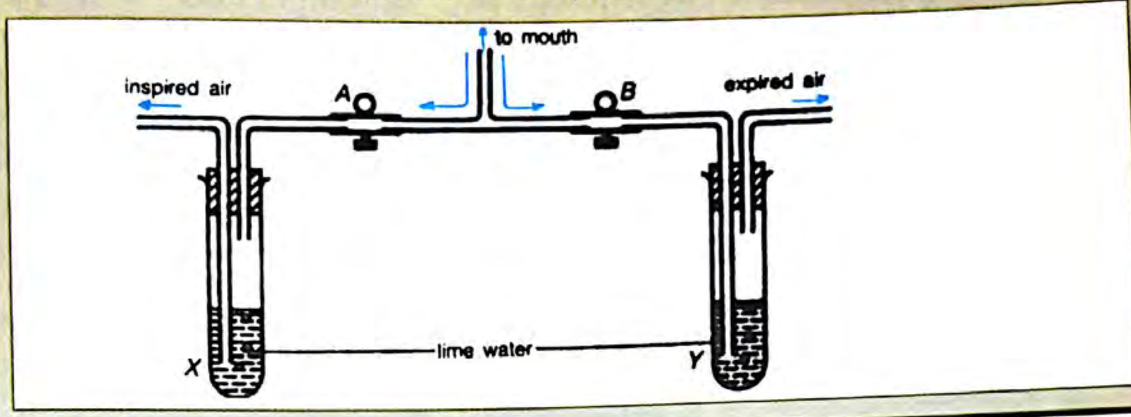
1 Argon is used in gas-filled electric lamps because it helps to prevent the oxidation of the lamp filaments.

2 A mixture of krypton and xenon is used in the

Experiment 15.4 To show that expired air contains more carbon(IV) oxide than inspired air.

Method Set up the apparatus as shown in fig. 15.8, and place an equal amount of lime water in both tubes *X* and *Y*.

Fig. 15.8 Expired air contains more carbon(IV) oxide than inspired air.



Open clip *A* and close clip *B*. Then breathe in through the mouth-piece. Air will enter the system through the lime water in tube *X* only. Now, close clip *A* and open clip *B*, and then breathe out. The expired air will now pass through the lime water in tube *Y* only. Repeat the breathing in and breathing out processes several times.

Result The lime water in tube *Y* turns milky in a shorter period of time than that in tube *X*.

Conclusion Expired air contains more carbon(IV) oxide than inspired air.

photographer's flash tube for taking highspeed pictures.

3 Helium, neon and argon will give out coloured lights when a high-voltage current is passed through them under low pressure. Neon gives a beautiful reddish-orange colour; argon, in the presence of mercury, gives a blue colour; and helium gives a white light which appears golden through a yellow tube. These gases are usually used in advertisement signs. Neon lights are also used in aerodrome beacons as they have a high power of fog penetration.

4 Helium, being non-combustible and yet almost as light as hydrogen, is often used in observation balloons. Mixtures of helium and oxygen are also used by divers.

5 Radon is radioactive. Its radiation is used in medicine for treating some forms of cancer.

Water Vapour in the Air

Water vapour is present in the atmosphere as a result of evaporation from water bodies like rivers, lakes and the oceans. Its presence in the air can be easily shown by using a deliquescent substance like calcium chloride. Such a substance would turn into a solution if it is left exposed to the atmosphere for a couple of days. The quantity of water vapour in the air varies from time to time and from place to place, depending on the amount of evaporation. The water vapour content in the air is also likely to be higher on rainy days. The atmosphere is then described as being humid.

For every temperature, there is a saturation pressure of water vapour in the air. This saturation pressure is the maximum vapour pressure of water at

Noble gases are used to produce colourful advertisement signs that particular temperature. When the pressure of water vapour in the air becomes greater than the saturation pressure, for example when the atmosphere is cooled at night, dew or fog may form as a result of the condensation of the excess water vapour from the air. Clouds are formed in this way when moist warm air rises and is subsequently cooled. The formation of large droplets results in rain.

Air Dissolved in Water

Air is sparingly soluble in water, dissolving more readily in cold water than in warm water. All the natural waters contain dissolved air because their surfaces are exposed to the atmosphere. Oxygen and carbon(IV) oxide in air are necessary for the existence of all living organisms. Oxygen is essential for respiration in both plants and animals while carbon(IV) oxide is needed by plants for photosynthesis. Most aquatic organisms cannot make use of atmospheric oxygen and carbon(IV) oxide. Therefore, the presence of dissolved air is vital for the existence of aquatic life.

The composition of dissolved air is marked different from that of atmospheric air. This is due the different solubilities of the constituent gases water. At 15 °C, dissolved air contains as much 33% by volume of oxygen and 0.5% by volume carbon(IV) oxide, as compared to 21% and 0.03 respectively in atmospheric air. In ponds, lakes, and rivers where there are aquatic plants, the percentage of oxygen may rise to about 40% due to the evolution of oxygen during photosynthesis.

Table 15.1 Percentage of gases in atmospheric air and in air dissolved in water

Constituent gases	% by volume in the atmosphere	% by volum dissolved in water
Oxygen	21	33
Nitrogen	78	66
Carbon(IV) oxide	0.03	0.50

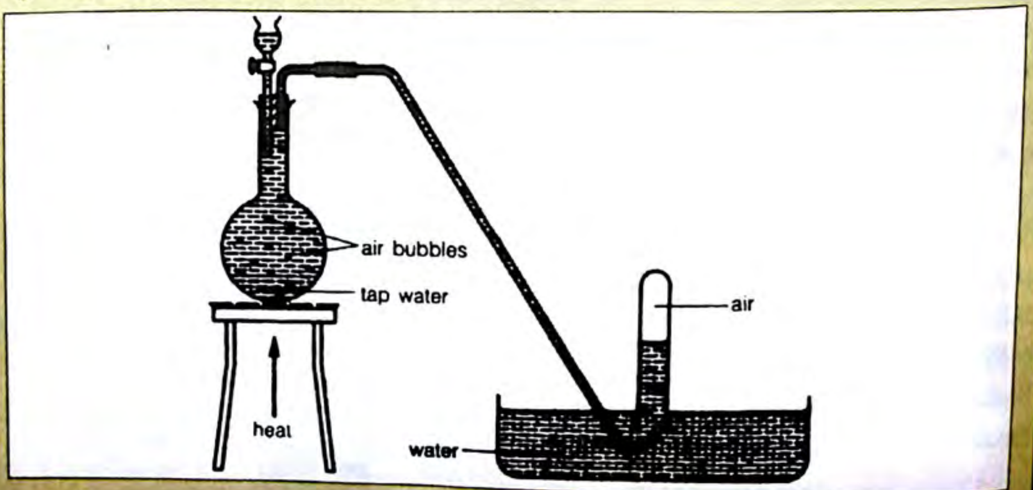
Experiment 15.5 To find out if tap water dissolved air.

Method Set up the apparatus as shown in fig. 15.9. Fill the flask and delivery tube completely with tap water via the thistle funnel. Close the tap of the funnel. Next, fill a test-tube to the brim with tap water. Invert and clamp it over the end of the delivery tube. Heat the water in the flask.

Result Air bubbles form in the water in the flask, rise and eventually collect in the test-tube.

NOTE Air bubbles form because the solubility of gases in water decreases with increasing temperature.

Fig. 15.9 Tap–water contains dissolved air.



Conclusion Tap water contains dissolved air.

NOTE This experiment can be repeated with pond water, river water, sea-water or other types of natural water to show that these, too, contain dissolved air.

AIR POLLUTION

The composition of the air we breathe in is determined by a delicate balance in nature. Processes such as photosynthesis, respiration, combustion and decay play an important role in maintaining this balance. Many of our activities

- increase the amount of carbon(IV) oxide in air;
- introduce undesirable substances known as *pollutants* into the air.

Within limits, the natural processes can remove the pollutants. Over the last few decades, however, industrialization has caused a tremendous increase in the release of pollutants into the air. In many places, these pollutants are present in concentrations that cause harm to human, animal and plant life, and to property (the non-living environment). Such a change in the air, where it is made impure, is known as *air pollution*.

Cause of Air Pollution

The main cause of air pollution is the combustion of fossil fuels such as coal, petrol, gasoline and gases. Most factories, power plants and vehicles such as motor-cars, trains and aircraft use fossil fuels to obtain energy. In the process, many pollutants are released into the air. Other causes of pollution include the release of freons from aerosol cans and poisonous gases from chemical warfare.

Pollutants

The main air pollutants are as follows:

- particulate matter (tiny solids),
- oxides of carbon,
- oxides of sulphur and nitrogen,
- gaseous hydrocarbons and chlorofluoro-carbons.

Particulate matter

Smoke, soot and dust are emitted mainly by industrial processes and the burning of coal and wood fires. They damage the respiratory system, especially the lungs.

Another very poisonous solid pollutant is lead (and lead(II) bromide) which is emitted in the exhaust of motor-cars using leaded petrol. Lead dust can cause lead poisoning and injury to the nervous system. The lead that is inhaled accumulates in the body. Over a long period, the amount of accumulated lead reaches levels that are toxic to the body.

Smog Usually the air next to the earth's surface is the warmest. As it rises, it cools. Sometimes, a temperature inversion occurs and we get a warm layer of air above the earth's surface. When this happens, pollutants become trapped underneath. This can lead to the formation of smog. Smog usually occurs over cities which burn a lot of coal.

Smog reduces visibility and causes respiratory diseases. In severe cases, many deaths occur.

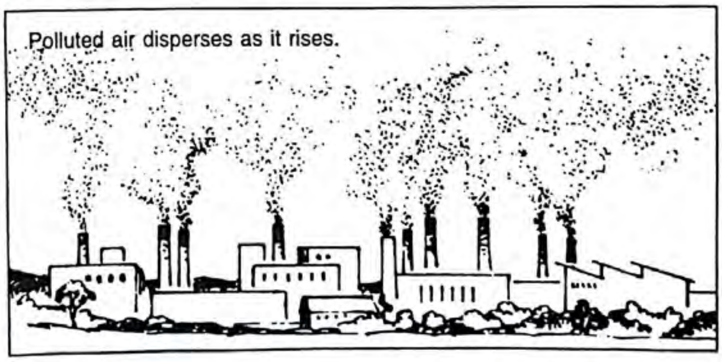
Oxides of carbon

Carbon(II) oxide is a colourless, odourless and poisonous gas. It is produced in large amounts when the carbon in fuel is burnt incompletely.

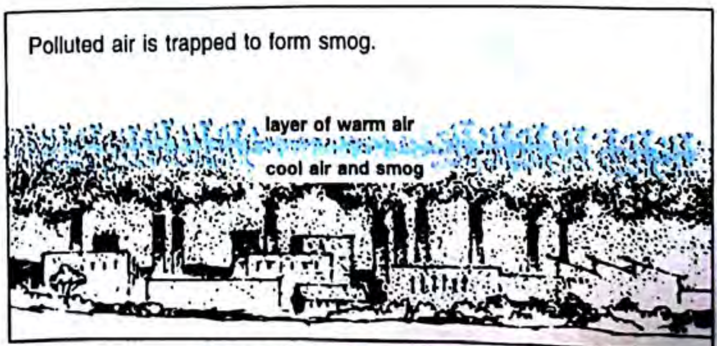
Motor vehicles are the largest single source of carbon(II) oxide emission. We know that carbon(II) oxide, if inhaled, competes with oxygen for the haemoglobin in the blood. This causes a reduction in the amount of oxygen that is carried to the body tissues. A carbon(II) oxide concentration of 0.005% in the atmosphere could, over prolonged periods, cause brain damage. At lower concentrations, carbon(II) oxide causes dizziness, headaches, fatigue and lethargy.

Carbon(IV) oxide is produced by many processes which use fossil fuel as a source of energy. This excessive production of the gas, together with deforestation, has caused an increase in the level of atmospheric carbon(IV) oxide. Carbon(IV) oxide helps to retain a certain amount of the infrared ray (heat ray) that is radiated by earth. An increase in the level of atmospheric carbon(IV) oxide would result

Polluted air disperses as it rises.



Polluted air is trapped to form smog.



Formation of smog

in a greater retention of infrared ray, giving rise to the *greenhouse effect*—a gradual warming of our planet. Such an occurrence would cause the polar caps to melt and submerge many of the coastal regions and islands on earth.

Oxides of nitrogen and sulphur

Oxides of sulphur are acidic, corrosive and poisonous. When sulphur-containing coal is burnt, it gives off sulphur(IV) oxide. Most of the sulphur(IV) oxide comes from electric power stations and industrial plants.

Oxides of nitrogen are produced when combustion of fuels occurs at high temperatures. The major sources of these pollutants (e.g. NO, NO_2) are from the exhaust of transportation vehicles.

Oxides of sulphur and nitrogen dissolve in rainwater to produce acids. This results in the fall of *acid rain* which is harmful to plant and animal life, buildings and metal structures.

Oxides of nitrogen react with sunlight to produce secondary pollutants such as ozone, nitrogen(IV) oxides and alkanals. These, together with the solid pollutants and water droplets in air, form the constituents of smog.

The oxides of nitrogen and sulphur cause irritation of the eyes, nose, throat and respiratory tissues.

Hydrocarbons

Hydrocarbons are released into the air when fuels evaporate from storage tanks. They are also found in the exhaust of motor vehicles when fuel is burnt incompletely.

Many hydrocarbons are believed to cause cancer. By 'reacting' with nitrogen oxides in the presence of light, they tend to produce smog or heavily stagnant air.

Chlorofluorocarbons

Chlorofluorocarbons or CFCs are a group of man made chemicals such as freon which are used as propellants for spray cans, coolants in refrigerators and air conditioners, and for making plastic foams. In the upper atmosphere, the ultra-violet light breaks off a free chlorine atom, Cl, from a chlorofluorocarbon molecule. The free chlorine atom is very reactive and attacks a molecule of ozone, O_3, to produce an ordinary oxygen molecule, O_2, and an unstable oxide of chlorine, ClO. The latter readily reacts with atomic oxygen, O, (usually present in this layer of the atmosphere) to form an oxygen molecule, O_2, and release the chlorine atom, which then attacks another ozone molecule. Thus, the process is repeated numerous times, causing a depletion in the ozone layer.

The ozone layer is found in the stratosphere. Data from satellites show a definite drop in ozone levels and revealed an 'ozone hole' over the Antarctic.

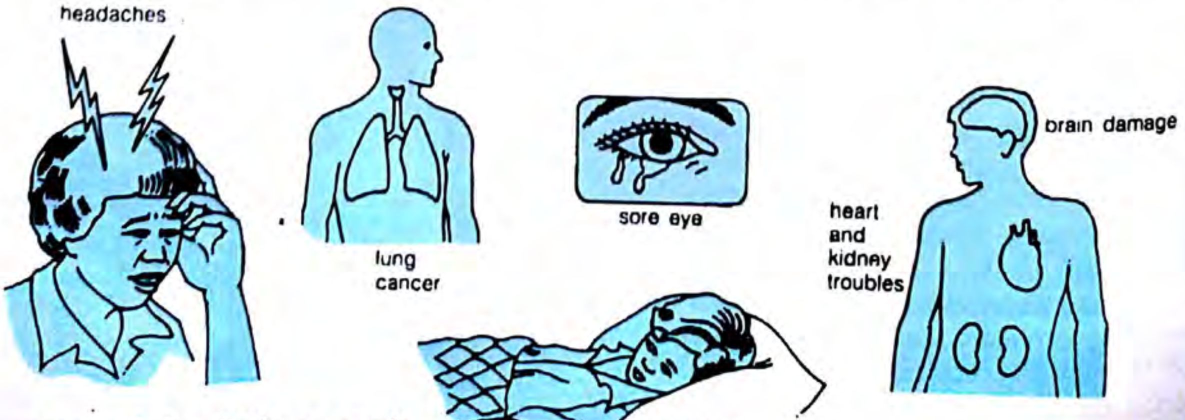
The ozone layer is important because it acts as a shield preventing too much ultra-violet light from reaching the earth's surface.

A diminishing ozone layer means an increase in the level of ultra-violet radiation that reaches earth. This poses a danger to human health and may cause an increase in cataracts, skin cancer and sunburns. It may also damage our body's defence system, thus lowering our resistance to diseases.

Control of Air Pollution

Some methods of controlling air pollution are as follows:

1 Strict laws should be passed to make factories and users of motor-vehicles keep air pollution down by using anti-pollution devices and taking anti-pollution measures.
2 Machinery should be improved so that more efficient fuel combustion occurs.
3 People should be educated to make them aware of the causes and dangers of pollution.



Effects of air pollution on people

SUMMARY

- Air is a mixture of gases, composed mainly of nitrogen and oxygen. It makes up the earth's atmosphere.
- Oxygen is needed for respiration, burning, corrosion and decay.
- A flame is a region where gases combine chemically to produce heat and light. Luminosity of a flame is due to the presence of solid particles in the flame.
- Rusting is the corrosion of iron which occurs in the presence of water and oxygen (or moist air). Rust is hydrated iron(III) oxide.
- Carbon(IV) oxide is formed during respiration, burning and decay. It is needed for photosynthesis, the food-making process carried out by green plants.
- Nitrogen is a relatively inactive gas which acts as an important diluent of air to slow down combustion and corrosion.
- Noble gases make up 1% by volume of air. Krypton and argon are used to produce coloured lights. Helium is used in observation balloons. Mixtures of helium and oxygen are also used by divers. Radon, being radioactive, is used as a tracer in medicine.
- Air pollution takes place when air is made impure by the presence of harmful substances in concentrations that cause injury to human, animal and plant life, and property. The main cause of air pollution is the combustion of fossil fuels. The main air pollutants are particulate matter, carbon(II) oxide, oxides of sulphur and nitrogen, and gaseous hydrocarbons and chlorofluorocarbons.

EXERCISES

1. Combustion is a chemical reaction which is always accompanied by

A heat.
B heat and light.
C heat and energy.
D heat and power.

2. All these are the causes of luminousity in flames except

A solid particles.
B solid particles and increased temperature.
C solid particles and increased pressure.
D size of materials burnt.

3. These gases burn with blue flame except

A H_2
B CH_4
C C_2H_2
D CO

4. Which of these is not necessary for metallic corrosion?

A Water
B Oxygen
C Heat
D Sulphur IV oxide

5. What chemical process is represented by the following equation?

$$4Fe(s) + 3O_2(g) + 2xH_2O\ (l) \rightarrow 2Fe_2O_3 . xH_2O(s)$$

A Combustion
B Oxidation
C Hydration
D Rusting

6. The most abundant noble gas in nature is

A Neon.
B Radon.
C Helium.
D Argon.

7. The following are major gaseous pollutants except

A oxides of carbon e.g. CO.
B oxides of sulphur e.g. SO_2.
C chlorofluorocarbon.
D carbon IV oxide.

8. (a) Give the constituents of atmospheric air, and indicate its approximate percentage composition.
(b) Give any two reasons to support the claim that air is a mixture.
(c) How would you demonstrate that rainwater contains dissolved air?
(d) Compare the percentage composition of atmospheric air with that of dissolved air, and explain why dissolved air contains more oxygen than atmospheric air.

. (a) List four examples of noble gases and give their uses.
(b) What happens when a beaker of air is inverted over a trough of water containing dissolved alkaline pyrogallol and left overnight?

10. (a) The atmosphere over industrial areas is said to be polluted and impure. Explain and justify this statement.
(b) What are the products of the combustion of a candle? Describe an experiment to identify the products of the burning candle.

11. (a) Define a flame.
(b) Describe the structure of a candle flame and explain the formation of the products obtained during the burning.
(c) Compare the structures of the luminous and the non-luminous Bunsen flames.
(d) What is strike-back of a Bunsen flame?

12. (a) What are the main pollutants in air?
(b) What is acid rain?

WATER • SOLUTIONS • 16
SOLUBILITY

NATURAL AND TREATED WATER

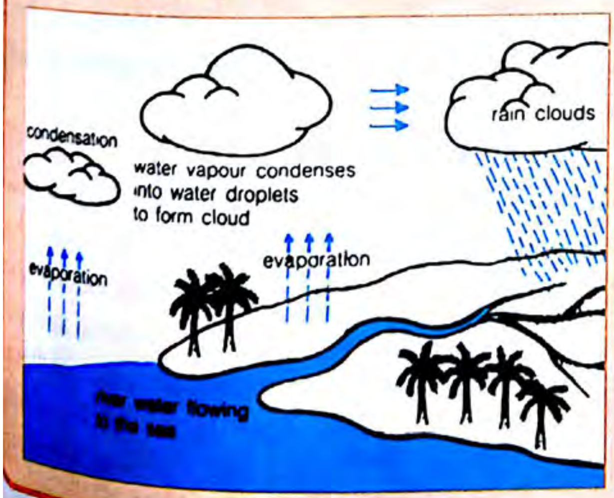
Water is one of the most common substances known. It is a good solvent for many substances and rarely occurs in its pure form in nature.

Natural Water

Natural water includes rainwater, spring water, well-water, river water, lake water and sea-water. Rainwater is the purest form of natural water because it is formed as a result of the condensation of water vapour in the atmosphere, i.e. it is a natural form of distilled water. Spring water contains a considerable amount of mineral salt; but very little suspended impurities such as dust and bacteria, so it is a good source of drinking water. Well-water contains a lot of clay and other mineral salts. A well that is used as a source of drinking water should be

- sited away from sources of underground water pollution such as pit latrines; and
- lined with bricks and covered.

Fig. 16.1 Water cycle.



Water from deep wells tend to be less polluted than that from surface wells. Generally, it is safer to boil well-water before drinking. River water, lake water and sea-water contain a lot of dissolved air, mineral salts, bacteria and organic remains. These waters have to be specially purified before they can be used for drinking.

All the types of natural water are in constant circulation, forming a gigantic *water cycle.*

Treated Water

Treated water is usually prepared for special purposes. Examples of treated water are distilled water, pipe-borne water for townships, and chlorinated water for use in swimming pools.

Distilled water

Distilled water is chemically pure water. It is prepared by condensing steam or using clean vessels. Water prepared using exchange resin is called deionized water.

Distilled water is used in

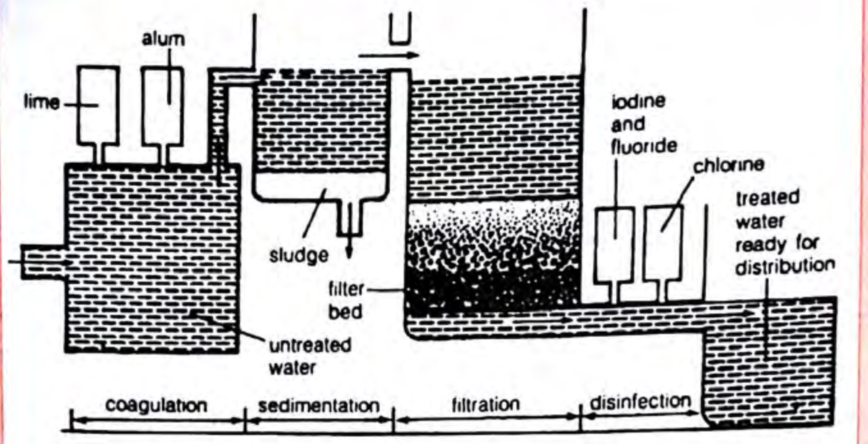
- the laboratory for preparing reagents and analytical work;
- certain industrial processes;
- the preparation of drugs;
- car batteries.

Water supply to a township

Pipe-borne water is prepared in a water-treatment plant. This water is usually germ-free but it contains mineral solutes like sodium chloride.

Water from rainfall, rivers or lakes is stored in reservoirs. This water is purified by various methods which include: *coagulation, sedimentation, filtration and disinfection.* The purified water is then distributed to towns and cities via underground pipes for domestic and industrial uses.

Fig. 16.2 The treatment of water



The treatment of water to make it fit for our use can be done in the following way: First, the untreated water is passed through large settling tanks where chemicals like potash alum, $KAl(SO_4)_2$, or sodium aluminate(III), $NaAlO_2$, are added to cause coagulation or flocculation. The impurities clump together to form big particles of dirt or *flocs* which settle down rapidly. Next, the water is passed through a filter bed to remove the remaining fine particles of dirt. Then, the water is treated with chemicals like chlorine to kill germs. Other useful chemicals, such as iodine and fluorine, may be added in the correct amounts as food supplements to prevent goitre and tooth decay respectively. Finally, the treated water, which is now clear and free from germs, is stored in a reservoir and distributed to the town for use.

HARDNESS OF WATER

Hard water will not form lather readily with soap. It contains a number of dissolved salts, the most important being calcium tetraoxosulphate(VI), magnesium tetraoxosulphate(VI) and calcium hydrogentrioxocarbonate(IV). Soap is the sodium or potassium salt of an organic acid. Ordinary soap is usually sodium octadecanoate. When soap is added to hard water, the dissolved salts in the water will immediately react with the soap molecules in the following way:

dissolved calcium or magnesium salts soluble	+	soap or sodium octadecanoate soluble
	↓	
calcium or magnesium octadecanoate insoluble scum	+	sodium salts soluble

The insoluble calcium and magnesium salts form an unpleasant scum which sticks to clothes and is difficult to rinse away. Hard water is wasteful, as a large amount of soap has to be used in precipitating and removing the calcium and magnesium ions, after which more soap has to be used for the actual washing. In recent years, this problem has been overcome by the introduction of detergents for domestic and laundry purposes. These detergents are not affected by hard water because they form calcium and magnesium salts which are soluble in water.

Origin of Hard Water

Water acquires hardness when it dissolves gypsum, $CaSO_4.2H_2O$, or limestone, $CaCO_3$, from the soil over which it flows. Gypsum is sparingly soluble in water but limestone is not. However, water which contains carbon(IV) oxide is capable of dissolving small quantities of limestone. The reaction is as follows:

$$\underset{\text{insoluble}}{CaCO_3(s)} + CO_2(g) + H_2O(l) \rightarrow \underset{\text{soluble}}{Ca(HCO_3)_2(aq)}$$

Types of Hard Water

There are two types of hard water: temporarily hard water and permanently hard water.

Temporary hardness

Temporary hardness of water can be easily removed by boiling. This hardness is caused by the presence of dissolved calcium hydrogentrioxocarbonate(IV), $Ca(HCO_3)_2$, which decomposes on heating. The calcium trioxocarbonate(IV), $CaCO_3$, formed is insoluble and this brings the calcium ions out of the solution as a precipitate. Once the calcium ions are out of the solution, the soap that is added to the water will be available for the, formation of lather.

$$\underset{\text{soluble}}{Ca(HCO_3)_2(aq)} \xrightarrow{\text{boil}} \underset{\text{insoluble}}{CaCO_3(s)} + H_2O(l) + CO_2(g)$$

Temporary hardness can also be removed by using slaked lime, $Ca(OH)_2$.

$$\underset{\text{soluble}}{Ca(HCO_3)_2(aq)} + \underset{\text{slightly soluble}}{Ca(OH)_2(s)} \rightarrow \underset{\text{insoluble}}{2CaCO_3(s)} + 2H_2O(l)$$

The soluble calcium hydrogentrioxocarbonate(IV) is precipitated as the insoluble calcium trioxocarbonate(IV), thus removing out of the solution calcium ions, which are responsible for the hardness of water.

Effects of temporary hardness

Furring of kettles and boilers When a kettle or boiler has been used to boil temporarily hard water for some time, the inner surface becomes coated with a white fur-like layer. This layer is due to the gradual deposition of calcium trioxocarbonate(IV), from the decomposition of calcium hydrogentrioxocarbonate(IV).

Stalagmites and stalactites These are pillars of limestone found in hot caves. When hard water flows temporarily over the top of a cave, drops of water tend to drip through cracks in its roof. The calcium hydrogentrioxocarbonate(IV) in the water then

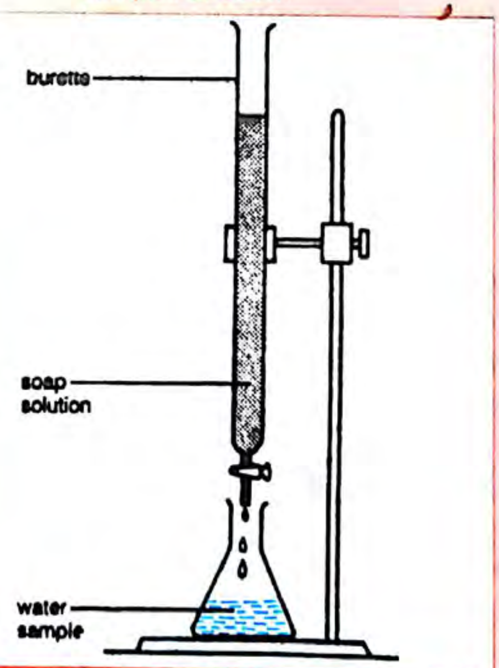
Experiment 16.1 To compare the hardness of various samples of water.

Method and results Dissolve 5 g of soap in 1 dm^3 distilled water. Fill a burette with soap solution and set it up as shown. Pipette 25 cm^3 of distilled water into a conical flask. Add 1 cm^3 of the soap solution at a time to the distilled water. Shake the flask after each addition. Continue adding soap solution until a permanent lather is formed. Note the volume of soap solution used. Using this value as a rough estimate of the amount of soap solution required to give a permanent lather, repeat the experiment very carefully to obtain an accurate result. Note this volume.

Repeat the process with 25 cm^3 of rainwater, tap-water, sea-water, well-water and any other samples of water. Record your results in the form of a table.

Conclusion Distilled water needs only a small amount of soap solution to produce a lather while sea-water needs a large amount. Since the degree of hardness of a water sample is directly proportional to the amount of soap solution needed, we can roughly assess the hardness of each sample.

Fig. 16.3 Comparing the hardness of various samples of water.



Type of water	Volume of soap solution used (cm^3)

becomes decomposed by the heat inside the cave, leaving deposits of calcium trioxocarbonate(IV) on the roof and the floor of the cave. A calcium trioxocarbonate(IV) structure growing downwards from the roof is known as a *stalactite* while one growing upwards from the floor is known as a *stalagmite*. These may grow towards each other to form one solid pillar inside the cave

Permanent hardness

Permanent hardness of water can only be removed by using chemicals. It is caused by the presence of calcium and magnesium ions in the form of soluble tetraoxosulphates(VI) and chlorides.

Removal of permanent hardness Permanent hardness can be removed by precipitating the calcium and magnesium ions from solution. The chemicals employed are all soluble sodium compounds which will form insoluble precipitates with the calcium and magnesium ions. Washing soda, caustic soda and permutit or zeolite are some of the common chemicals used in the removal of permanent hardness.

The addition of washing soda removes the calcium and magnesium ions as the insoluble calcium and magnesium trioxocarbonates(IV) respectively.

$$Na_2CO_3(aq) + \underset{\text{soluble}}{CaSO_4(aq)} \rightarrow \underset{\text{insoluble}}{CaCO_3(s)} + Na_2SO_4(aq)$$

$$Na_2CO_3(aq) + \underset{\text{soluble}}{MgSO_4(aq)} \rightarrow \underset{\text{insoluble}}{MgCO_3(s)} + Na_2SO_4(aq)$$

In the same way, the addition of caustic soda removes the calcium and magnesium ions as the insoluble calcium and magnesium hydroxides respectively.

$$2NaOH(aq) + \underset{\text{soluble}}{CaSO_4(aq)} \rightarrow \underset{\text{insoluble}}{Ca(OH)_2(s)} + Na_2SO_4(aq)$$

$$2NaOH(aq) + \underset{\text{soluble}}{MgSO_4(aq)} \rightarrow \underset{\text{insoluble}}{Mg(OH)_2(s)} + Na_2SO_4(aq)$$

Permutit or zeolite is an ion-exchange resin used industrially and in the home for softening water. It is naturally occurring sodium aluminium trioxosilicate(IV) (commonly known as sodium zeolite) which can also be prepared artificially. As the hard water is passed through the resin, the sodium ions will go into solution while the unwanted calcium and magnesium ions take their place in the complex salt. For example,

$$\underset{\text{soluble}}{\text{calcium tetraoxosulphate(VI)}} + \underset{\text{pemutit}}{\text{sodium zeolite}} \downarrow \underset{\text{insoluble}}{\text{calcium zeolite}} + \underset{\text{soluble}}{\text{sodium tetraoxosulphate(VI)}}$$

When the permutit is used up, it can be regenerated by pouring a strong solution of common salt through the resin.

$$\text{sodium chlorite} + \text{calcium zeolite} \downarrow \underset{\text{permutit}}{\text{sodium zeolite}} + \underset{\text{soluble}}{\text{calcium chloride}}$$

Advantages of hard water

1. Hard water tastes better than soft water because of the dissolved minerals in it.
2. The calcium salts present in hard water, when taken in by animals, help to build strong teeth and bones.
3. Hard water helps animals such as snails and crabs to make their shells. These shells are made mainly of calcium trioxocarbonate(IV).
4. Hard water can be supplied in pipes made of lead as this type of water does not dissolve lead. Soft water dissolves lead. If supplied in lead pipes, it will cause lead poisoning.

Disadvantages of hard water

1. For washing, hard water requires a lot of soap before it can form a lather. Soft water is ideal for washing as soap lathers readily in it.
2. Hard water causes furring of kettles and boilers while soft water does not.
3. Hard water cannot be used in dyeing and tanning as the salts in it interfere with the modes of action of these processes.

WATER POLLUTION

Water pollution is a big problem in the present day world. It threatens aquatic life and changes water bodies into unsightly, foul-smelling scenes. It also affects our health because of the harmful substances that accumulate in aquatic animals, one of our main sources of food.

The main cause of water pollution is the indiscriminate dumping of solid and liquid wastes into water bodies.

Pollutants

The common pollutants are as follows:

- Refuse and sewage
- Industrial and agricultural wastes
- Crude oil spills

Refuse and sewage

Many towns and villages are located near rivers for convenience since transport is easy and water supply is available. As a result, it is a common practice to dump refuse and human wastes into the river for easy disposal. Nowadays, many homes in towns have water-closet (WC) lavatories. The human waste and liquid from these lavatories are emptied either into septic tanks or sewers. (Sewers are large underground pipes for carrying waste or sewage.) In many cases, sewers empty the waste directly into rivers and seas without any treatment.

The waste or sewage is mostly organic matter. It is broken down into simple substances by decomposers, mainly bacteria. In the process, the bacteria use up the dissolved oxygen. Too much sewage in a water body causes an increase in the bacterial population. This reduces the level of oxygen in the water. If the oxygen level falls too much, the aquatic organisms start to die and eventually the water body becomes clogged up and foul-smelling. Water polluted by sewage contains many disease-causing organisms.

Industrial and agricultural wastes

Many factories empty their chemical wastes directly into rivers and seas without converting them into harmless substances. These chemicals include acids, alkalis, mercury compounds, organic solvents and detergents.

Fertilizers and insecticides used in agriculture are washed by rain into the soil and eventually reach the lakes, ponds and rivers.

Many harmful chemical wastes like detergents and insecticides are non-biodegradable, i.e. they cannot be broken down into harmless compounds by living organisms. They remain in water and harm aquatic life. Mercury compounds tend to accumulate in the body of aquatic organisms like fish. If we eat such fish regularly, the mercury accumulates in our bodies and eventually leads to mercury poisoning.

Fertilizers initially stimulate the growth of aquatic plant life. The level of oxygen in the water increases so that the populations of other forms of aquatic life too increase. However, all living organisms must eventually die. As the plants and animals die, decomposers come in and use up the oxygen for their activities. The level of oxygen in the water body drops and the aquatic animals start to die. Large masses of undecomposed plants settle to the bottom of the water body and eventually clog it up if it is a pond or a lake.

Thermal pollution Several industries like oil refineries, steel mills and breweries use water for cooling. Usually water from a nearby river or lake is pumped in and used for the cooling process. The resulting warm water is then emptied back into the river or lake. This causes an increase in the temperature of the water. As a result, less oxygen dissolves in it. Many types of fishes cannot live under such conditions and start to die.

Crude oil spills

Accidents and carelessness in oil rigs and tankers cause crude oil spills mainly in the coastal waters. The oil floats on water and kills most of the marine life in the affected area. The oil is then washed up on the beach, temporarily preventing people from using the water and the beach for recreation. Cleaning up large oil spills is an extremely expensive process. The rehabilitation of the affected areas may take many years.

Control of Water Pollution

Some methods of controlling water pollution are as follows:

1 Refuse should be buried or burnt in an incinerator with built-in devices to prevent air pollution.
2 Sewage should be processed, treated and converted to useful fertilizers in sewage plants.
3 Chemical wastes should be converted to harmless biodegradable substances before being dumped in the sea.
4 Safety measures must be implemented to prevent crude oil spills.
5 Strict laws must be passed to control water pollution by individuals and companies.

Education is also an important anti-pollution measure. It makes each of us aware of the dire consequences of polluting our precious water supplies. This knowledge acts as a major preventive measure in controlling water pollution.

Pollution has turned this water body into an ugly rubbish dump

COMPOSITION OF WATER

Priestley (1781) was the first to observe that the explosion of a hydrogen-and-oxygen gas mixture yields water vapour. Later, Cavendish established that the ratio by volume of hydrogen to oxygen in that reaction, at constant temperature and pressure, was 2:1.

Water as an oxide of hydrogen

When dry hydrogen gas is ignited in air, it burns with a faint blue flame to give steam, which will condense on contact with any cold surface to form water.

$$\underset{\text{hydrogen}}{2H_2(g)} + \underset{\text{oxygen}}{O_2(g)} \rightarrow \underset{\substack{\text{hydrogen oxide}\\ \text{(i.e. water)}}}{2H_2O(g)}$$

PROPERTIES OF WATER

Physical properties

Pure water is a clear, colourless, tasteless and odourless liquid with the following properties.

- A boiling point of 100 °C.
- A freezing point of 0 °C.
- Maximum density of 1 g cm^{-3} at 4 °C.
- Neutral to litmus.

Unusual physical properties of water Water has some unique physical properties. For example, the melting point and boiling point of water are unexpectedly high for a molecule of its size. This is due to the fact that water molecules tend to form aggregates where the molecules are linked by hydrogen bonds. Although hydrogen bonds are weak forces, their abundance in water makes it difficult for water to boil and ice to melt. The hydrogen bonds are also responsible for the high surface tension in water producing a skin-like effect on water surfaces.

When most liquids solidify, the solids are usually more dense than the liquids. In the case of water, however, ice is less dense than water, i.e. it floats on water. This is because the molecules in ice are held together by hydrogen bonds to form an open lattice structure. The molecules in this solid structure are not crowded together as in liquid water. Therefore, ice is less dense than water.

Since ice floats on water, ponds and lakes do not freeze completely during winter. This prevents aquatic life from being killed.

Chemical properties

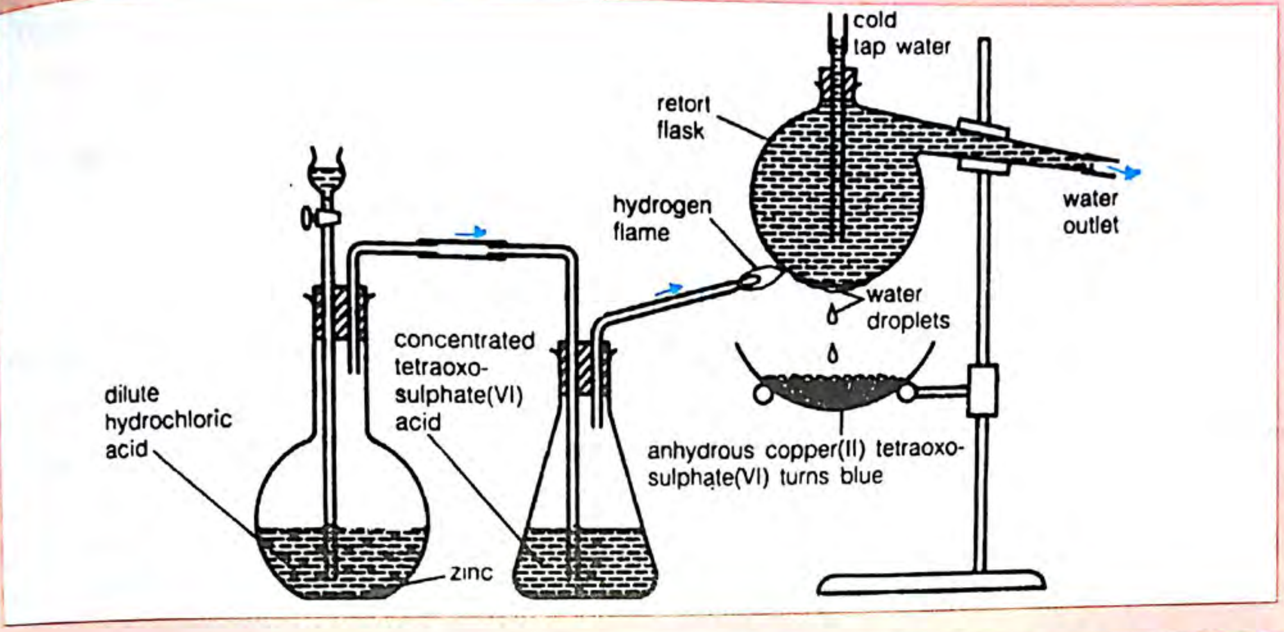
Water reacts with metals in a number of ways, with the degree of reactivity depending on the position of the metal in the electrochemical series. Thus,

- sodium, potassium and calcium react with cold water to form alkalis and liberate hydrogen;

periment 16.2 To find out that when hydrogen burns in air, water is produced.

Method Set up the apparatus as shown. Add dilute hydrochloric acid to metallic zinc to produce hydrogen gas. Dry the gas by passing it through concentrated tetraoxosulphate(VI) acid and let it flow out of a delivery tube that ends in a jet. Ignite the gas at the jet and direct the flame towards the bottom of a retort flask containing cold tap water. Place an evaporating dish containing some anhydrous copper(II) tetraoxosulphate(VI) underneath the retort flask.

Fig. 16.4 Hydrogen bums in air to produce water.

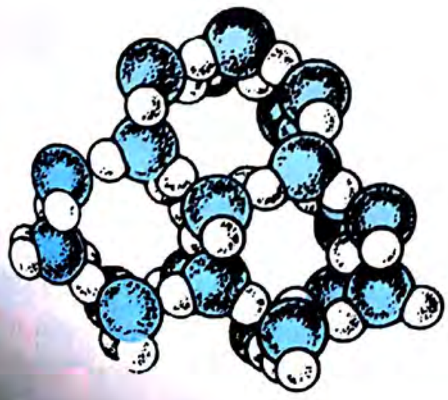


CAUTION Since a mixture of hydrogen and air is explosive, do not ignite the gas at the jet until a tube of gas collected at the jet burns silently when ignited with a burning splint.

Result Drops of condensed water are formed on the bottom of the retort flask, near the jet where the hydrogen is burning. These drops of water turn the white anhydrous copper(II) tetraoxosulphate(VI) blue.

Conclusion Since water is formed when hydrogen burns in air, we can infer that water is an oxide of hydrogen. This fact can also be confirmed by the electrolysis of acidified water which yields hydrogen and oxygen only.

Fig. 16.5 Open lattice structure of ice.



- magnesium and zinc react only with steam to liberate hydrogen and form oxides;
- iron reacts only with excess steam at red heat;
- copper, gold, silver and mercury do not react with water in any form.

Non-metals like chlorine, oxygen and silicon also react with water.

Oxides of alkaline metals readily form strong alkalis or hydroxides with water. Calcium oxide partially dissolves in water to form calcium hydroxide or slaked lime.

Certain oxides of non-metals like carbon, sulphur and nitrogen form acids with water.

Water reacts with organic and inorganic compounds. Such reactions are generally described as hydrolysis. For example,

$Al_2S_3(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s) + 3H_2S(g)$

Test for water

When a few drops of water are added to

- white anhydrous copper(II) tetraoxosulphate(VI), it turns blue;
- blue cobalt(II) chloride, it turns pink.

However, these two tests are not specific for water. They only indicate the presence of water. Any aqueous solution or substance containing water will give a positive test for water.

$$\underset{\text{white anhydrous}}{CuSO_4(s)} + 5H_2O(l) \rightarrow \underset{\text{blue hydrate}}{CuSO_4.5H_2O(s)}$$

$$\underset{\text{blue anhydrous}}{CoCl_2(s)} + 6H_2O(l) \rightarrow \underset{\text{pink hydrate}}{CoCl_2.6H_2O(s)}$$

SOLUTIONS

A *solution* is formed when a solid, such as crystals of copper(II) tetraoxosulphate(VI), dissolves in a liquid, such as water, to produce a homogeneous mixture. The solid is called the solute and the liquid the *solvent.*

$$\underset{\text{solute}}{CuSO_4(s)} + \underset{\text{solvent}}{5H_2O(l)} \rightarrow \underset{\text{solution}}{CuSO_4.5H_2O(s)}$$

A solution is a uniform or homogeneous mixture of two or more substances. A solute is a dissolved substance which may be a solid, liquid or gas. A solvent is a substance (usually a liquid, although it may be a solid or a gas) which dissolves a solute.

Water as a universal solvent

The most common solvent in nature is water. It is usually referred to as the *universal solvent.* Water molecule has a structure which is polar in nature, i.e. one side of the molecule is positively charged while the other side is negatively charged.

As a result of this polar structure, water is an excellent solvent for electrovalent solutes such as mineral salts, mineral acids and bases. These are mainly inorganic substances. All covalent compounds which contain the hydroxyl group will also dissolve easily in water. Examples are organic solids like sugar, and organic liquids like alkanol and propane-1,2,3-triol (glycerol).

Besides these, all gases can dissolve in water to some extent. Gases which ionize in solution, or which react with water are found to be very soluble, e.g. ammonia, hydrogen chloride and nitrogen(IV) oxide. Other gases like sulphur(IV) oxide, carbon(IV) oxide and chlorine, which ionize only slightly, are found to be fairly soluble in water. Gases which do not ionize at all in water are only sparingly soluble. Examples of such gases are oxygen, hydrogen, nitrogen and carbon(II) oxide. In general, the solubilities of gases decrease with an increase in the temperature.

Organic solvents

Water and other polar solvents dissolve most inorganic substances, but only a few organic ones. Organic substances dissolve readily in solvents like kerosene, petrol, benzene and turpentine. These are known as organic or non-polar solvents and are obtained from crude oil.

Types of solutions

Familiar solutions are those where the solutes are dissolved in a liquid solvent. When the liquid is water, the solution is known as an *aqueous solution.*

In some cases, the apparent solution of a solute in a solvent is accompanied by a chemical reaction. This is often known as a chemical solution. For example, when magnesium appears to dissolve in dilute hydrochloric acid, what actually happens is that the magnesium attacks the acid to form magnesium chloride, which dissolves in the water present.

Table 16.1 Examples of solutions

Solution	Solute (state)	Solvent (state
Brine	Sodium chloride(s)	Water(l)
Anti-freeze	Alkanol(l)	Water(l)
Soda water	Carbon(IV) oxide(g)	Water(l)
Brass	Zinc(s)	Copper(s)
Air	Mainly oxygen(g)	Nitrogen(g)

Experiment 16.3 To show that certain solutes dissolve only in certain types of solvents.

Requirements *Solutes* (a) Sodium chloride crystals, (b) copper(II) tetraoxosulphate(VI) crystals, (c) sugar (sucrose), (d) iodine crystals, (e) naphthalene, (f) grease, (g) sulphur, (h) rubber, (i) paint and (j) quicklime.

Solvents Water, ethanol, petrol, turpentine, benzene and carbon(IV) sulphide.

Method Arrange 6 rows of 10 test-tubes each. Add the relevant solvent (5.0 cm^3) and solute (0.5 g) to each tube and shake the mixture vigorously to dissolve the solute. Record your results for each pair of solute and solvent as either soluble or insoluble.

Arrangement of test-tubes

Solute / Solvent	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
Water										
Ethanol										
Petrol										
Turpentine										
Benzene										
Carbon(IV) sulphide										

Result The results may be summarized as follows:

Solute	Suitable solvent	Solute	Suitable solvent
Sodium chloride	Water	Grease	Paint
Copper(II) sulphate(VI)	Water	Sulphur	Carbon(IV) sulphide
Sugar	Water	Rubber	Benzene
Iodine	Ethanol	Paint	Turpentine
Naphthalene	Ethanol	Quicklime	None

Conclusion Water, a polar solvent, dissolves the inorganic salts and sugar, while the non-polar dissolve the organic substances.

Uses of solvents

Solvents play an important role in our everyday life. Some common uses of solvents are listed below.

1 In laundries and dry cleaners,
  - fat, oil and grease stains are removed by solvents like petrol, kerosene or ammonia solution;
  - paint stains are removed by turpentine;
  - coffee or tea stains are removed by a solution of borax in water.

2 For the general cleaning of household or office furniture and equipment, petrol is used to remove stains of wax, grease, fat and oil.

3 In the manufacture of perfumes, aromatic (i.e. sweet-smelling) oils are dissolved in ethanol.

4 In the laboratory, chlorophyll (the green pigment in leaves) is extracted by boiling the leaves in ethanol.

5 The vulcanizer's solution for mending punctures in the inner tubes of car tyres is prepared by dissolving rubber and certain other substances in benzene.

6 The iodine solution for dressing wounds in the dispensary is prepared by dissolving solid iodine in ethanol.

7 Turpentine is used to mix water-proof paints for the painting of walls.

8 Water, being the universal solvent, serves as a very suitable medium for most chemical reactions especially in living systems.

COLLOIDS

True solutions and colloidal solutions

When solute particles dissolve such that they are able to get in between the solvent particles, the resultant

Experiment 16.4 To find out whether true and false solutions can pass through the pores of a filter paper (filtration).

Method Make a true solution of common salt in water and a false solution of starch in boiling water. Filter the solutions separately. Then test the filtrates for the presence of common salt and starch respectively as follows:

(a) *To test for sodium chloride* Add a few drops of silver trioxonitrate(V) solution to the filtrate of the salt solution. What do you observe?
(b) *To test for starch* Add a few drops of iodine solution in alkanol to the filtrate of the starch solution. What do you observe?

Result **(a)** A white precipitate is formed indicating the presence of sodium chloride in the filtrate of the salt solution.
(b) The filtrate of the starch solution turns blue indicating the presence of starch.

Conclusion The solute particles of both the true and false solutions can pass through the pores of a filter paper.

Experiment 16.5 To find out whether dialysis can take place with both true and false solutions.

Theory Dialysis is the passage of both water and crystalloid solutes through a semi-permeable membrane. A semi-permeable membrane is a membrane which allows only the solvent molecules of a solution to pass through its pores.

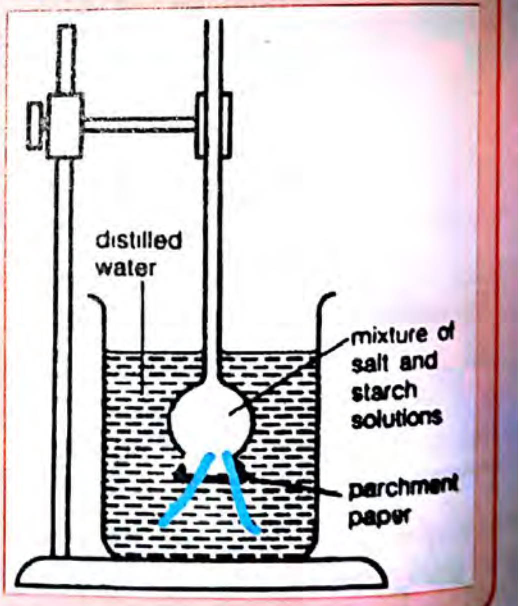
A suitable semi-permeable membrane for dialysis is parchment paper. It has pores big enough to be permeable to water molecules and some solute molecules which are slightly bigger than that of water, but impermeable to other larger solute particles like those in starch colloids.

Method Mix a salt solution and a starch solution. Cover a thistle funnel with a piece of parchment paper and pour the mixture into the funnel. (Where a thistle funnel cannot be obtained, make a bag out of the parchment paper and fill it with the mixture.) Suspend the mixture in a beaker of distilled water and allow it to stand. After a few days, take samples of the water in the beaker and test them for sodium chloride and starch as before.

Result Only sodium chloride particles pass through the parchment membrane to the surrounding water.

Conclusion Only solutes of true solutions can be dialyzed.

Fig. 16.6 Dialysis.



homogeneous mixture is called a true solution. The solute particles, which are simple molecules or ions, are too small to be seen by the naked eye and are called *crystalloids*. Examples of true solutions are aqueous solutions of sodium chloride and copper(II) tetraoxosulphate(VI).

In *false solutions* or *colloidol solutions*, the individual solute particles are larger than the particles of the true solution, but not large enough to be seen by the naked eye. Some examples of colloids are starch and albumen.

Table 16.2 True and false solutions.

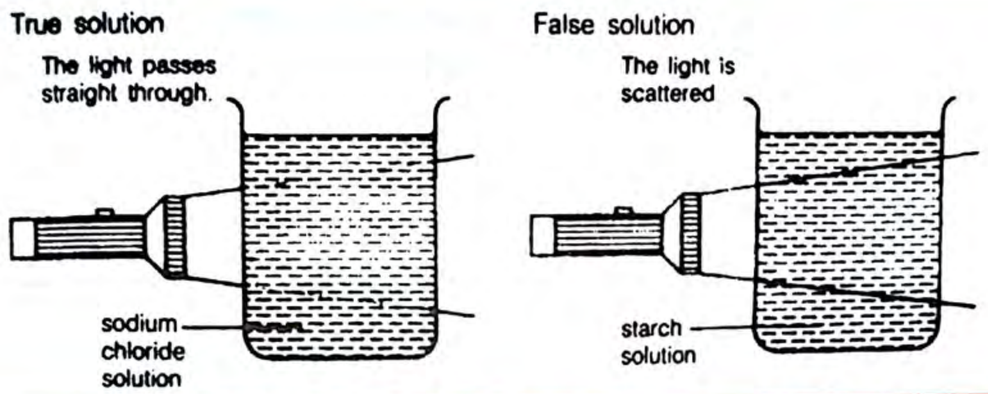
True solution	False solution
• The solutes can pass through a filter paper.	The solutes can pass through a filter paper
• The solution can be dialyzed, i.e. the solutes can diffuse through a semi permeable membrane.	The solution cannot dialyzed.
• The solutes do not scatter light rays.	The solutes can scat light rays. i.e. the solution exhibits the Tyndall effect.

Experiment 16.6 To demonstrate that false solutions scatter light while true solutions do not.

Theory Colloidal particles, unlike the crystalloids of true solutions, are large enough to block the path of light rays and scatter them. This scattering of light by a colloidal solution is known as the *Tyndall effect.*

Method Place a true solution (sodium chloride or copper(II) tetraoxosulphate(VI) solution) and a colloidal solution (starch solution) in separate beakers in a dark room. Shine a beam of light from a torch into each solution as shown.

Fig. 16.7 Tyndall effect.



Result The light beam can be clearly seen in the beaker containing the false solution, but not in the beaker containing the true solution.

Conclusion Only false solutions can scatter light rays, i.e. exhibit the Tyndall effect.

Types of colloids

In a colloidal or false solution, the liquid solvent is more appropriately known as the *dispersion medium* while the solid solute particles constitute the *dispersed substance.* As in the case of solutions, in colloids too, the dispersion medium and dispersed substance may be a solid, a liquid or a gas. The most important colloid is protoplasm, the living matter in cells.

Sols and gels The most common type of colloid is one where solid particles are dispersed in liquid medium. Such solid-liquid colloidal system are called *sols.* Most sols can solidify under certain conditions to form gels. Examples of sols are starch, glue, agar, jelly, gelatin and clay.

Aerosols These are systems where liquid particles are dispersed in a gas. Fog and smoke are aerosols. Examples of aerosols are the sprays of insecticides and deodorants from aerosol cans.

Emulsion In this colloidal system, a liquid is dispersed in another liquid. Examples of emulsions are milk, hair cream and cod liver oil emulsion. Butter is a solid emulsion, i.e. liquid particles are dispersed in a solid medium. The cleaning action of soap and detergents is due to their ability to form emulsions.

Table 16.3 Examples of aolloids.

Examples of colloids	Solvent or dispersion medium	Solute or dispersed substance
Fog	Gas	Liquid
Smoke	Gas	Solid
Foam or lather	Liquid	Gas
Emulsions	Liquid	Liquid
Sols	Liquid	Solid

Coagulation of colloids

The dispersed particles in colloids cannot be separated from the medium by fiitration. However, they can be precipitated or coagulated by the addition of solutions containing metal ions. This is what happens at the mouth of a river, when river-water and sea-water mix. The ions in the sea-water precipitate the mud particles in the river-water. As a result, mud settles at the mouth of a river to form a delta.

SUSPENSIONS

In a suspension, the dispersed particles can be seen with the naked eye. If the suspension is left undisturbed, the dispersed particles eventually settle down, leaving the solvent or dispersion medium clear.

A suspension is a heterogenous mixture of undissolved particles in a given medium. The particles are usually large enough to be seen without the aid of an instrument, and they eventually settle down if left standing.

The Harmattan is a dusty north-easterly wind which blows across the Sahara Desert towards West Africa during the dry season between January and March. It is an example of a suspension of dust and fine sand particles in the air. It produces a haze which reduces visibility. The suspended sand particles usually settle on exposed surfaces especially on the leaves of plants, buildings and vehicles.

In some suspensions, the particles are too small to be seen. They appear to have dissolved in the medium and may not settle on any exposed surface. Such examples are border-line cases between suspensions and colloidal solutions. They are described as colloidal suspensions. They have the characteristics of both a colloidal solution and a suspension. Examples are clouds, fog, smoke and aerosol sprays.

Table 16.4 Particle sizes of solutions, colloids and suspensions.

True solution	The particles are less than 10^{-9} m in size. They exist in their simplest forms, i.e. as molecules or ions. They are not visible to the naked eye and are homogeneously distributed in the solvent.
Colloidal solution	The particles are between 10^{-9} m and 10^{6} m in size. They are large but not big enough to be seen with the naked eye. They are usually formed by a large collection of molecules clinging to one another.
Suspension	The particles are larger than 10^{-6} m. They are heterogeneously distributed in the solvent and will settle down if left standing for some time.

The characteristics of true solutions, colloidal solutions and suspensions are due to the sizes of their dissolved or dispersed particles.

SOLUBILITY

Although most substances are soluble in water, some are more soluble than others, i.e. their solubilities differ. Solubility is a means of comparing the extent to which different solutes can dissolve in a particular solvent at a definite temperature.

Saturated and unsaturated solutions

A given volume of water can only dissolve a certain amount of salt in it at room temperature. If more salt is added to such a solution, the salt will remain undissolved. Such a salt solution is said to be saturated.

A saturated solution of a solute at a particular temperature is one which contains as much solute as it can dissolve at that temperature in the presence of undissolved solute particles.

The composition of a saturated solution is not affected by the presence of excess solute particles. On the other hand, an unsaturated solution can continue to dissolve more solutes, if added, until the solution becomes saturated. The concentration of a saturated solution varies with the solute, the solvent, and with the temperature.

In a saturated solution, the dissolved solutes and the undissolved solutes are in equilibrium at a particular temperature. Any change in temperature will disturb this equilibrium and the system must alter to counter the change. Since the solution of many substances is accompanied by heat absorption, an increase in temperature will result in a corresponding increase in the solubility of these substances. On the other hand, when a saturated solution is cooled, excess solute will crystallize out, i.e. solubility generally decreases with a decrease in the temperature.

Supersaturated solutions

It is possible to cool saturated solutions of certain substances, for example,

- sodium trioxothiosulphate(VI)-pentahydrate, $Na_2S_2O_3.5H_2O$, and
- sodium tetraoxosulphate(VI)-decahydrate, $Na_2SO_4.1OH_2O$,

without the excess solute crystallizing out, provided no undissolved solids or dust particles are present. This cooled solution which contains more of the solute than is present in a saturated solution at that particular temperature is said to be *supersaturated*.

A supersaturated solution is one which contains more of the solute than it can normally hold at that temperature.

Supersaturated solutions are unstable and the excess solute will separate out if the solution is disturbed slightly by shaking or if a tiny crystal of the solute or even a dust particle is dropped into it. Even scratches inside the container can serve as centres of crystallization for the excess solute.

Determination of solubility

The solubility of a solute in a solvent at a particular temperature is the maximum amount of the solute in moles or grams that will saturate 1 dm³ of the solvent at that temperature.

Experiment 16.7 To find the solubility of potassium trioxonitrate(V) in water at room temperature.

Method ***Stage 1*** To half a boiling-tube of distilled water, add excess potassium trioxonitrate(V) crystals and stir for some time. When no more of the salt can dissolve, filter the solution. The filtrate is a saturated solution of potassium trioxonitrate(V) at the prevailing room temperature.

Stage 2 Pour some of the saturated solution into a weighed evaporating dish. Weigh the dish again and find the mass of the saturated solution. Heat the solution to dryness on a water-bath. Cool and dry the residue in a desiccator and weigh again. Find the mass of the solvent that was evaporated, and hence the amount of solute that dissolved in that amount of the solvent. Express this concentration in terms of moles per dm^3.

NOTE Use dry apparatus to avoid diluting the saturated solution.

Speciment result

Mass of the saturated solution = 55.27 g

Mass of the solvent evaporated = 43.40 g

Mass of the dry residue (KNO_3) = 11.87 g

Molar mass of KNO_3 = 101 g

Mass of dissolved KNO_3 = 11.87 g

$$\therefore \text{ molarity of dissolved } KNO_3 = \frac{11.87}{101} = 0.118 \text{ mole}$$

1 g of water = 1 cm^3 of water

$\therefore$ 43.4 g or cm^3 of water is saturated by 0.118 mole of KNO_3.

$$1\,000 \text{ cm}^3 \text{ of water will be saturated by } \frac{1\,000 \times 0.118}{43.4} \text{ mole of } KNO_3. = 2.7 \text{ moles of } KNO_3.$$

Conclusion Solubility of KNO_3 in water at room temperature is 2.7 moles dm^{-3}.

NOTE To determine the solubility of potassium trioxonitrate(V) at 60°C, heat the salt solution in a water-bath. Add the solute, stirring at intervals, until the water-bath reaches a temperature of 65 °C. Then remove the flame, stir the solution continously, always maintaining some undissolved potassium trioxonitrate(V) crystals at the bottom of the tube. At exactly 60 °C, decant some of the saturated solution, determine the amount of solute in it and calculate the solubility

The method of determining the solubility of a given solute involves two stages:

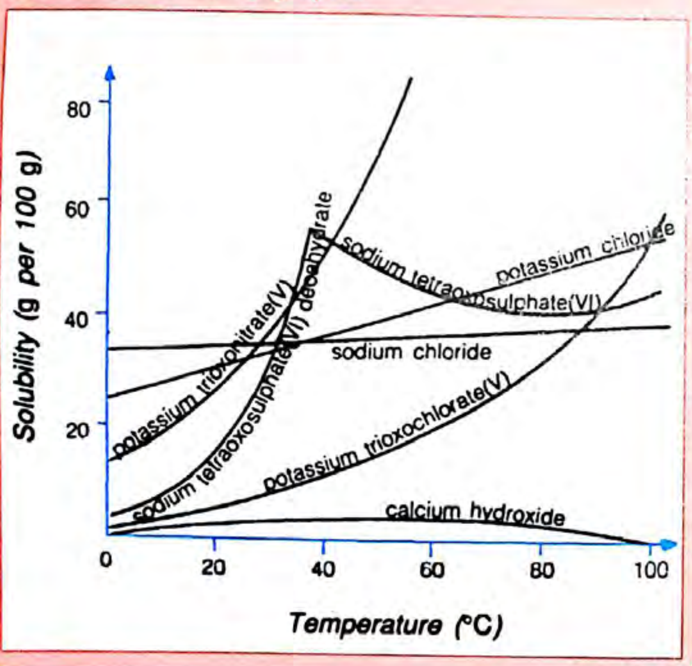
Stage 1 Preparing a saturated solution of the given solute at the specified temperature.

Stage 2 Taking a known mass of the saturated solution and heating it to dryness so that the exact mass of the solvent and the solute in the saturated solution at that temperature can be calculated.

Solubility graphs or curves

If the solubilities of a solute in a given solvent are plotted against their respective temperatures, *a solubility graph* or *curve* showing the effect of temperature on the solubility of the substance will be obtained. For comparing the solubilities of different solutes in a given solvent, several curves can be plotted on the same axes (see fig. 16.8).

Fig. 16.8 Solubility graphs.



Deductions from the solubility curves

From fig. 16.8, we can deduce the following for the temperature range of 0 °C to 100 °C.

1 Solubilities of potassium trioxochlorate(V) and potassium trioxonitrate(V) increase very rapidly with increase in temperature.

2 Solubilities of sodium chloride and calcium hydroxide are independent of temperature.

3 Sodium tetraoxosulphate(VI) shows a sol curve with a sharp break at 36 °C. This is bec the salt exists in solution as sodium tetrao sulphate(VI)-decahydrate, $Na_2SO_4.10H_2O$, temperatures below 36 °C but gives up its wat of crystallization to become anhydrous temperatures above 36 °C. Thus, 36 °C is referre to as the *transition point*. If cooled, a saturated solution of sodium tetraoxosulphate(VI) wil deposit

- the hydrated crystals, $Na_2SO_4.10H_2O$, temperatures below 36 °C, and
- the anhydrous salt, Na_2SO_4, at temperature above 36 °C.

4 At all temperatures between 0 °C and 100 °C calcium hydroxide has the lowest solubility of the six compounds. It also shows a decrease i solubility at temperatures over 70 °C.

5 The solubility of potassium chloride increases a a constant rate with the rise in temperature.

Applications of solubility curves

1 Solubility curves enable pharmacists to determine the amounts of solid drugs that must be dissolved in a given quantity of solvent to give a prescribed drug mixture.

2 The curves also enable chemists and research workers to determine the most suitable solvents to be used at various temperatures for the extraction of essential chemicals from various natural sources.

3 With the help of solubility curves, a given mixture of solutes can be separated or purified by fractional crystallization. When a saturated solution of such a mixture is cooled, those fractions with very low solubilities will be the first to crystallize out of solution while those solutes that are still within their limits of solubility will remain in solution.

Solubility of gases

The solubility of most solid solutes increases with rise in temperature. The solubility of most common gases, however, decreases with a rise in temperature. Hydrogen chloride gas is an exception. Gases which do not react with water are only slightly soluble i water. Gases like ammonia and hydrogen chloride which are verv soluble in water forrn alkali and acid solutions respectively. Air is sparingly soluble in water.

The solubility of a gas is directly proportional to the pressure of the gas. Aerated drinks are made by dissolving carbon(IV) oxide under pressure. When an aerated drink can or bottle is opened, the pressure is released and bubbles of carbon(IV) oxide gas are given off.

EXAMPLES

1 *If 12.2 g of lead(II) trioxonitrate(V) were dissolved in 21 g of distilled water at 20°C, calculate the solubility of the solute in mol dm^{-3}.*

Molar mass of $Pb(NO_3)_2$ = 331 g

12.2 g of $Pb(NO_3)_2$ $= \frac{12.2}{331} = 0.037$ mole.

21 g of water at 20 °C dissolved 0.037 mole of $Pb(NO_3)_2$,

$\therefore$ 1000 cm^3 of water at 20 °C dissolved $\frac{1000 \times 0.037}{21}$

= 176 moles of $Pb(NO_3)_2$.

$\therefore$ at 20 °C, the solubility of $Pb(NO_3)_2$ in water is 1.76 moles dm^{-3}.

2 *The solubility of potassium trioxonitrate(V) is exactly 1 800 g per 1 000 g water at 83 °C and 700 g per 1 000 g water at 40° C. Calculate the mass of potassium trioxonitrate(V) that will crystallize out of solution if 155 g of the saturated solution at 83 °C is cooled to 40 °C.*

	solvent +	solute =	solution
Masses involved at 83 °C:	1 000 g	1 800 g	2 800 g
Masses involved at 40 °C:	1 000 g	700 g	1 700 g

Solute deposited on cooling
from 83 °C to 40 °C = 2 800 − 1 700 = 1 100 g

On cooling from 83 °C to 40 °C,
2 800 g of saturated solution deposit 1 100 g of solute.

$\therefore$ 155g of saturated solution will deposit $\frac{1\,100 \times 155}{2800}$

= 60.89 g of solute.

SUMMARY

- Rain, springs, wells, rivers, lakes and seas are natural sources of water. Most natural water con dissolved mineral salts, suspended impurities and germs.
- Distilled water is chemically pure water. It is used in the laboratory, in the preparation of drugs an certain industrial processes.
- In a water treatment plant, water from natural sources undergoes coagulation, sedimentation, filtration disinfection to make it safe for domestic and industrial uses.
- Hard water does not lather readily with soap. This is due to the presence of certain calcium and magnes salts.
- Temporary hardness of water is due to the presence of calcium hydrogentrioxocarbonate(IV). It can removed by boiling and using slaked lime.
- Permanent hardness of water is mainly due to the presence of calcium and magnesium ions in the fo of soluble tetraoxosulphates(VI) and chlorides. These ions are removed by adding washing soda or caus soda, or by passing the hard water through an ion exchange resin.
- Water pollution is caused by oil spills and the indiscriminate dumping of refuse, sewage, and indust and agricultural wastes into water bodies. It threatens aquatic life and changes water bodies into fo smelling, unsightly scenes.
- Water is composed of the elements hydrogen and oxygen combined in the ratio 2:1.
- The presence of water can be tested with the following two compounds:
  - (a) Anhydrous copper(II) tetraoxosulphate(VI) which turns from white to blue.
  - (b) Cobalt(II) chloride which turns from blue to pink.
- The unusual physical properties of water such as high boiling point, melting point and surface tension a due to the presence of hydrogen bonding.
- The water molecules in ice form an open lattice structure, where the water molecules are not as closel packed together as in liquid water. This makes ice less dense than water.
- Water is the universal solvent. It is polar in nature and dissolves most inorganic solutes and some pola organic solutes to form aqueous solutions.
- Organic solvents like kerosene, petrol and benzene dissolve non-polar organic solutes.
- A solution is formed when a solute dissolves in a solvent to form a homogeneous mixture. The solu particles are less than 10^{-9} m in size.
- A colloid is a false solution where the particles are between 10^{-9} m and 10^{-6} m in size. The particles a said to be dispersed in a given medium. The particles cannot be seen by the naked eye and they do no settle down on standing.
- Colloid particles can pass through filter paper but not through parchment paper. Colloids can also scatt light rays unlike true solutions. This is known as the Tyndall effect.
- Sols, gels, aerosols and emulsions are colloids. Colloidal particles can be precipitated or coagulated b the addition of metal ions.

A suspension is a heterogeneous mixture of undissolved particles in a given medium. The particles are larger than 10^{-6} m. They can be seen with the naked eye and they eventually settle down on standing.

A saturated solution of a solute at a particular temperature is one which contains as much solute as it can dissolve at that temperature in the presence of undissolved solute particles.

A supersaturated solution is one which contains more of the solute than it can normally hold at that temperature.

The solubility of a solute in a solvent at a particular temperature is the maximum amount of solute in moles or grams that will saturate 1 000 dm^3 or grams of the solvent.

The solubility of gases generally decreases with a rise in temperature, while that of most solid solutes increases.

EXERCISES

Distilled water is different from deionized water because

A distilled water is a product of condensed steam while deionized water is filtered laboratory water.

B distilled water is always pure and sold in packs while deionized water is not packaged for consumption.

C distilled water is a condensed steam but deionized water is produced using exchange resins which absorb undesired ions.

D distilled water is man made while deionized water is both natural and artificial.

Treated town water undergoes the following steps except

A co-agulation. B sedimentation.
C precipitation. D chlorination.

Water is temporarily hard because it contains

A $CaSO_4$. B $MgSO_4$.
C chlorine. D $Ca(HCO_3)_2$.

Temporary hardness of water is removed by the use of the following except

A boiling.
B use of $Ca(OH)_2$.
C use of Na_2CO_3.
D use of alum.

5. One of these is not a water pollutant:

A Petroleum.
B Domestic liquid and solid water.
C Industrial effluents.
D Biodegradable chemicals.

6. These are abnormal physical properties except

A turns to ice when cooled below 0°C.
B high boiling point.
C solid water contracts when heated.
D solid water is less dense than liquid water.

7. Which is the odd-man-out?

A HCl B NH_3
C NO_2 D CO

8. Coffee stains are removed with

A turpentine.
B ammonia.
C borax in water.
D petrol.

9. The following are characteristics of colloids except

A tyndall effect on light beam.
B solid phase are removed by dialysis.
C colloidal particles are larger than that of suspensions.
D colloidal particles are separated using parchment membranes.

10. Solute is to true solution as ______ is to colloids.
- A dispersion medium
- B dispersed phase
- C crystalloids
- D aerosol

11. The following are examples of colloids except
- A smoke.
- B foam.
- C emulsion.
- D paints.

12. A saturated solution is a solution
- A in which the solute is in equilibrium with the solvent.
- B in which the solute saturates the solution.
- C the solvent can still accept more solute except when the temperature is lowered.
- D whose solvent has low solubility at a given temperature.

13. A graph of solubility against temperature is called
- A sigmoid curve.
- B supernant curve.
- C solubility curve.
- D dispersion curve.

14. On heating 25 g of a saturated solution to dryness at 60°C, 4 g of anhydrous salt was recovered. Calculate its solubility in grammes per 100 g of solvent.
- A 25 g/100
- B 19.05 g/100
- C 40 g/100
- D 38.1 g/100

15. The solubility of alcohols in water is due to
- A their covalent nature.
- B hydrogen bonding.
- C their low boiling point.
- D their low freezing point.
- E their ionic character.

16. A common solvent of sulphur is
- A water.
- B carbon(IV) sulphide.
- C alcohol.
- D methanol.
- E ethanoic acid.

17. (a) Describe how river water is treated a rendered suitable for human consump

(b) Some samples of hard water can be softe easily by boiling while others requir chemical treatment for softening. Justify the statement. Give three chemical methods for removing the hardness of water. Write the respective equations.

18. Distinguish between true and false solutions. Explain the differences between them. Write briefly on the following:
- (a) Fog
- (b) The Harmattan
- (c) Sol
- (d) Smoke
- (e) Cloud
- (f) Coagulation

19. Describe the common causes of water pollution in Nigeria.

20. 1.33 dm^3 of water at 70 °C are saturated by 2.25 moles of lead(II) trioxonitrate(V), $Pb(NO_3)_2$; and 1.33 dm^3 of water at 18 °C are saturated by 0.53 mole of the same salt. If 4.50 dm^3 of the saturated solution are cooled from 70°C to 18 °C, calculate the amount of solute that will be deposited in
(a) moles, (b) grams.
(Pb = 207, N = 14, O = 16)

21. What is a supersaturated solution? Define the term solubility of a solute. How would you determine the solubility of potassium trioxonitrate(V) at 60 °C? How would you calculate the solubility from your results?

22. (a) What are solubility curves? Give three uses of solubility curves. A solubility curve of sodium tetraoxosulphate(VI) for a temperature range of 0 °C to 100 °C has a break at 36 °C. Explain why this is so.

(b) Water was added to 120.0 g of a salt, MCl_2, to produce 60.0 cm^3 of a saturated solution at 25 °C. Its solubility at 25 °C is 8.0 mol dm^{-3}. Calculate the mass of the salt which remained undissolved.

(M = 24, Cl = 35.5)

SHAPES OF MOLECULES AND SOLIDS

17

POLAR AND NON-POLAR MOLECULES

Some substances are attracted by a non-uniform electrostatic field while others are not. We can show this by carrying out the following experiment. Fill a burette with water, open the tap and bring

- a positively-charged rod near the thin jet of water; then
- a negatively charged rod near the jet of water.

In both cases, the jet of water is deflected towards the rod.

If we replace the water with trichloromethane, we get the same result. However, if we replace it with tetrachloromethane, there is no deflection.

Substances which are deflected by a non uniform electrostatic field are said to be *polar*, while those which are not deflected are said to be *non-polar.*

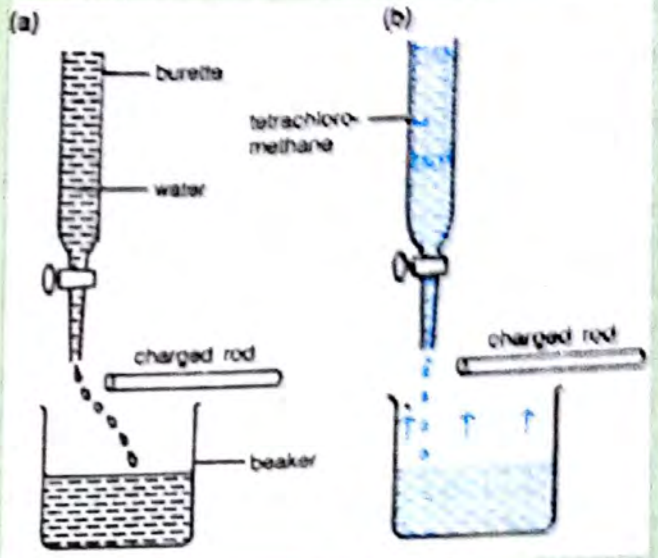
Table 17.1 [illegible] liquids.

Liquids deflected by charged rod (polar)	Liquids not deflected by charged rod (non-polar)
Water	Tetrachloromethane
Trichloromethane	Benzene
Ethanol	Cyclohexane

Polar substances consist of polar molecules. A polar molecule is one that contains positive and negative poles. There is a partial positive charge δ+, at one point in the molecule and a partial negative charge, δ–, at another point (see fig. 17.2)

Let us consider hydrogen chloride, a simple polar molecule. In the hydrogen chloride molecule the bonding electrons will not be shared equally by the hydrogen and chlorine atoms, because the chlorine atom has a greater attraction for the electrons than the hydrogen atom. We say that chlorine is more electronegative than hydrogen.

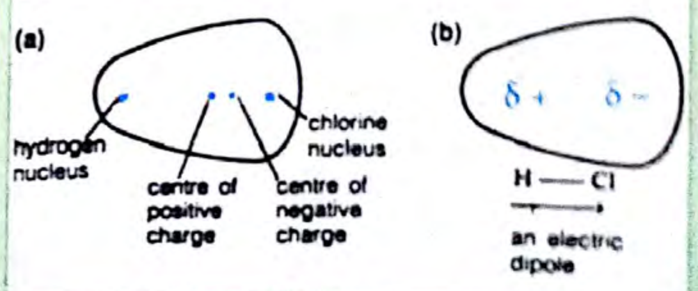
Fig. 17.1 Effect of a charged rod on a jet of liquid.



The centre of the negative charge in the hydrogen chloride molecule is closer to the chlorine atom than to the hydrogen atom. This overall distortion of charge in molecules such as hydrogen chloride, which results from the unequal sharing of electrons, is known as *polarization.* Such molecules are said to be *dipolar* and the separation of charges in the molecule is referred to as a *dipole.*

The uneven distribution of electrons in hydrogen chloride is represented as an electron cloud. As the centre of the positive charge and that of the negative charge do not coincide, a permanent *electric dipole* results.

Fig. 17.2 Electric dipole in a hydrogen chloride.



NOTE Conventionally, an electric dipole is represented by +→, with the arrow pointing towards the negative end.

When polar liquids flow from a burette past a positively charged rod, the negative ends of the polar molecules are attracted towards it. With a negatively charged rod, the positive ends of the polar molecules are attracted.

Trichloromethane, $CHCl_3$, is deflected by a non-uniform electrostatic field, whereas tetrachloromethane, CCl_4, is not. To explain this difference in behaviour between the molecules, we have to examine their structures first.

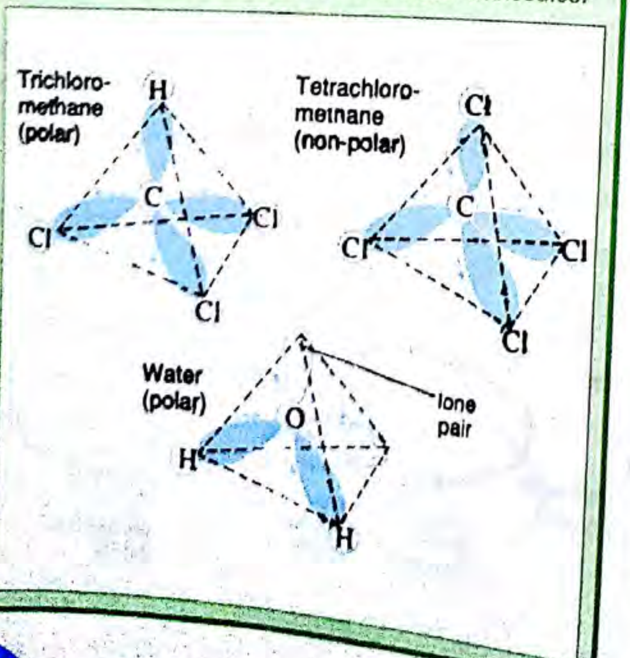
Tetrachloromethane has a symmetrical distribution of similar atoms. Each of its four bonds is a dipole, C+→Cl. In such a distribution, the equal dipoles cancel each other and the compound is non-polar. The structure of trichloromethane is not symmetrical. We note that the dipoles do not cancel each other. Thus, the compound is polar.

Water molecule is also polar. In this case, the covalent bonds and the lone pair of electrons contribute to its polar nature.

From these examples, we note that three factors determine whether a molecule is polar or non-polar. These are

- the polarity of the covalent bond;
- the number and position of lone pairs; and
- the shape of the molecule.

Fig. 17.3 Electric dipoles in trichloromethane, tetrachloromethane and water molecules.



A study of the polarity of a molecule may help t deduce the structure of the compound. For example, from the fact that carbon(IV) oxide is non-polar, we can assume that it has a linear structure (so that the two C+→ H dipoles cancel out). The fact that water is polar indicates that it cannot have a linear structure.

ELECTRONEGATIVITY

In non-symmetrical molecules such as hydrogen chloride and water, the centre of the positive charge and the centre of the negative charge do not coincide. The polarity in these molecules is due to the presence of highly electronegative elements such as oxygen and chlorine.

The electron attracting power, or *electronegativity* of an atom is different in different compounds since it will depend on the atoms to which it is attached. One of the most widely used scales of electronegativity values is that devised by Linus Pauling. Pauling defined the *electronegativity of an atom as the power of that atom in a molecule to attract electrons to itself.* Regardless of the scale used, electronegativity of the elements in the Periodic Table generally increases across the Periodic Table and decreases down the groups. Thus, from the Periodic Table, we notice that the most electronegative element is fluorine, while the least electronegative element is caesium.

Electronegativity values can be used to estimate the polarity of different bonds. In general,

- bonds between elements of widely different electronegativities (e.g. between a metal and a non-metal, such as in sodium chloride) will be highly polar, i.e. ionic in nature;
- bonds between elements of similar electronegativities will be non-polar or only slightly polar and essentially covalent if the elements are non-metals, (e.g. the bonding between oxygen and sulphur).

The existence of a dipole confers partial ionic character to a covalent molecule. As the polarity of the molecule increases, the ionic character of the substance also increases.

In chapter 4, bonds are described as being wholly covalent or wholly ionic. However, we have just learnt that the equal sharing of electrons we would expect in a covalent bond is not true in most cases. Instead, in many covalent molecules, unequal electrons occurs, thus conferring a partial ionic character to the molecules.

Similarly, electron density maps (obtained by X-ray analysis) of many ionic compounds indicate varying degrees of covalent bonding. Thus, it is important to realize that the wholly ionic and wholly covalent bonds are extreme types. Generally, all ionic compounds have some covalent character, and most covalent compounds have some ionic character.

SHAPES OF SIMPLE COVALENT MOLECULES

We normally represent simple covalent molecules as flat structures. In reality, such molecules have definite shapes. We shall discuss the factors responsible for their shapes.

In covalent molecules, atoms combine by sharing electrons. The single covalent bond that is formed results from an overlap of two atomic orbitals, each occupied by a single electron. The bond will be orientated in the direction of the orbitals which provide the electrons, so it is said to be directional. Such bonds influence the shape and structure of the resulting molecule.

In a simple covalent molecule like methane, CH_4, the central atom is carbon. The shape of such a molecule is influenced by the total number of electron pairs in the valence shell of its central atom. The electron pairs include both shared (or bonding) pairs and lone (or non-bonding) pairs. The electron clouds of these pairs are negatively charged. Within a molecule, such electron clouds mutually repel each other and stay as far apart as possible. This affects the shape of the molecule.

Methane

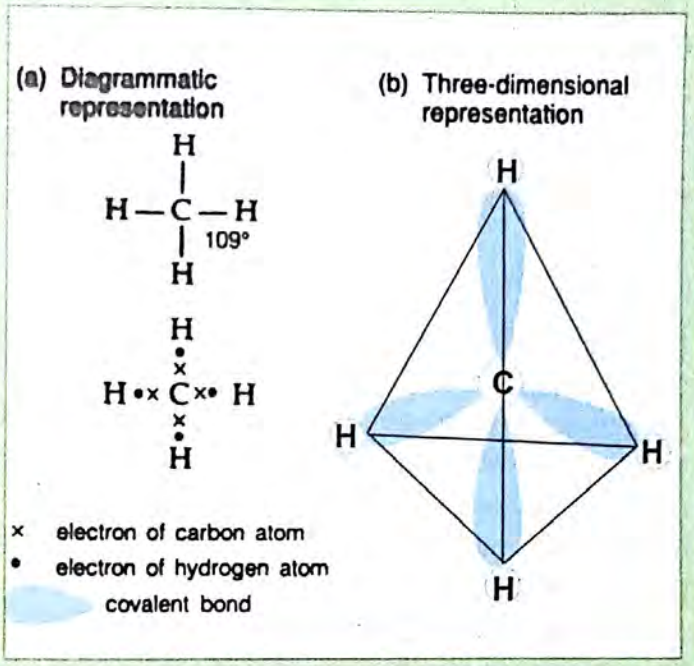
In a molecule of methane, CH_4, the central atom is carbon. Carbon has the following electronic configuration:

$1s^22s^22p^2$ (or ↑↓ ↑↓ ↓ ↓ ☐)
$1s^2$ $2s^2$ $2p_x^1$ $2p_y^1$ p_z

It has only two unpaired electrons available for bond formation in its valence shell. However, in methane and most carbon compounds, carbon shows a valency of four. To achieve this, one of the 2*s* electrons is "promoted" to occupy the empty $2p_z$ orbital, creating four unpaired electrons (one *s* and three *p*) in its valence shell as shown.

$1s^22s^12p^12p_x^12p_y^12p_z^1$ (or ↑↓ ↓ ↓ ↓ ↓)
$1s^2$ $2s^1$ $2\,p_x^1$ p_y^1 p_z^1

Fig. 17.4 Tetrahedral shape of the methane molecule.



In the methane molecule, each of the four unpaired electrons of the carbon atom forms a bond with an electron from a hydrogen atom. Altogether, the carbon atom in methane has four bond pairs of electrons in its valence shell, i.e. the octet electronic configuration is achieved.

The C–H bonds in methane are identical although the valence electrons in the carbon atom consist of one s and three p electrons. This can be explained if the 2s and three 2p orbitals merge or *hybridize* to form four new orbitals that are identical to each other. This new set of four hybrid orbitals are called sp^3 indicating that one *s* and three *p* orbitals are combined.

The electron clouds of the four bond pairs of electrons in methane are equally negatively charged, so they tend to repel one another to an equal extent. To minimize the repulsion, the four bond pairs become widely spread so that the four electron pairs are directed towards the corners of a regular tetrahedron. In this spatial arrangement, carbon lies in the centre with the four hydrogen atoms situated at the apices of the tetrahedron. The bond angle between any two covalent bonds is approximately 109°.

Ammonia

In a molecule of ammonia, NH3, the central atom is nitrogen, with the following configuration:

$$1s^22s^22p^3 \text{ (or } \underset{1s^2}{\boxed{\uparrow\downarrow}}\ \underset{2s^2}{\boxed{\uparrow\downarrow}}\quad \underset{2p_x^1}{\boxed{\downarrow}}\ \underset{p_y^1}{\boxed{\downarrow}}\ \underset{p_z^1}{\boxed{\downarrow}}\text{)}$$

It has three unpaired electrons in the $2p$ orbitals and one lone pair in the $2s$ orbital of its valence shell. Each of the three unpaired electrons forms a covalent bond with an electron of a hydrogen atom. Altogether, the nitrogen atom in ammonia has three bond pairs of electrons and one lone pair in its valence shell. Thus, the octet rule for stability is satisfied.

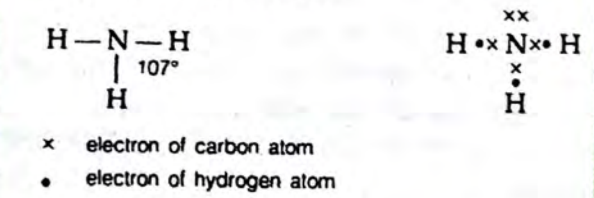
Like the methane molecule, the electron clouds of the four pairs of electrons are also spaced out but into a slightly different shape. This is because ammonia contains one lone pair of electrons, whereas methane contains no lone pair of electrons. Lone pair electrons have a greater repelling effect than bond pairs. The relati repelling strengths of electron pairs are as shown belo

Lone pair-lone pair repulsion > Lone pair-bond pair repulsion > Bond pa bond pai repulsion

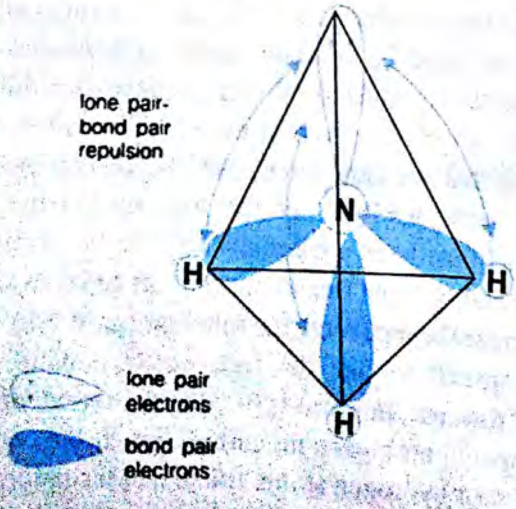
Due to the large repulsive force exerted by th lone pair on the three neighbouring bond pairs o electrons, the ammonia molecule has a trigon pyramidal shape, where the three hydrogen atom occupy the corners of the triangular base, with th lone pair electrons occupying a large space at the ape The bond angle between two N—H bonds i approximately 107°.

Fig. 17.5 The trigonal pyramidal shape of the ammonia molecule.

(a) Diagrammatic representation



(b) Three-dimensional representation



Water

In a molecule of water, H_2O, the central atom i oxygen. Oxygen has the following electroni configuration:

$$1s^22s^22p^4 \text{ (or } \underset{1s^2}{\boxed{\uparrow\downarrow}}\ \underset{2s^2}{\boxed{\uparrow\downarrow}}\quad \underset{2p_x^2}{\boxed{\downarrow\uparrow}}\ \underset{p_y^1}{\boxed{\downarrow}}\ \underset{p_z^1}{\boxed{\downarrow}}\text{)}$$

Its valence shell has two lone pairs of electron ($2s^22p_x^2$) and two unpaired electrons ($2p_y^12p_z^1$). Each unpaired electron forms a covalent bond with a electron from a hydrogen atom. The water molecul has two lone pairs of electrons and two bond pairs of electrons in the valence shell of its central atom thereby satisfying the octet rule for stability.

Ideally, the four electron pairs should be directe towards the corners of a tetrahedron as in methan However, when one lone pair of electrons is locate near another lone pair, the repulsion between them i so great that they "squeeze" the other two bond pai of electrons closer together. As a result, the bond angl in water is compressed to approximately 105°, su that the structure of the water molecule is V-shape (or angular).

Carbon(IV) oxide

In the three covalent molecules just discussed, on single covalent bonds have been described. Th carbon(IV) oxide molecule, CO_2, has double bon

By forming two double bonds with neighbour oxygen atoms, the carbon atom achieves the oc

Fig. 17.6 The angular shape of the water molecule.

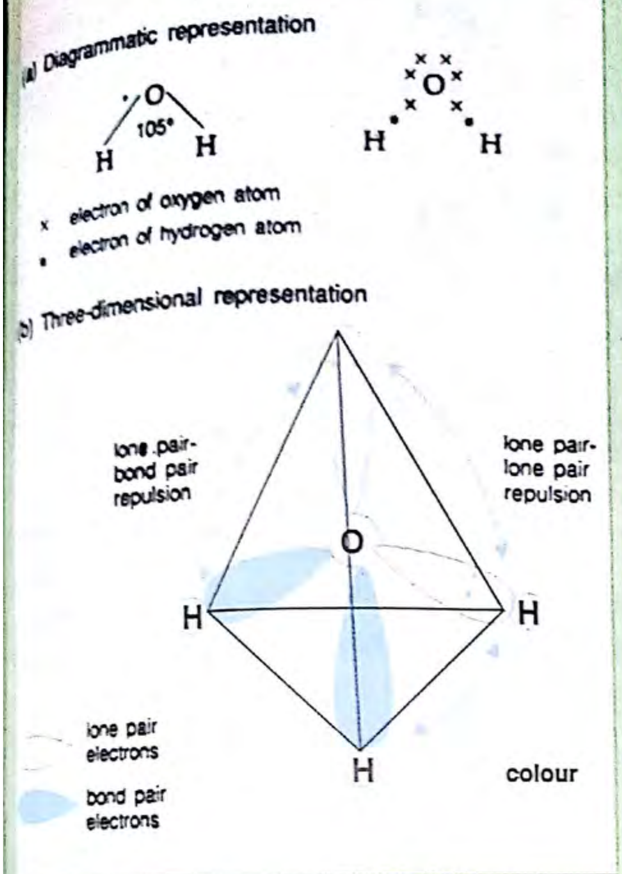
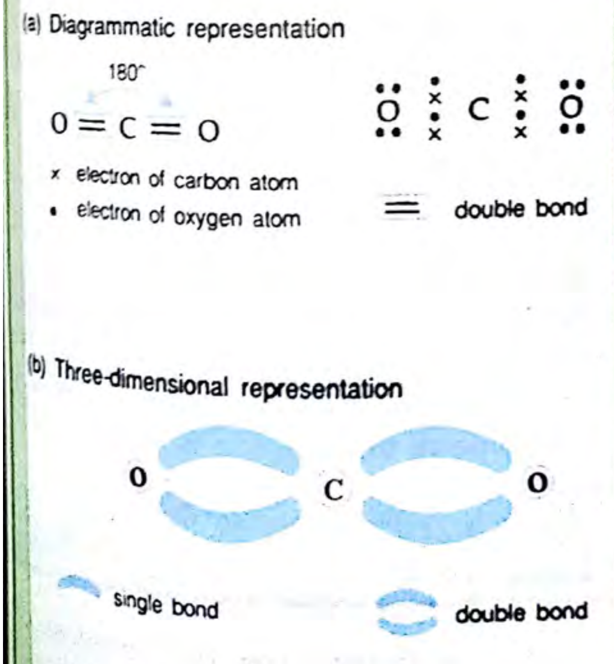


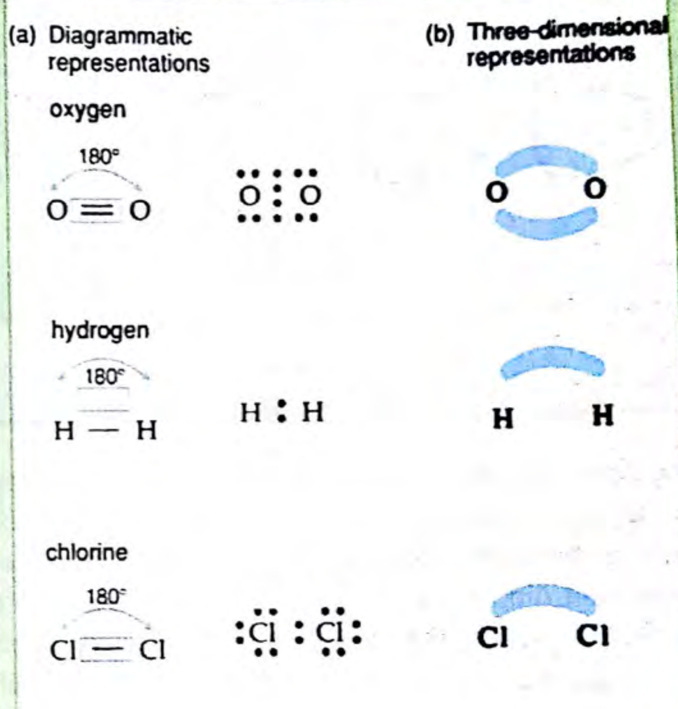
Fig. 17.7 The linear shape of the carbon(IV) oxide molecule.



electronic configuration. However, electron clouds of the double covalent bonds repel each other because of their similar charge and close proximity. As such, the bonds are distorted and under strain, giving the molecule a linear shape (i.e. all the three atoms lie in a straight line).

Other examples of covalent molecules with linear shapes are the molecules of oxygen, O_2, hydrogen, H_2, and chlorine, Cl_2.

Fig. 17.8 The linear shapes of oxygen, hydrogen and chlorine molecules.



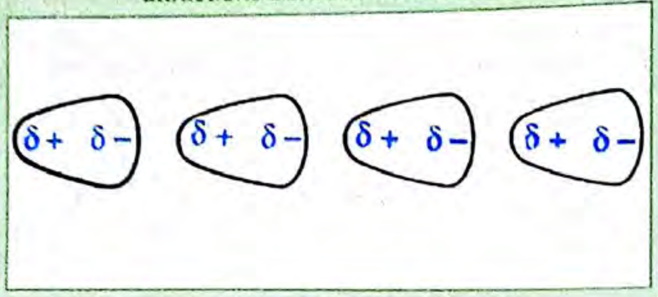
INTERMOLECULAR FORCES

The forces existing between molecules are known as intermolecular forces. These forces are much weaker than electrovalent and covalent bonds. They can be classified into three types: *dipole-dipole attractions, van der Waals forces and hydrogen bonding*. More than one type of intermolecular force may be present between molecules.

Dipole-dipole attractions

Trichloromethane molecules are polar because of the non-symmetrical distribution of charge within each molecule. The interactions between the permanent dipoles explain the attraction between neighbouring trichloromethane molecules. The positive end of one polar molecule attracts the negative end of another molecule. These attractions are called *permanent dipole-permanent dipole attractions.* The existence of these dipole-dipole attractions explains the forces holding together the polar molecules in liquids such as trichloromethane. As a result of dipole-dipole interaction, polar molecules are generally held to each other more strongly than non-polar molecules of comparable mass.

Fig. 17.9 Permanent dipole-permanent dipole attractions between molecules.

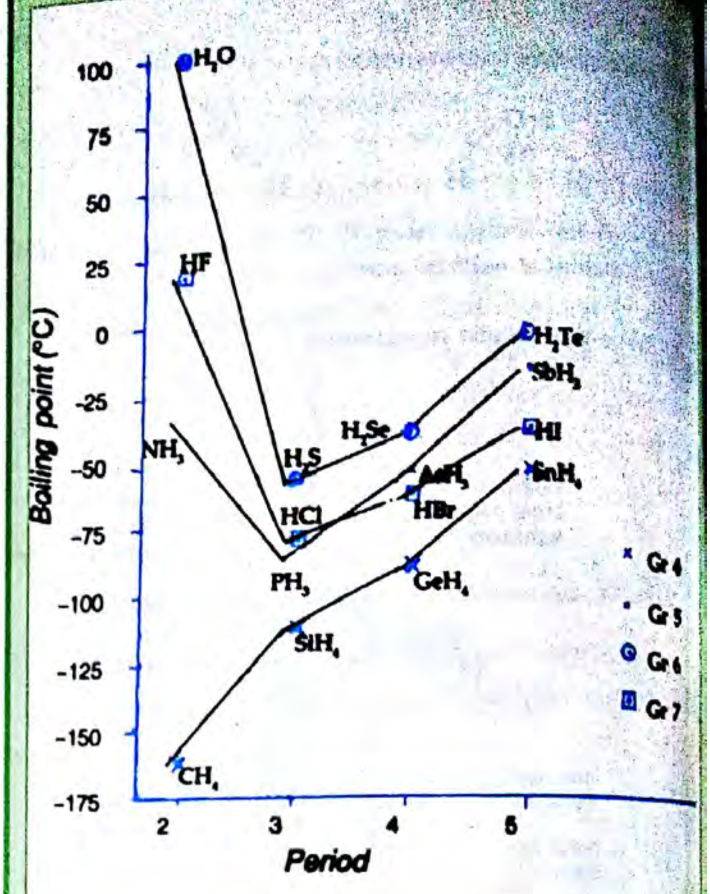


Van der Waals forces

The dipole-dipole attractions cannot be used to account for the forces between non-polar molecules in liquids such as tetrachloromethane, because they have no permanent dipole. In 1873, the Dutch physicist, van der Waals, postulated the existence of weak, short-range forces of attraction, which are independent of normal bonding forces, between non-polar molecules. He came to this conclusion after studying the behaviour of real gases at low temperatures and high pressures These forces are known as *van der Waals forces.*

On the average, electrons in a non-polar molecule such as hydrogen are close to one nucleus as to the other. However, at a given instant, the electron cloud may be concentrated at one end of the molecule. This momentary concentration of the electron cloud on one side creates a temporary dipole in the hydrogen molecule, i.e. one side of the molecule acquires a partial negative charge while the other side acquires a partial positive charge of equal magnitude. The temporary dipole induces a similar dipole in an adjacent molecule. This results in a temporary dipole-induced dipole attraction between the positive and negative ends of the adjacent molecules. Electron movements in the molecules cause the concentration of the electron clouds to shift sides continually but the attractive force between the adjacent molecules remains constant. This is how weak van der Waals forces are set up. These forces generally exist between atoms and between molecules in the solid, liquid and gaseous states.

Fig. 17.10 Graphs of the boiling points of the [illegible] of Groups 4, 5, 6 and 7.



As the size of a molecule increases, the number of constituent electrons increases. As a result, the temporary dipole-induced dipole attractions become stronger. This is illustrated by the increase in the boiling points of the halogens and the boiling points of the alkanes.

Usually van der Waals forces are weak forces which are between one-tenth to one-hundredth the strength of covalent bonds.

The van der Waals force between layers in graphite is strong enough to hold the layers together, but sufficiently weak to allow them to slide over each other. Because of this, graphite is used as a solid lubricant.

Hydrogen bonds

Fig. 17.10 shows the boiling points of the hydrides of Groups 4, 5, 6 and 7 elements. We notice that the boiling points of the hydrides in Group 4 decrease with decreasing relative molecular mass from tin(IV) hydride (SnH_4) to methane (CH_4). However, when we look at the boiling points of the hydrides of the elements in Group 5, we note that although there is a general decrease from antimony hydride (SbH_3) through arsenic hydride (AsH_3) to phosphorus hydride (PH_3), ammonia (NH_3) has a much higher boiling point than one would expect. A similar pattern is observed in the hydrides of Groups 6 and 7 elements.

The unusually high boiling points of hydrogen fluoride, water and ammonia are due to the presence of *hydrogen bonds*. A hydrogen bond is a strong dipole-dipole attraction which occurs between

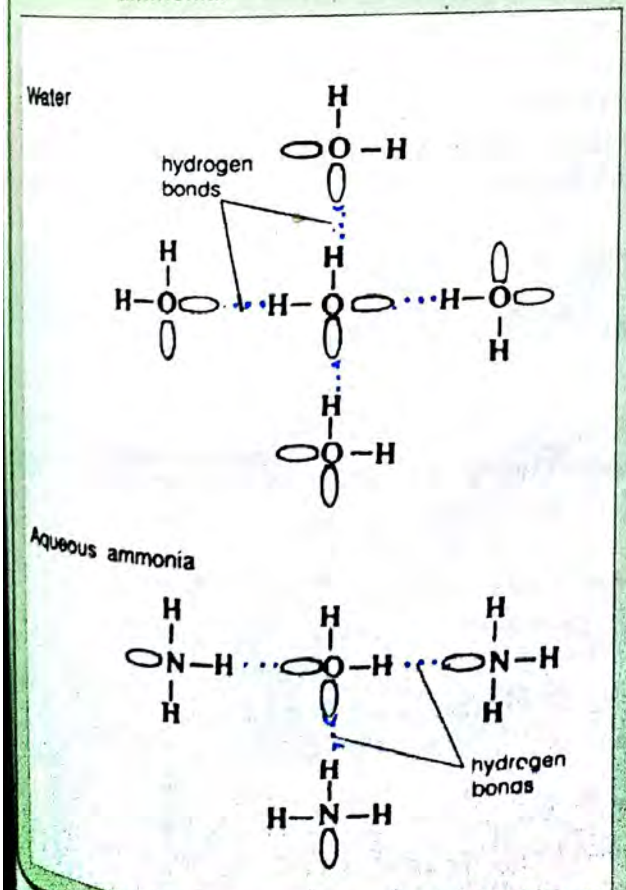
- the hydrogen atom attached to a strongly electronegative atom, and
- another strongly electronegative atom with a lone pair of electrons.

Hydrogen fluoride, water and ammonia contain the three most electronegative elements, fluorine, oxygen and nitrogen respectively, linked directly to hydrogen. In addition, lone pairs of electrons are present in the fluorine, oxygen and nitrogen atoms of the three hydrides. Thus, hydrogen bonds form readily between the molecules of each hydride in the following way:

:X—H   :X—H   where X = N, O or F
↑   : = lone pair of electrons
hydrogen bond

Hydrogen bonding causes the molecules of the hydrides to aggregate, forming chains. This accounts for their higher boiling points. The hydrogen bonds, however, are weak and break off easily when heat is applied. The strongest hydrogen bonds are found in hydrogen fluoride, since fluorine is the most electronegative element.

Fig. 17.11 Hydrogen bonding in water and aqueous ammonia.



SOLIDS—THEIR STRUCTURES AND PROPERTIES

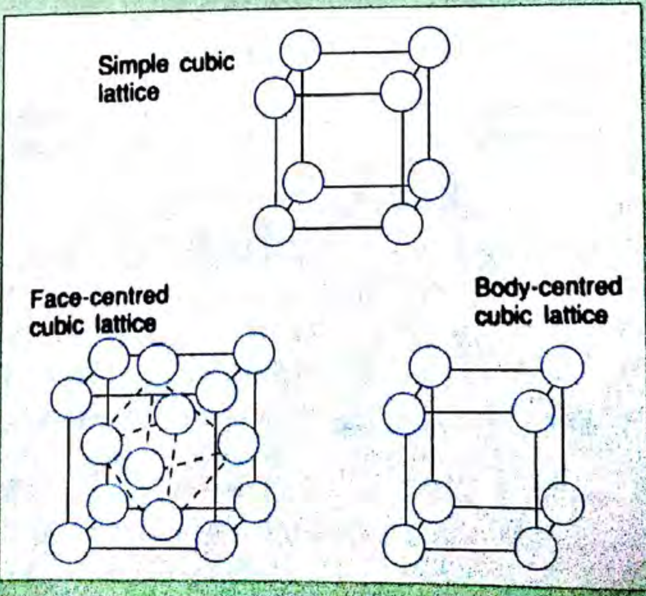
In chapter 5, we learnt that particles in a solid are packed closely together in a fixed pattern. These particles can vibrate about a fixed position but they cannot translate. Thus, solids are rigid and have definite shapes and volumes.

Many solids have definite geometric shapes. Such solids are said to be crystalline.

General Structures of Crystals

The external shape of a crystal is the result of the spatial arrangement of the particles that make up the crystal. This three-dimensional arrangement of the particles is

Fig. 17.12 The three types of cubic unit cells



called the *crystal lattice*. The crystal lattice may be considered to be made up of *unit cells* which are each the smallest portion of the crystal lattice which shows the complete pattern of the particles in their relative positions.

The shape of the unit cell, and therefore of the crystal, depends on

- the force of attraction between the particles; and
- whether the particles are the same or different, and, if they are different, on their relative sizes.

There are three kinds of unit cells based on the cubic structure. These are as follows:

1. *Simple cubic* structure in which the particles are placed one at each corner of the cube.
2. *Face-centred cubic* structure in which there is a particle at each corner and one in the centre of each face of the cube.
3. *Body-centred cubic* structure in which there is a particle at each corner and one at the centre of the cube.

Types of Crystalline Solids

We have just seen that crystals can be grouped according to their structure. Crystals can also be classified according to the chemical nature of their particles, i.e. as covalent, ionic, molecular and metallic.

Covalent solids

Covalent solids are made up of atoms joined to one another by covalent bonds to form a giant lattice. The covalent bonds are quite strong. As a result, these solids are quite hard and have a high melting point. They are also poor conductors of electricity.

The best example of a covalent solid is a diamond crystal which is usually octahedral in shape. The crystal lattice is built up from a basic three-dimensional tetrahedral unit cell. In this unit cell, a carbon atom is linked to four other carbon atoms by covalent bonds (of equal lengths) which are directed towards the apices of a regular tetrahedron. This basic unit cell is repeated indefinitely, forming a giant three-dimensional molecule.

As a result of the strength and uniformity of the bonds, and the stable and rigid crystal lattice, diamond is the hardest substance known. It is also very resistant to high temperatures and chemical attack. Because of the compactness of its crystal structure, diamond has a relatively high density of 3.5 g cm^{-3}. It is a non-conductor of electricity because there are no free valence electrons in the crystal, all the four valence electrons of each atom being effectively used to form covalent bonds.

In graphite, on the other hand, each carbon atom is joined to only three others by covalent bonds. The three covalent bonds lie in the same plane with an angle of 120° between them. The carbon atoms arrange themselves at the corners of adjacent hexagons, forming planes or layers. The layers are arranged in parallel, one above the other to form a crystal lattice.

Fig. 17.13 The diamond crystal.

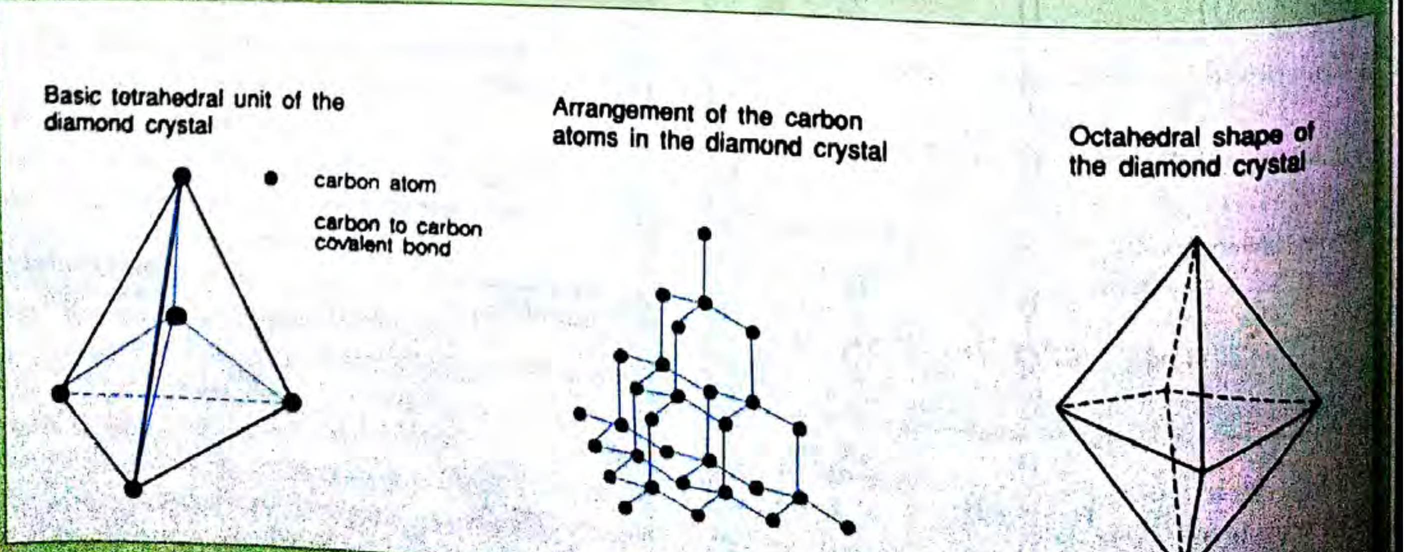


Fig. 17.14 Arrangement of carbon atoms in the graphite crystal.

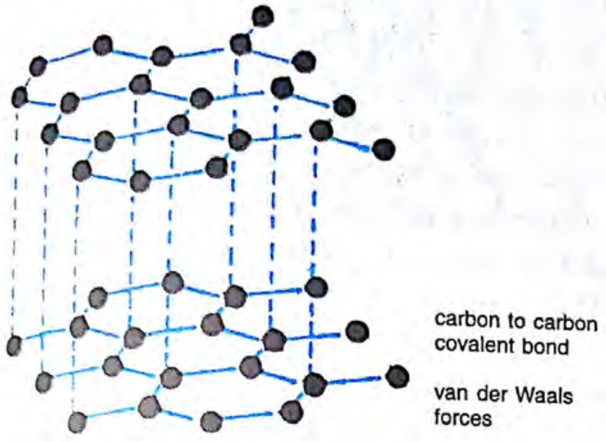
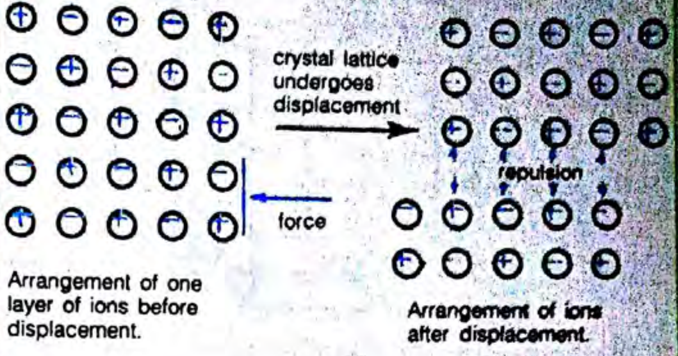


Fig. 17.15 The breaking up of a crystal lattice when struck.



The atoms in a given layer are held together by strong covalent linkages, but the forces between the layers are the weak van der Waals forces. Thus, the layers can slide readily past one another, making graphite a lubricant in the solid state. It is also very soft, slippery and flakes easily. Because of its more open structure, graphite is less dense and slightly more prone to chemical attack than diamond, e.g. it can be oxidized to six carbon-atom organic compounds under suitable conditions. Only three of the four valence electrons are held in definite bond formation. One electron is free to move about. Thus, graphite is a good conductor of electricity because of the presence of mobile electrons in the crystal lattice.

Ionic solids

Positive and negative ions are arranged in a regular pattern to give a giant crystal lattice in an ionic solid. The strong electrostatic attractions that occur between these ions of opposite charges provide the binding force that holds the crystal together. As a result, the lattice formed is determined mostly by the relative sizes of the ions and their charges. When the crystal is formed, the ions arrange themselves to maximize attractions and minimize repulsions. Examples of ionic solids are crystals of sodium chloride and copper(II) tetraoxosulphate(VI).

Ionic crystals are hard and have high melting points because the electrostatic forces holding the ions are strong. In the solid state, ionic compounds are poor conductors of electricity because the ions are held rigidly in place and so cannot move about. When melted or when dissolved in water, the ions are free to move about and the ionic substances become good conductors of electricity. Ionic solids are also brittle. When struck, they tend to shatter because as planes of ions slip by one another, they pass from a condition of mutual attraction to one of mutual repulsion.

Molecular crystals

In molecular solids, molecules are arranged in regular patterns to give crystal lattices. The molecules are held together by weak intermolecular forces such as van der Waals forces, dipole-dipole attractions and hydrogen bonds.

Generally, van der Waals forces are present in all molecular solids. In naphthalene, iodine and dry ice crystals, these are the only forces that hold the molecules together. In crystals of polar molecules such as sulphur(IV) oxide, the dominant forces are the dipole-dipole attractions; and in solids such as ice, ammonia and hydrogen fluoride, the molecules are held in place by hydrogen bonding. Since these are relatively weak forces (compared to the covalent or ionic bonds), molecular crystals tend to have small lattice energies and are easily deformed. They have low melting points and are poor conductors of electricity because the electrons are bound to individual molecules and are not able to move freely through the solid.

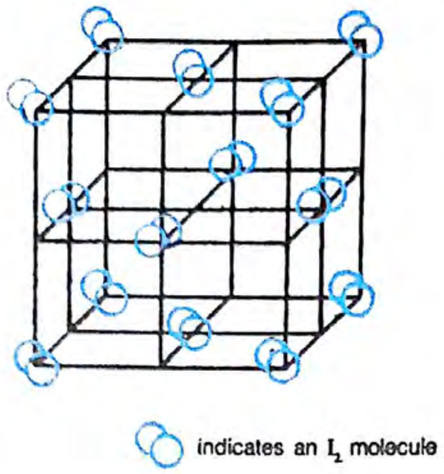


Fig. 17.16 The crystal structure of iodine.

Metallic solids

X-ray analysis reveals that metal particles are held together in a lattice of closely-packed spheres. In metallic atoms, there are relatively few valence electrons and hence, they are unable to form normal covalent bonds with the eight or twelve nearest neighbours in a solid metallic crystal. However, these valence electrons are very loosely held and they tend to separate from their particular nuclei and move at random through the crystal lattice, forming a combined electron cloud. The resultant positively charged metallic ions tend to repel one another but are held together by the attractive force of this electron cloud. It is this attraction which constitutes the *metallic bond*. (The exact nature of the bond is still unclear.)

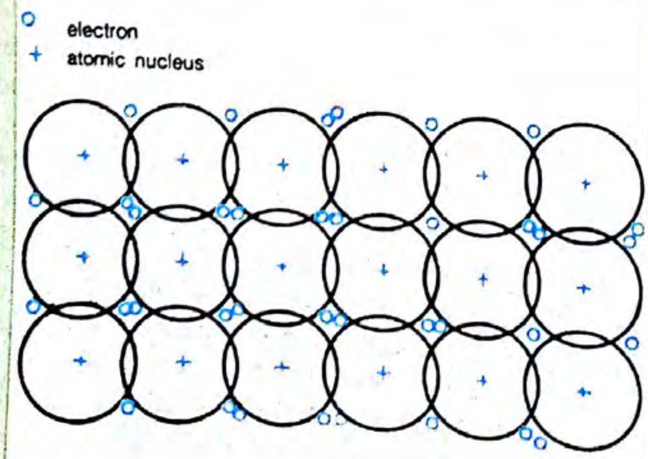


Fig. 17.17 Diagrammatic representation of metallic bonding.

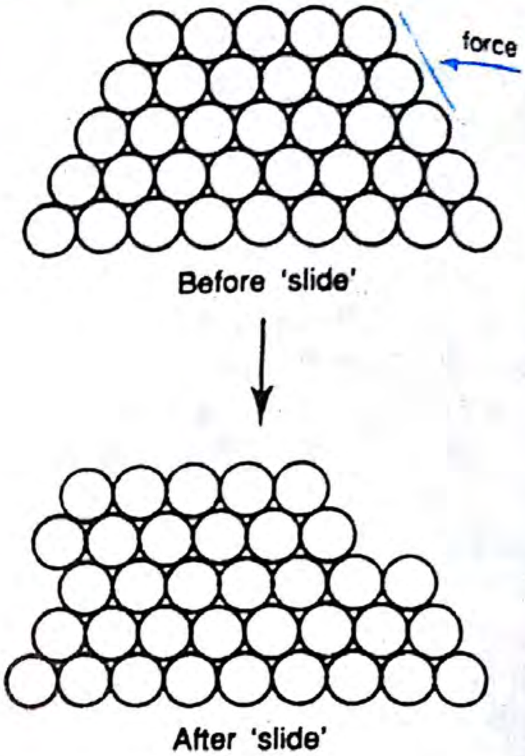


Fig. 17.18 How layers of metallic ions slide when a force is applied.

The strength of the metallic bonds varies considerably among different metals. It is much stronger in iron than in sodium or potassium, both of which can be cut easily with a knife. Metals like iron,

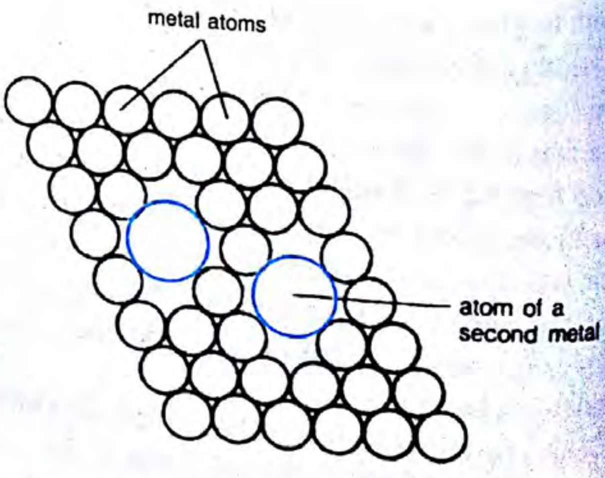


Fig. 17.19 How sliding of layers of metallic ions is prevented by alloying.

copper, tin and zinc are very malleable and ductile. This can partly be accounted for by metallic bonding. When a force is applied, the layers of metallic ions can slide over one another without shattering the crystal lattice. This is because there are no rigid, directed bonds in a metallic crystal — the bonding agent is a moving electron cloud which can easily readjust itself when the metallic layers achieve a new stable arrangement. The sliding action, however, can be hindered by the addition of a small amount of another metal. As such, alloys are generally less malleable but have greater mechanical strength than pure metals.

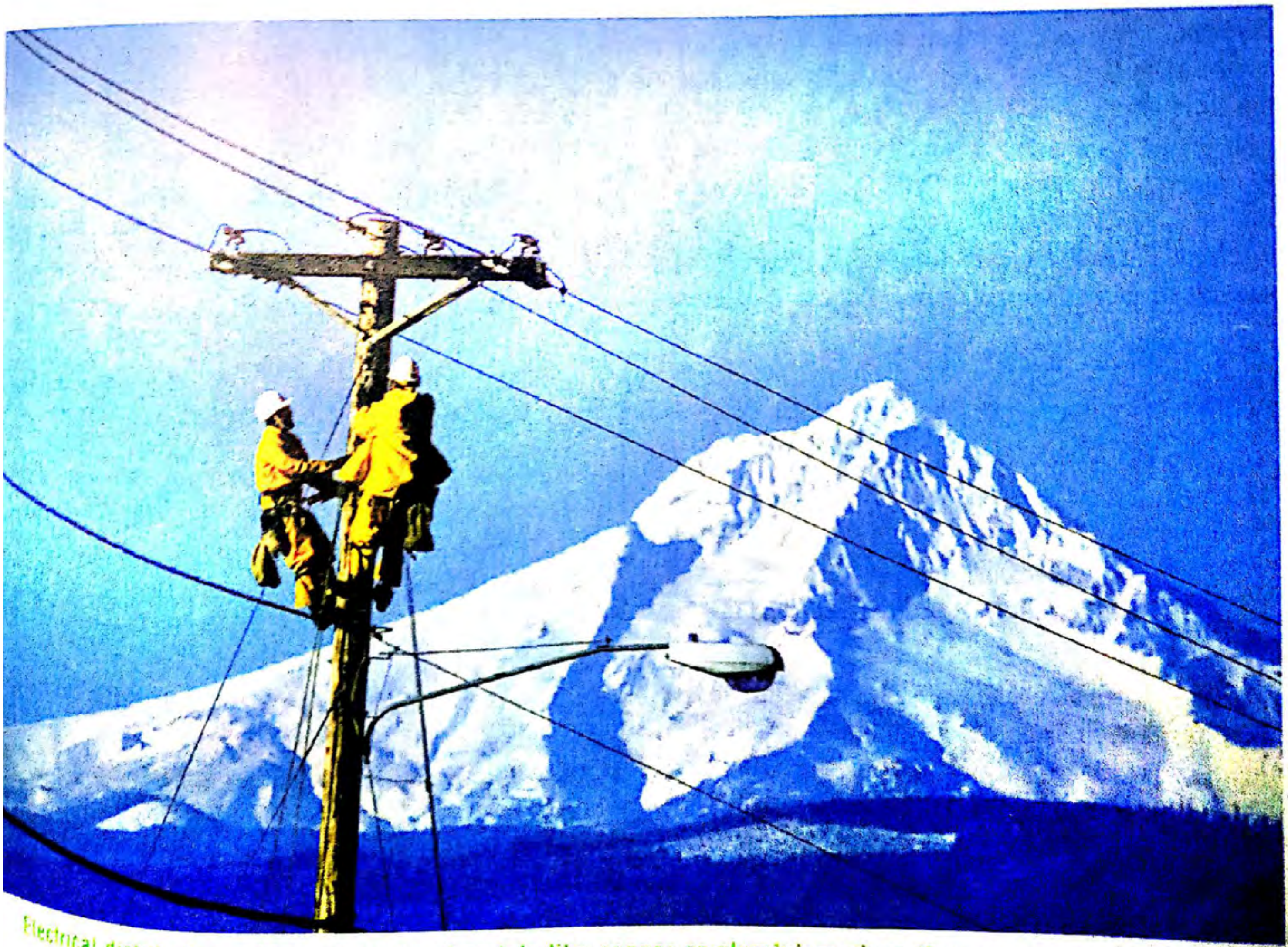
Metals are also good electrical conductors because when a metal wire is connected to the terminals of a car battery (i.e. when a potential difference is applied to the two ends of the metal wire), the electrons in the electron cloud will lose their random movement and flow through the wire in a particular direction (i.e. along the potential gradient). Metals are also good conductors of heat, since the freely moving electrons can also convey heat energy.

Table 17.2 Some common metals and their structures

Metallic structure	Metal
Face-centred cubic packing	Copper, aluminium, lead, silver, gold, strontium, iron, cobalt, nickel, platinum.
Hexagonal close packing	Magnesium, zinc, cadmium, calcium, nickel.
Body-centred cubic packing	Lithium, sodium, potassium, barium, tungsten, vanadium, chromium, iron.

The structure of metals is dependent on the different ways in which the atoms are packed together. There are three main types of metallic structures. They are *face-centred cubic packing, hexagonal close packing and body-centred cubic packing.*

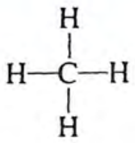
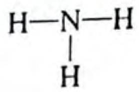
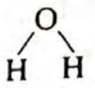
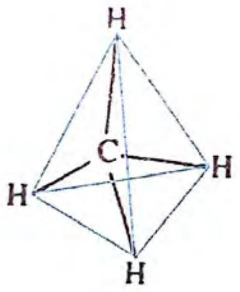
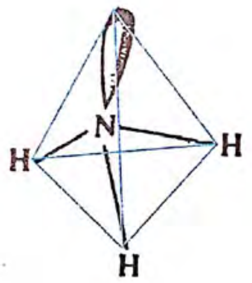
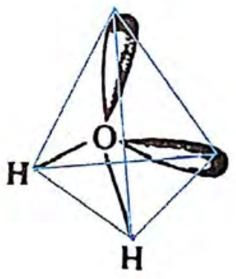
Some metals can exist in more than one type of structure. Iron has a body-centred cubic lattice below 906 °C but exists as a face-centred cubic structure between 906 °C and 1 400 °C.



Electrical distribution cables are made of metals like copper or aluminium since they are good conductors of electricity.

SUMMARY

- Molecule is polar when there is unequal sharing of electrons between the component atoms resulting in an overall distortion of charges within it. The three factors which determine whether a molecule is polar or non-polar are
  (a) the polarity of the covalent bond which in turn depends on the relative electronegativities of the atoms involved,
  (b) the number and position of lone pairs, and
  (c) the shape of the molecule.
- The electronegativity of an atom is defined as the ability of that atom to attract electrons to itself. In the Periodic Table, the value of electronegativity increases across the period and decreases down the group.
- The shapes and structural properties of some simple covalent molecules are as follows:

	CH_4	NH_3	H_2O	CO_2
Structural formula				O=C=O
Shape	Tetrahedral	Trigonal pyramidal	V-shaped (angular)	Linear
				
Bond angle	109 °	107 °	105 °	180 °
Types of bond pair	4 bond pairs	3 bond pairs 1 lone pair	2 bond pairs 2 lone pair	4 bond pairs
Types of covalent bond	Single bond	Single bond	Single bond	Double bond

- Intermolecular forces are forces that exist between molecules. There are basically three types of intermolecular forces.
  (a) Permanent dipole-permanent dipole attractions occur in polar molecules where there is a non-symmetrical distribution of charges within each molecule.
  (b) Van der Waals forces are weak, short-range forces of attraction, arising from induced dipole-induced dipole attractions.
  (c) Hydrogen bonds are weak forces that occur when a hydrogen atom is attached to an atom with high electronegativity or to an electronegative atom with at least one lone pair of electrons.

Types of crystalline solids and their properties are given below.

Type of solid	Covalent	Ionic	Molecular	Metallic
Examples	Diamond, graphite, quartz	Sodium chloride, calcium oxide	Iodine, water, methane, hydrogen chloride	Sodium, iron, copper
Type of substance	Group 4 non-metallic element or its compounds	Metallic or non-metallic compounds	Non-metal or non-metallic compounds	Metal with low electronegativity
Particles at lattice points	Atoms	Positive and negative ions	Molecules	Positive ions
Bonding in the solid	Atoms linked by strong covalent bonds	Electrostatic attraction of positive and negative ions giving strong ionic bonds	Atoms held by covalent bonds; molecules held by hydrogen bonds, van der Waals forces, etc.	Attraction between positive nuclei and mobile electrons giving rise to metallic bonds
Properties a) State at room temperature	Solids	Solids	Gases or volatile liquids	Usually solids
b) Volatility	Non-volatile with very high melting and boiling points	Non-volatile with high melting and boiling points	Volatile with low melting and boiling points	Non-volatile with high melting and boiling points
c) Hardness	Very hard and brittle	Hard and brittle	Soft	Hard yet malleable
d) Conductivity	Non-conductors except for graphite	Non-conductors as solids but good conductors in molten or aqueous state	Usually non-conductors	Good conductors as solids or liquids
e) Solubility	Insoluble in all solvents	Soluble in polar solvents	—	Soluble only in liquid metals

EXERCISES

1. These are factors which determine whether a molecule is polar or non-polar.
   A The shape of the molecule.
   B Number of lone pairs in an atom.
   C The number of electronegative elements present.
   D Polarity of the covalent bond.

2. Major contribution of dipole to covalent molecule is to
   A confer partial ionic character.
   B confer partial non-polar character.
   C confer basic character.
   D confer acidic character.

3. Covalent molecules are directional because
   A there is sharing.
   B there is overlap of two atomic orbitals.
   C there is overlap of shared clouds.
   D most of them face x and y axes.

4. Which of them is false about shapes of molecules/ions?
   A Methane is tetragonal.

B Ammonium is tetragonal.
C Ammonia is trigonal.
D Water is a linear molecule.

5. The valence shell of water molecule contains
A one lone pair and two unpaired electrons.
B two lone pairs and two unpaired electrons.
C two lone pairs and a single unpaired electrons.
D single lone pair and a single unpaired electrons.

6. These have linear molecular shapes except
A Cl_2 B HCl
C CO_2 D H_2O

7. These are intermolecular bonds or attractions except
A metallic bond.
B dipole – dipole attractions.
C van-der-Waal's forces.
D hydrogen bond.

8. These except one has no hydrogen bond.
A NH_3 B HF
C H_2O D CH_4

9. These are examples of unit cell cubic structure.
A Simple cubic structure.
B Non-linear cubic structure.
C Face-centred cubic structure.
D Body centred cubic structure.

10. Basic particles constituting different solids ar
A ions. B molecules.
C atoms. D radicals.

11. Which of the following molecules are polar?
(a) SiF_4 (b) CH_2Cl_2 (c) CS_2 (d) CH_4

12. Define electronegativity. Arrange these elements in increasing order of electronegativity.
Cl, Rb, Mg, Br, S, O, Na

13. Give the meaning of crystal lattice and unit cell. What are the three types of cubic cells?

14. Why is diamond so hard and graphite so much softer? Account for the fact that graphite conducts electricity while diamond does not.

15. Why are metals good conductors of electricity? What is the main cohesive force in metals?

16. What are the types of attractive forces present in each of the following substances at room temperature and pressure?
(a) Methane (d) Diamond
(b) Argon (e) Water
(c) Carbon(IV) oxide (f) Aluminium
For example, sulphur(IV) oxide, SO_2 contains covalent bonds within the molecules and van der Waals forces between the molecules.

RADIOACTIVITY • NUCLEAR ENERGY

18

RADIOACTIVITY

n 1896, Becquerel observed that a crystal of a *uranium salt* spontaneously emitted *radiation*, which could penetrate through opaque material to affect a photographic plate. Further experiments showed that the metal uranium and all its compounds possessed the same property. Becquerel concluded that the uranium atoms were responsible for the emission of this unknown radiation and called this phenomenon *radioactivity*.

In 1898, Pierre and Marie Curie detected some radioactivity in the element *thorium*. They also noted that the level of radiation in a naturally occurring uranium ore, called *pitchblende*, was much higher than could be explained by its uranium content. Suspecting the presence of other radioactive elements in pitchblende, they analyzed it and isolated two new radioactive elements, *polonium* and *radium*. The latter was found to be several million times as radioactive as the same mass of uranium.

These discoveries led to further investigations by scientists. Since then, more than 40 naturally occurring radioactive substances have been found.

Studies on radioactivity soon revealed that this phenomenon could not be explained by ordinary chemical reactions, which involved only the electrons of atoms. Instead, it could only be explained in terms of special changes which involved the nuclei of atoms.

Radioactivity is the spontaneous emission of radiation by an element. Such an element is called a radioactive element.

An element may have stable and radioactive isotopes, e.g. ^{12}C and ^{14}C are the stable and radioactive isotopes of carbon respectively.

Characteristic of Radioactivity

A radioactive substance emits radiation continually and spontaneously. Temperature and pressure have no effect on the rate at which this radiation is emitted. The radiation, unlike light rays, can penetrate through opaque matter. However, like visible light rays, it affects photographic plates. It also ionizes the gases through which it passes, causing fluorescence in certain substances, e.g. zinc sulphide, and leaving tracks in a cloud chamber.

Radioactivity is always associated with a release of energy. The energy of radioactivity is about a million times as great as that liberated during any chemical reaction. This type of energy is known as *nuclear energy*.

Types of Radiation

Radioactive radiation consists of three main components of different penetrating power: *alpha*- (α-), *beta*- (β-) and *gamma*- (γ-) rays. These three components can be separated and distinguished by their behaviour in an electrostatic field.

Fig. 18.1 Using an electrostatic field to separate the three types of radiation.

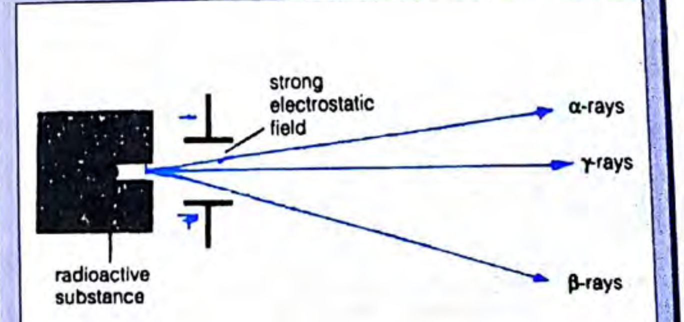


Table 18.1 Summary of the properties of α-, β- and γ-rays.

	Alpha-ray, α-ray	Beta-ray, β-ray	Gamma-rays, γ-ray
Nature	Helium nuclei, ^4_2He	Electrons, $^{0}_{-1}e$	Electromagnetic radia
Electrical charge	+2	−1	No charge
Mass	4 units	$\frac{1}{1\,840}$ unit	No mass
Velocity	About $\frac{1}{20}$ the speed of light	Varies (from 3–99% of the speed of light)	Speed of light
Relative penetration	1	100	10 000
Absorber	Thin paper	Metal paper	Large lead block

Alpha-rays

α-rays are fast-moving streams of positively charged particles, each having a mass number of four, an atomic number of two and two units of positive charge. Thus, each α-particle is actually a helium nucleus, ^4_2He. Since they are positively charged and fairly heavy, α-particles are deflected slightly towards the negative plate in an electrostatic field.

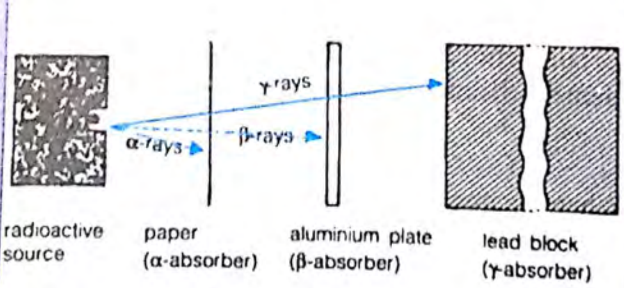
α-rays have very low penetrating power. They travel only a few centimetres in air and are stopped or absorbed by a thin sheet of paper or an aluminium foil which is only 0.1 mm thick. They exert a very powerful ionizing effect upon any gas through which they pass. In addition, α-rays can cause fluorescence in some materials, e.g. zinc sulphide.

Beta-rays

β-rays are very fast-moving streams of electrons. Since they are negatively charged and have a relatively small mass, they are quite markedly deflected towards the positive plate in an electrostatic field. Each particle has a mass number of zero and a charge of −1 and is represented by the symbol $^{0}_{-1}e$.

β-rays are much more penetrating than α-rays. Their range is about 3 m in air, and about 4 mm in aluminium. In air, the ionization power of β-particles is only about one-thousandth of that of α-particles. They also cause fluorescence in certain substances like anthracene, but not zinc sulphide.

Fig. 18.2 The three types of radiation and their absorbers.



Gamma-rays

γ-rays are not particles but electromagnetic waves similar to visible light and X-rays, but with very short wavelengths. They travel at the speed of light, and are unaffected by an electrostatic field. Of the three types of radioactive emissions, γ-rays have the least ionization power but they are the most penetrating. They can penetrate about 100 m through air and can pass through 0.5 m of iron or lead. They can also cause fluorescence in certain substances like sodium iodide and zinc sulphide.

X-rays

X-rays are electromagnetic waves, like visible light but with a shorter wavelength. They are produced by allowing fast-moving electrons to bombard metals such as tungsten. The fast-moving electrons knock electrons out of the inner shells of the metal atoms. The dislodged electrons are replaced by electrons moving in from the outer shells. This movement of lectrons is accompanied by the emission of X-rays.

X-rays can penetrate easily through most solid ubstances which are opaque to visible light, such as netal foils, flesh, wood and paper. Hard X-rays have greater penetrating ability than soft X-rays.

Soft X-rays are used in medicine to photograph uman body parts. The X-rays pass through the flesh ut are absorbed by the dense bones and produce a hadow photograph of the bones. Hard X-rays are sed for destroying cancerous cells.

In chemistry, X-rays are used to study the rrangement of particles in crystal lattices and in big rganic molecules like proteins.

Detection of Radiation

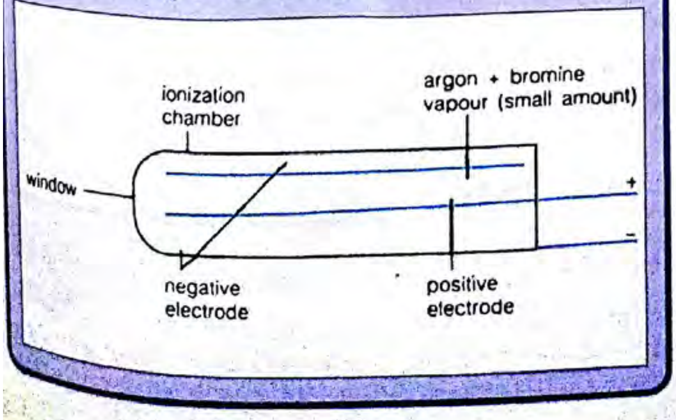
ifferent types of devices have been developed over e years for detecting radiation. The most commonly sed detectors are the *Geiger-Muller counter, the cintillation counter* and the *diffusion cloud chamber.*

Geiger-Muller counter

he Geiger-Muller counter is based on the ionizing ffect of radiation on gases. The device consists of an onization chamber into which two metal electrodes re sealed, and which is filled with a gas, usually rgon, at very low pressure, together with a little romine vapour. A potential difference of about 450 volts is maintained between the electrodes. When n ionizing particle or radiation enters the chamber, ome argon atoms are ionized. The electrons produced hen drift to the positive terminus while the positive ons migrate to the negative one. A small current, nown as a pulse current, is obtained for a short while. This current is amplified and may be detected by uitable equipment, for example, in the form of

- audible clicks from a loudspeaker;
- movement of the needle of a ratemeter; or
- reading recorded in the register of a scaler.

Fig. 18.3 Geiger–Muller counter.



The Geiger-Muller counter is a widely used detector of radioactivity. It can also be used to measure the intensity of radiation since the count rate is proportional to the intensity of the radiation.

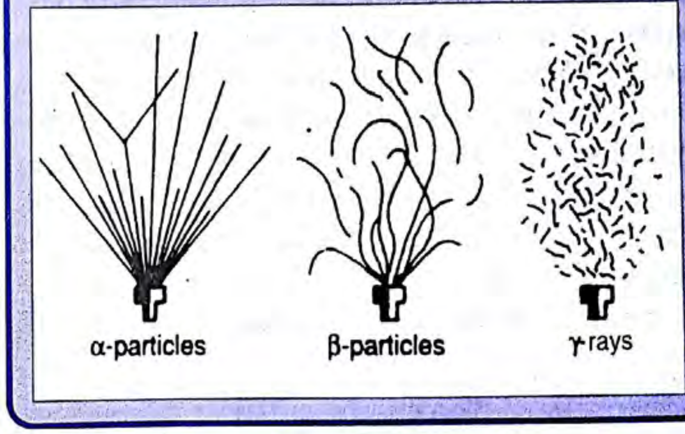
Scintillation counter

Certain minerals, such as zinc sulphide, fluoresce or glow when exposed to radiation. The glow is made up of tiny flashes of light or scintillations, and these may be seen under a microscope or counted with a suitable device.

Diffusion cloud chamber

The diffusion cloud chamber is used for detecting the actual paths followed by individual α- and β-particles.

Fig. 18.4 Cloud chamber tracts.



These ionizing particles are allowed to pass through a gas which has been supersaturated with water vapour. The ions formed in the track of the ionizing particles act like dust, serving as centres for the condensation of the water vapour. As a result, the path of the particle is revealed as a visible vapour trail. The tracks persist long enough to be photographed so that a permanent record of the movements of each α- or β-particle through the gas can be obtained.

Radioactive Disintegration

Radioactivity is the *spontaneous disintegration* of the nucleus of an atom. When a certain quantity of a radioactive material disintegrates spontaneously, the word *decay* is used. During disintegration, a radioactive atom emits either an α-particle or β-particle. Sometimes, γ-rays accompany the emission of these particles. As a result, the parent nucleus (i.e. the disintegrating nucleus) undergoes a change in atomic number and becomes the nucleus of a different element. This new nucleus is called the *daughter nucleus* and this process is called the *transmutation of an atom.*

Radioactive decay is a random process as we cannot predict which atom will disintegrate at a given instant. The rate of decay depends on the radioactive material and varies widely from material to material. No physical or chemical process can alter or affect the rate at which the disintegration of atoms proceeds. But in all cases, the element disintegrates at a certain definite rate which follows an exponential law whereby a certain definite fraction of the atoms present in the element disintegrates every second.

Alpha decay

When the nucleus of an atom loses an α-particle (a helium nucleus, $^{4}_{2}He$) during disintegration, the atomic number of the atom is reduced by two units and its mass number by four units. Thus, an atom of a new element is formed with an atomic number and a mass number smaller than those of the original atom by two units and four units respectively. In the Periodic Table, this new element will be placed two places to the left of the original element.

Alpha decay can be represented as follows:

$$\underset{\text{parent nucleus}}{^{A}_{Z}X} \rightarrow \underset{\text{daughter nucleus}}{^{(A-4)}_{(Z-2)}Y} + \underset{\alpha\text{-particle}}{^{4}_{2}He}$$

For example, if a uranium nucleus, $^{238}_{92}U$, emits an α-particle, its nucleus changes to the nucleus of a new element, thorium-234, $^{234}_{90}Th$, whose atomic and mass numbers are smaller than those of the uranium nucleus by two and four units respectively.

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$$

In the Periodic Table, thorium whose atomic number is 90 is found two places to the left of uranium.

NOTE Just like ordinary chemical reactions, nuclear reactions too must balance. In this case, the [illegible] the atomic numbers and mass numbers on the [illegible] side of the equation must balance with those [illegible] right side.

Beta decay

When the nucleus of an atom emits a β-particle, it is equivalent to the splitting of a neutron in the nucleus to form an electron, which is the, β-particle and a proton which remains in the nucleus. Thus, the atomic number of the atom increases by one unit, but the mass number remains unaltered. Consequently, a new element is formed and it has properties similar to those of an element which is situated one place to the right of the parent nucleus in the Periodic Table.

Beta decay can be represented as follows:

$$\underset{\text{parent nucleus}}{^{A}_{Z}X} \rightarrow \underset{\text{daughter nucleus}}{^{A}_{(Z+1)}Y} + \underset{\beta\text{-particle}}{^{0}_{-1}e}$$

For example, if a thorium nucleus, $^{234}_{90}Th$, emits a ß-particle, its nucleus changes into a nucleus of the element protactinium-234, $^{234}_{91}Pa$, whose mass number is the same as that of thorium but whose atomic number is increased by one unit from 90 to 91.

$$^{234}_{90}Th \rightarrow {}^{234}_{91}Pa + {}^{0}_{-1}e$$

Radioactive decay series

Very often, the nuclei of the new elements which are formed by transmutation during radioactive decay are themselves unstable, and will undergo further disintegration after an interval of time which may vary from a few microseconds to millions of years. Thus, a series of changes may occur until a stable nucleus is finally produced. Several such series of radioactive decay exist in nature, e.g. the *uranium series*, the *thorium series* and the *actinium series*, each of which is named after the longest-lived element in the series.

Nuclear stability and radioactive decay

The nuclei of a radioactive element tend to disintegrate spontaneously because they are unstable. The stability of an atomic nucleus is related to the ratio of neutrons to protons in the nucleus. The *neutron-proton ratio* ble 18.2 … in the uranium series.

lement and adiation emitted	Isotope	Half-life
ranium	$^{238}_{92}U$	4.5 × 10⁹ years
→ α		
Thorium	$^{234}_{90}Th$	24.1 days
→ β		
rotactinium	$^{234}_{91}Pa$	1.18 minutes
→ β		
ranium	$^{234}_{92}U$	2.5 ×10⁵ years
→ α		
Thorium	$^{230}_{90}Th$	8.0 × 10⁴ years
→ α		
Radium	$^{226}_{88}Ra$	1.622 years
→ α		
Radon	$^{222}_{88}Rn$	3.8 days
→ α		
olonium	$^{218}_{84}Po$	2.05 minutes
→ α		
ead	$^{214}_{82}Pb$	26.8 minutes
→ β		
Bismuth	$^{214}_{83}Bi$	19.7 minutes
→ β		
Polonium	$^{214}_{84}Po$	1.6 × 10⁻⁴ seconds
→ α		
Lead	$^{210}_{82}Pb$	19.4 years
→ β		
Bismuth	$^{210}_{83}Bi$	5 days
→ β		
Polonium	$^{210}_{84}Po$	138 days
→ α		
Lead	$^{206}_{82}Pb$	stable

NOTE Half-life is a measure of the rate of disintegration of an element.

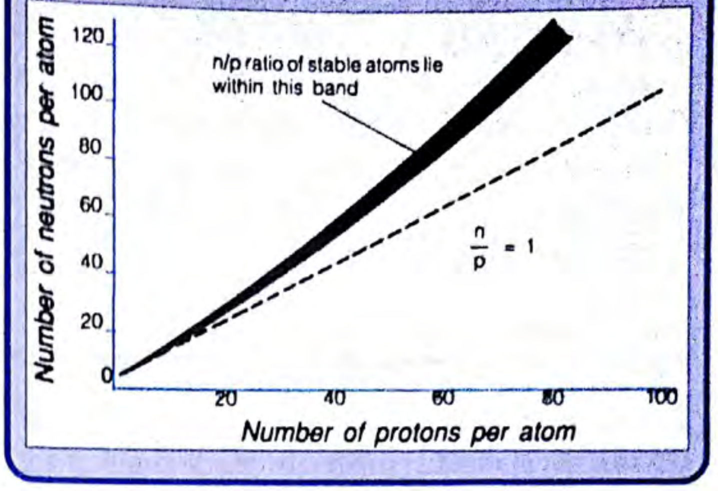
or stable atoms varies between unity for the lighter lements and a value of about 1.5 for those heavier lements with atomic numbers around eighty. Atoms ith a neutron-proton ratio less than 1 or greater than 1.5 tend to be unstable and undergo radioactive decay.

In general, most naturally occurring light elements have stable nuclei and are not radio active. There are some notable examples of light elements with naturally occurring radioactive isotopes, e.g. potassium-40 and carbon-14, but it is much more common to observe radioactivity in the heavier elements from lead (atomic number, 82) to uranium (atomic number, 92).

Rate of radioactive decay

Radioactive elements decay at varying rates. The rate of radioactive decay is used to characterize a radioactive element. This is usually expressed in terms of the *half-life* of a radioactive element.

Fig. 18.5 Neutron–proton ratio in stable nuclei.

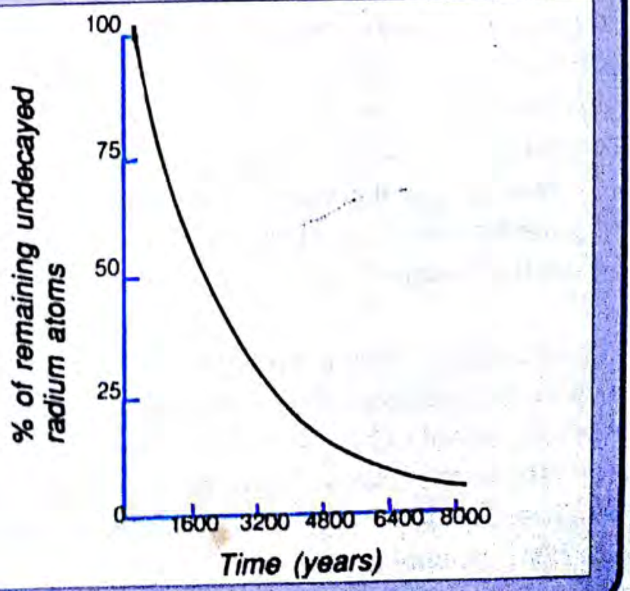


> *The half–life of a radioactive element is the time taken for half of the total number of atoms in a given sample of the element to decay.*

For example, the half-life of radium-226 is 1 622 years. This means that if we have 1 000 000 radium atoms at the beginning, then at the end of 1 622 years, 500 000 atoms would have disintegrated, leaving 500 000 undecayed radium atoms. In the next 1 622 years, half the remaining atoms, i.e. 250 000 atoms would have disintegrated, leaving 250 000 undecayed atorns of radium and so on.

The half-life of a radioactive element may vary from a fraction of a second to millions of years. For

Fig. 18.6 Radioactive decay curve of radium.



example, polonium-212 which is very unstable has a half-life of 3.0×10^{-7} second. On the other hand, the half-life of carbon-14 is 5.76×10^3 years while that of uranium-238 is 4.51×10^9 years. The radioactive isotopes of most common light element have short half-lives (a few days or weeks) and decay rapidly to vanishing point. That is why they are not found in nature to any noticeable extent.

Biological Effects of Radiation

Exposure to radioactive radiations has harmful physiological effects, especially since some of these effects are cumulative. Mild doses of radiation can cause changes in cell structure and body chemistry. Anaemia, cancer, especially leukaemia, and genetic mutations are common in these cases. Death usually results from heavier doses. Thus, great care has to be taken when handling radioactive material. The best shields against the most penetrating radioactive rays are thick blocks of lead, iron and high-density concrete. Workers in radiological laboratories are checked regularly to ensure that they have not been exposed to a dangerous dose of radiation. We are also exposed to some radiation from the radioactive material in the earth's crust and from cosmic rays from outer space, but this amount is so small that there are no harmful effects. This radiation is known as *background radiation.*

Uses of Radioisotopes

Medical uses Intense γ-radiation can be used to destroy cancerous growths. However, great care must be taken to regulate the dosage and confine the irradiation to only cancerous tissues. Cobalt-60 is commonly used for this treatment. Iodine-131 and phosphorus-32 are used in treating cancer of the thyroid gland and leukaemia respectively.

Heart pacemakers used to maintain the heartbeat of patients with heart diseases can now be powered by nuclear batteries, which can last for about 10 years.

Sterilization When an object is irradiated with γ-radiation, germs are killed, leaving it perfectly sterile with no trace of radioactivity. This is particularly useful for sterilizing surgical equipment which can be irradiated after it is sealed so that there is no risk of further contamination.

Workers in radiological laboratories wear pr
clothing to shield themselves from radia

Industrial uses β- and γ-radiations are used to monitor and control the thickness of sheet material, such as plastic, paper and metal, during production by detecting for variations in the intensity of the radiation passing through the material. In the same way, these radiations are used to measure the wall thickness of pipes to check for internal corrosion. Pipelines may also be tested for leaks by adding a radioisotope to the flowing liquid and testing for activity along the length of the pipe.

β- and γ-radiations are also used to control the filling of packets, tins, tanks, etc. by machines. When the material reaches a pre-determined height in the container, the radiation supply is cut off and the filling stopped.

Cobalt-60 is widely used in industrial radiography for the rapid checking of faults in welds and castings. For example, a welded pipeline is tested by placing the gamma-source inside the pipe at the welded portion and wrapping a piece of film around the weld. After suitable exposure, the film is processed and any flaws detected in the pipe can be corrected.

Agricultural purposes Radioactive radiation is employed in agricultural research to induce mutations (modifications in the genetic constitution) in plants and animals in order to obtain new and improved varieties with desired characteristics such as earlie maturity, better nutritional value, higher yield or productivity and greater resistance to diseases.

Radiation is also used in insect and pest control, for example, the male pupae of an undesirable insect are sterilized by irradiation so that sterile male adults are produced. They are then released in large numbers to mate with the native female adults, which will lay unfertilized eggs. Consequently, the next generation of this insect will be greatly reduced in number.

Radioactive tracers The movement or behaviour of a radioactive atom can be traced because it emits radiation. Therefore, a radioactive isotope of an element can be used as a marker or tracer to trace what happens to the element during a chemical change. Using this technique, many metabolic processes in both plants and animals have been studied, e.g. the uptake of iodine by the thyroid gland using iodine-131 and the course of photosynthesis using carbon-14 in the form of carbon(IV) oxide. In medicine, such techniques are used in diagnosis. Tracers are also of vital importance to the chemist in studying the mechanisms and kinetics of chemical reactions.

Dating techniques The presence of very long-lived radioisotopes (e.g. uranium-238 with a half-life of 4.5×10^9 years) in the earth's crust is utilized to estimate the age of rocks. This is done by comparing he radioactivity of rocks now with that which they were presumed to have had when first formed. From he proportions of radioactive uranium, radium and lead occurring in some of the oldest rocks, the earth itself is estimated to have been in existence for at least 2 000 million years.

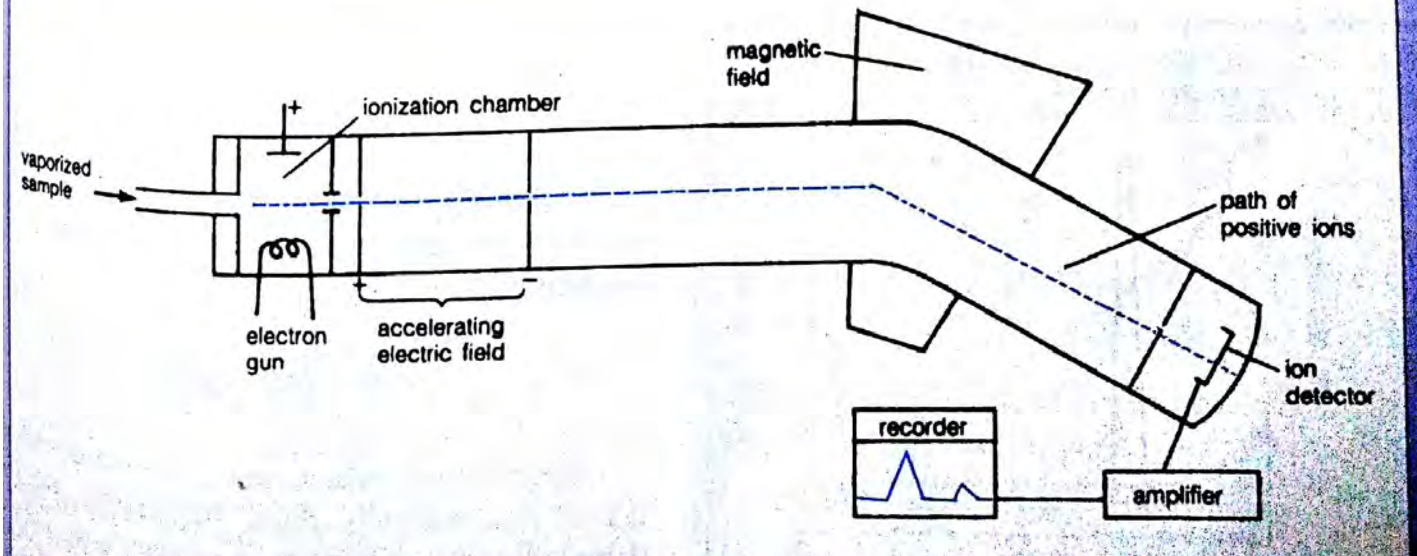
Radiocarbon dating is used to determine the age of the more recent organic remains found in archaeological excavations. Radiocarbon, carbon-14, is continually created by bombardment of carbon(IV) oxide by cosmic rays. The carbon-14 formed becomes evenly distributed throughout the atmosphere, the water-bodies and all living things, such that it maintains a constant ratio with carbon-12, which is its disintegration product. When plants and animals die, the carbon-14 content in their body is not renewed. Instead, the carbon-14 present decays at a known rate, its half-life being 5 760 years. Thus, by measuring the radioactivity of the remaining carbon-14, the age of the specimen can be determined. This method is accurate for ages up to about 30 000 years.

Mass spectrometer This instrument measures the masses of the various isotopes present in a sample of an element. It also gives the percentage abundance of each isotope. From these data, the relative atomic masses of elements can be calculated accurately.

The mass spectrometer works on the principle that all particles having the same mass and charge are deflected to the same extent by a fixed magnetic field.

There are five main stages in the operation of the mass spectrometer.

Fig. 18.7 How a mass spectrometer works.



1 A sample of the test element is vaporized and injected into the ionization chamber of the mass spectrometer.

2 The vaporized particles are bombarded by cathode rays (beam of fast-moving electrons). In this process, positively-charged ions are formed as electrons are knocked out of the vaporized particles.

$$e^- + X(g) \rightarrow X^+(g) + e^- + e^-$$

e^-	$X(g)$	$X^+(g)$	e^-	e^-
high-energy electron	atom of test element	positive ion	electron knocked out of X	high-energy electron

3 The positive ions are accelerated in an electric field.

4 Then, the ions are deflected by a magnetic field according to their mass and charge. For ions of the same charge, the lightest elements are deflected the most.

5 Finally, they are detected by an ion detector. The detector is connected to an amplifier and a recorder. The mass spectrum obtained is used to calculate the relative atomic mass of the test element.

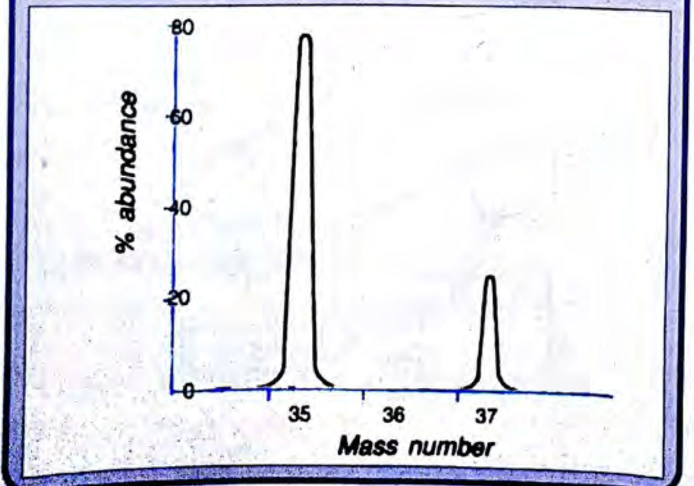
Fig. 18.8, shows that a sample of naturally occurring chlorine has two isotopes in the following amounts.

	Mass of isotope	% abundance
^{35}Cl	35	75.8
^{37}Cl	37	24.2

∴ the relative atomic mass of chlorine $= \dfrac{(35 \times 75.8) + (37 \times 24.2)}{100}$

$= 35.5$

Fig. 18.8 A mass spectrum for a sample of naturally occurring chlorine.



NUCLEAR ENERGY

We have learnt that natural radioactivity is du… spontaneous and uncontrolled decay of unstab… nuclei. Such decay is usually accompanied by th… evolution of a large quantity of heat. For example, f… every mole of radium-226 which decays to radon-22… by α-radiation, about 4×10^8 kJ of energy is released. Scientists realized that this nuclear energy could become a very important source of energy. However, they could only tap this source of energy if they could bring about radioactive decay or nuclear transmutations artificially. In addition, they had to be able to control these nuclear reactions so that their energy could be harnessed and used.

Artificial Transmutation

In 1919, Lord Rutherford succeeded in transmuting a nitrogen isotope into an oxygen isotope by bombarding the former with α-particles.

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}p$$

proton

Many different atomic transmutations can now be carried out by bombarding various elements with fast-moving atomic particles like neutrons, protons, deuterons (nuclei of deuterium atoms), and α particles. The neutron is a particularly effective bombarding particle for bringing about nuclear decay, since it is heavy and has no charge.

In general, light elements bombarded by neutrons yield new elements by ejecting charged particles.

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}p$$

neutron

If the nucleus being bombarded is heavy, it captures the neutron to produce an isotope of the original element.

$$^{59}_{27}Co + ^{1}_{0}n \rightarrow ^{60}_{27}Co$$

Many of the products formed are isotopes wh… do not exist naturally. Some 700 isotopes, m… them radioactive, have now been made artific… this way. For example, sodium-24, wh…

radioactive isotope, is produced from sodium-23 by neutron bombardment.

$$^{23}_{11}\text{Na} + ^{1}_{0}\text{n} \rightarrow ^{24}_{11}\text{N}$$

Many isotopes, such as cobalt-60, iodine-131 and phosphorus-32, are now manufactured on a considerable scale because of their many uses in industry, medicine and scientific research.

By suitable transmutations, scientists have also been able to make atoms with atomic numbers above 92, thereby synthesizing new artificial elements not known previously. For example, neptunium (atomic number, 93) is produced from uranium-238 by neutron bombardment.

$$^{138}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{239}_{92}\text{U} \rightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e}$$

Eleven artificial elements such as plutonium, curium and lawrencium have been made in the last forty years.

Binding Energy

If the mass of the helium atom and the total mass of the protons and neutrons that make up a helium atom are measured, it will be found that these values differ.

Mass of 2 protons = 2 × 1.0078 amu	= 2.015 6 amu
Mass of 2 neutrons = 2 × 1.0087 amu	= 2.017 4 amu
∴ total mass of 2 protons and 2 neutrons	= 4.033 0 amu
Actual mass of the helium atom	= 4.002 6 amu
∴ discrepancy in mass (*mass defect*)	= 0.030 4 amu

Hence, the mass of an atom is less than the sum of the masses of its constituent particles (i.e. protons and neutrons). This loss of mass is known as mass defect and can be accounted for by Albert Einstein's Theory of Relativity which states that mass and energy are interconvertible. The loss in mass corresponds to the release of energy according to the Einstein equation:

$$E = mc^2$$

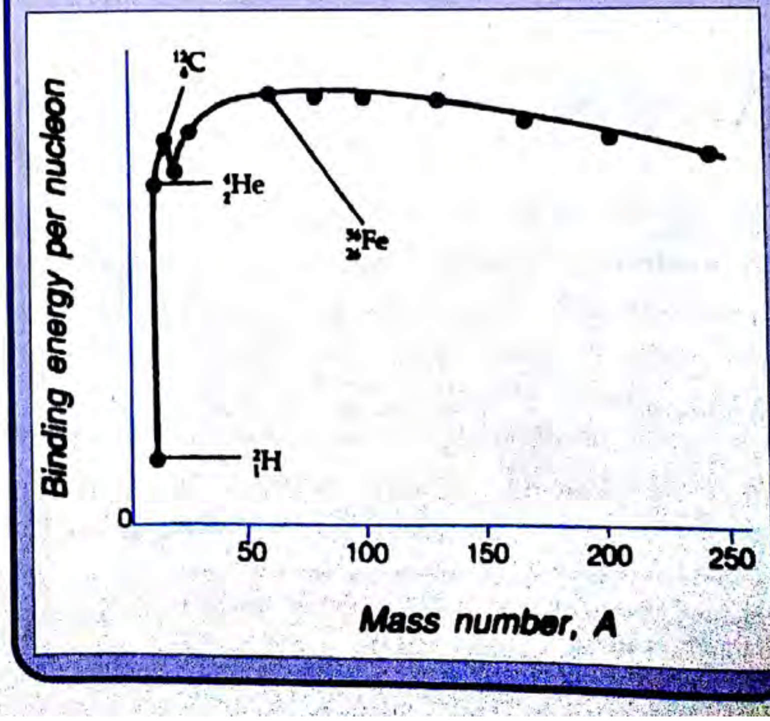
where E is the energy in J, m is the loss in mass of the substance in kg, c is the velocity of light in m s^{-1}.

In the process of binding the nucleus to form a helium atom, a certain amount of energy is evolved. This energy is released from the atom so that the total mass left in the helium atom is less than the total mass of the constituents of the atom. This energy, equivalent to the mass defect, is called the *binding energy* of the nucleus. In other words, binding energy is the energy evolved in the formation of a nucleus from free protons and neutrons. It varies for different nuclei.

Binding energy per nucleon The particles in a nucleus are collectively known as *nucleons*. If the total binding energy of a nucleus is divided by the number of nucleons it contains, we obtain the quantity called the *binding energy per nucleon*.

Fig. 18.9 shows a graph in which the binding energy per nucleon is plotted against the atomic mass number, A. The curve shows how the binding energy per nucleon varies with the size of the nucleus. The curve rises sharply at the beginning, reaches the maximum at around $A = 56$ (corresponding to the iron nuclei) and then declines gradually. Nuclei with mass numbers around 56 are those requiring the greatest amount of energy for their disintegration and hence, are the most stable ones. On the other hand, elements which have mass numbers near the two extremes of the mass range are least stable. This fact suggests that if heavy nuclei can be split into lighter ones, i.e. undergo *nuclear fission*, or if light nuclei can be combined to produce larger nuclei, i.e. undergo *nuclear fusion*, energy will be evolved.

Fig. 18.9 Binding energy per nucleon.



Nuclear Fission

In 1939, German scientists brought about nuclear fission by bombarding uranium-235 atoms with neutrons travelling at moderate speeds. The process resulted in a uranium-235 atom being split up into two fragments of about equal sizes, accompanied by the evolution of a tremendous amount of energy and the release of two or more fast-moving neutrons.

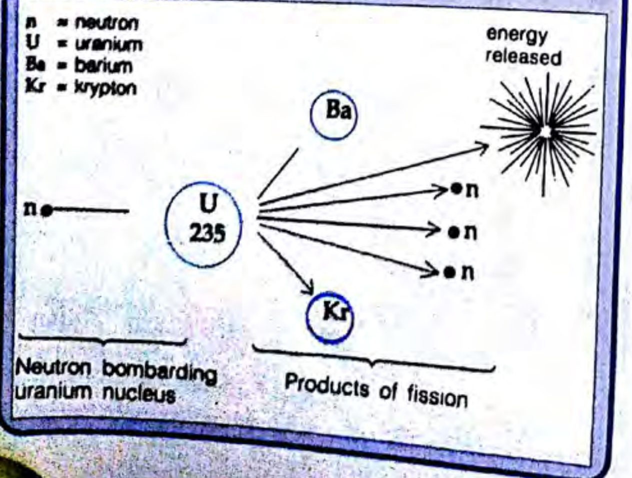
NOTE The two large fragments formed from the fission of each uranium-235 atom are usually unstable isotopes of some heavy elements (for example $^{94}_{38}Sr$, $^{139}_{54}Xe$, $^{145}_{56}Ba$ and $^{88}_{36}Kr$), and it is the radioactive disintegration of such atoms that accounts for the intense radiation (mainly β- and γ-trays) associated with nuclear fission

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{141}_{56}Ba \rightarrow ^{92}_{36}Kr + 3^{0}_{1}n$$

Nuclear fission is a process in which the nucleus of a heavy element is split into two nuclei of nearly equal mass with a release of energy and radiation.

In all cases of nuclear fission, the total mass of all the fragments and neutrons released differs from the total mass of the original atom of the element and the mass of the bombarding neutron. The difference in the mass is due to the conversion of mass to energy which is liberated during fission. The following calculations show the total amount of nuclear energy released at each fission of a $^{235}_{92}U$ atom as described by the equation given above.

Fig. 18.10 Nuclear fission.



Mass of $^{235}_{92}U$ = 235.040 amu
Mass of $^{1}_{0}n$ = 1.009 amu
Total mass of $^{235}_{92}U$ and $^{1}_{0}n$ = 236.049 amu
Mass of $^{141}_{56}Ba$ = 140.910 amu
Mass of $^{92}_{36}Kr$ = 91.910 amu
Mass of three $^{1}_{0}n$ = 3.027 amu
Total mass of $^{141}_{56}Ba$ and $^{92}_{36}Kr$ and three $^{1}_{0}n$ = 235.847 amu

$\therefore$ mass defect = (236.049 − 235.847) amu = 0.202 amu

Using Einstein's equation, energy released $E = mc^2$,

$$E = 0.202 \times 1.6 \times 10^{-27}\ \text{kg} \times (3 \times 10^{8}\ \text{m s}^{-1})^2$$
$$= 2.9 \times 10^{-11}\ \text{J}$$

NOTE 1 amu is 1.6×10^{-27} kg.

Thus, 2.9×10^{-11} J of energy are released for every atom of that undergoes fission.

The energy released when 1 g of uranium-2 undergoes fission can be calculated as follows:

235 g of uranium-235 contain 6.023×10^{23} ato (Avogadro's number).

$$\therefore 1\ \text{g of uranium-235 contains}\ \frac{6.023 \times 10^{23}}{235}$$
$$= 2.563 \times 10^{21}\ \text{atom}$$

Energy released for 1 g of $^{235}_{92}U$

$$= 2.563 \times 10^{21} \times 2.9 \times 10^{-11}$$
$$= 7.433 \times 10^{10}\ \text{J}$$

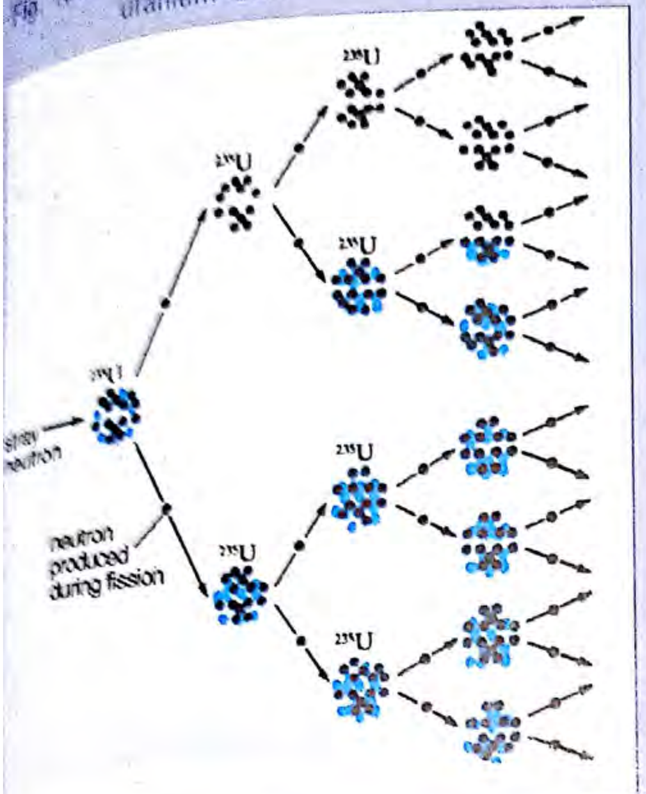
In comparison, the amount of energy liberated b the fission of 1 g of pure uranium-235 is the same a that liberated by the burning of 3×10^{6} kg of coal.

Atomic pile and atomic bomb If the neutrons produced during the fission of the uranium-235 atom could bombard other parent atoms (i.e. uranium-235 atoms) to produce more energy and more neutrons, and if this process could be repeated over and over again, then a self-maintaining or chain reaction could be obtained. This is the principle of the *atomic or fission bomb* and the *atomic pile* or *nuclear reactor* (as used in atomic power plants where nuclear energy is harnessed for the production of electrical energy).

An atomic explosion results when just the right amount of fissionable material is brought together to be split by neutrons in a chain reaction.

This amount is called the *critical mass* of the atomic bomb. The explosion of an atomic bomb is an

Fig. 18.11 Nuclear chain reaction in pure uranium-235.



tantaneous and uncontrolled chain reaction.

In an atomic pile, the same amount of energy may released, but the rate of nuclear fission is carefully ntrolled so that the heat evolved can be dissipated it is produced.

The rate of nuclear fission is controlled in an mic pile by using ordinary uranium-238 enriched th fissionable uranium-235. The atoms of uranium-8 capture fast-moving neutrons readily, while those uranium-235 readily capture slow-moving neutrons. nce fission results in the production of fast-moving utrons, most of the neutrons are captured by anium-238 atoms, while only a few are absorbed by anium235 to produce fission. Thus, the presence of anium-238 slows down the rate of absorption of utrons by uranium-235 atoms, and so helps to ntrol the fission rate.

In order to sustain the chain reaction, certain aterials called *moderators* are used to slow down e neutrons so that at least one neutron from each anium-235 fission will bring about the fission of e other uranium-235 atom. The best moderators re graphite and heavy water.

Rods of neutron-absorbing materials, like admium and boron steel, are introduced immediately o the atomic pile if the chain reaction shows signs f going out of control.

Nuclear Fusion

Another potential source of nuclear energy exists in nuclear fusion, in which the nuclei of the light atoms are made to combine to form heavier and more stable nuclei, with an accompanying release of energy. This energy is due to a slight loss in mass when the heavier nucleus is formed by the fusion of the lighter nuclei. The amount of energy per unit mass of nuclear fuel liberated by nuclear fusion is far greater than that liberated by nuclear fission. In practice, nuclear fusion occurs only at extremely high temperatures (at least 1.5 × 10^7 °C) and is described as a *thermonuclear reaction*. This is because very large energies have to be given to the positively charged nuclei to overcome the strong repulsion between them.

Nuclear fusion is a process in which two or more light nuclei fuse or combine to form a heavier nucleus with a release of energy and radiation.

Hydrogen bomb The high temperatures required for nuclear fusion can be obtained by nuclear fission. When a mixture of deuterium and tritium (the two heavy isotopes of hydrogen) is exposed to the heat from a fission bomb explosion, nuclear fusion occurs.

$$^{2}_{1}\mathrm{D} + {}^{3}_{1}\mathrm{T} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \text{energy}$$

This type of reaction is the basis of the *hydrogen* or *fusion bomb*. The lethal power of this bomb is partly due to the enormous amount of energy released (due to a small loss in mass) and partly to the large quantity of γ-radiation produced by the detonating agent, which is the fission bomb.

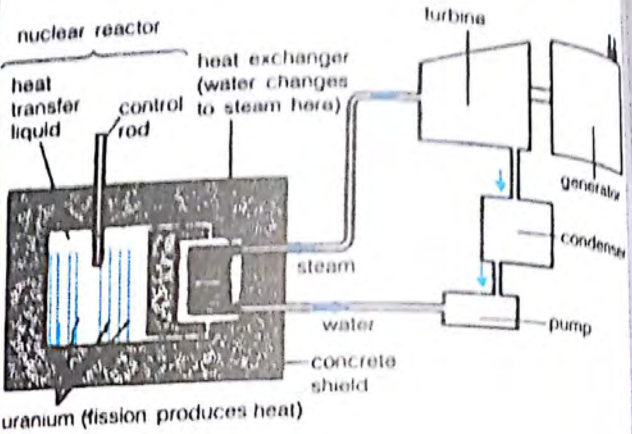
Possible source of cheap power Attempts are still being made at the present time to carry out the thermonuclear reactions under controlled conditions. If these are successful, a cheap source of power will be available. Heavy hydrogen forms about 1 part in 45 000 parts of water, and if it is extracted from sea-water, it can provide limitless power at a very economic price.

Energy of the sun Thermonuclear reactions are believed to be the source of energy of the sun and stars. these reactions mainly involve the nuclear fusion of hydrogen nuclei to form a helium nucleus, with the liberation of a very large amount of energy.

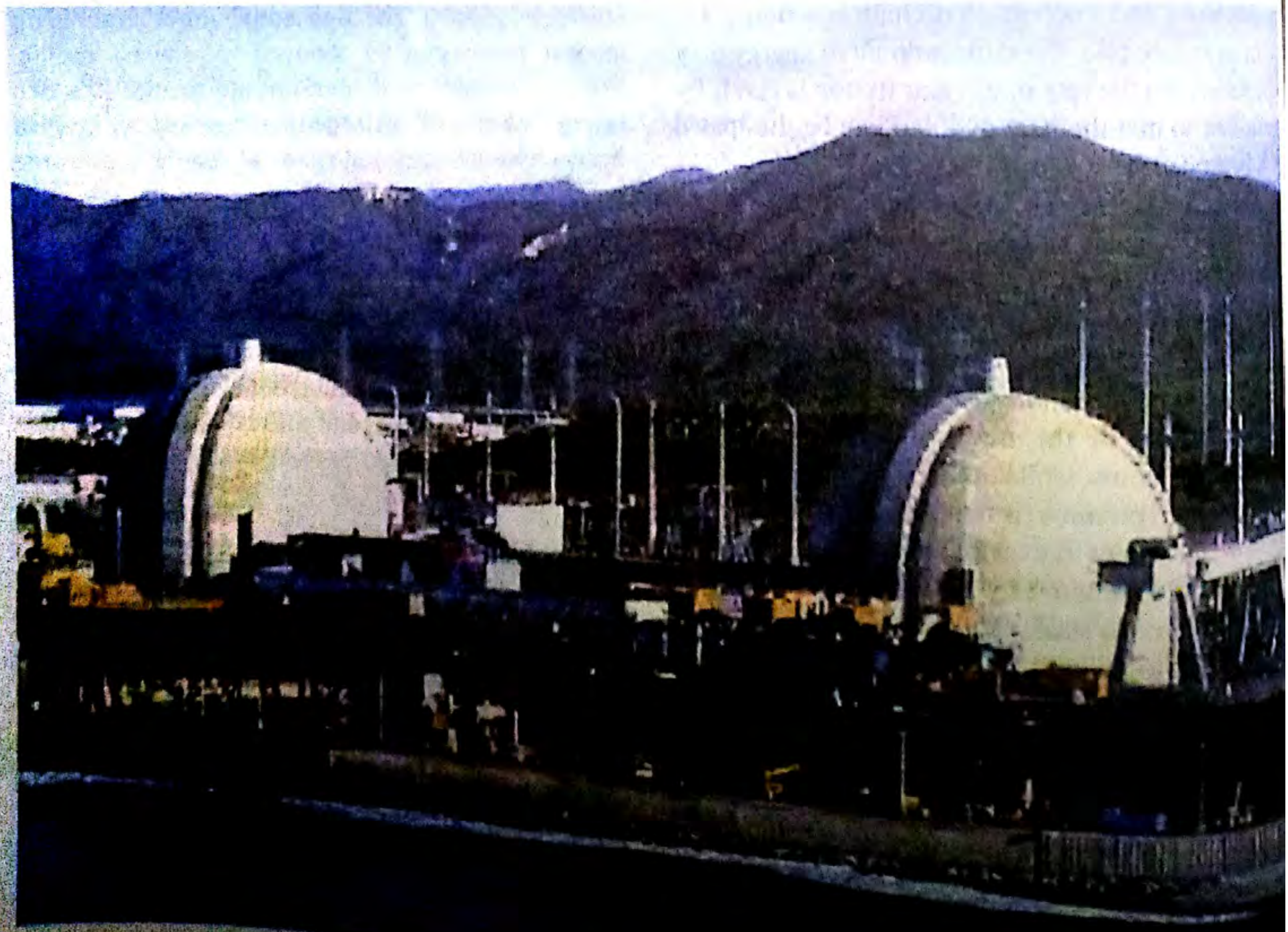
Nuclear Energy for Power

The heat developed in a nuclear reactor is used to produce power. A heat-transfer liquid or gas, such as heavy water or carbon(IV) oxide, is circulated through the reactor where it becomes heated. The heated liquid or gas is then pumped into a heat interchanger, where it converts water to steam. The steam produced can then be used to drive the turbines, which turn electrical generators to produce electricity. In order to control the nuclear reaction, a moderator is used to absorb the excess neutrons. In nuclear submarines, the energy produced is used to power the ship. A nuclear reactor can work day and night for a few years with the same uranium fuel.

Fig. 18.12 Power from a nuclear reactor



A nuclear reactor for generating electricity.



SUMMARY

Radioactivity is the spontaneous emission of radiation by an element. Such an element is said to be radioactive.

The three main types of radiation are alpha-rays, beta-rays and gamma-rays.

(a) Alpha-particles (α-particles) are positively charged nuclei of helium. Although they have low penetrating power and can be easily absorbed by matter, they exert strong ionizing effect during collision. Due to their heavy masses, they are only slightly deflected by magnetic or electric fields.

(b) Beta-particles (β-particles) are fast-moving electrons. They have weaker ionizing power than α-particles. Due to their very small masses, they are easily deflected by magnetic or electric fields.

(c) Gamma-rays (γ-rays) are electromagnetic waves. They are the most penetrating type of radiation. Unlike the α- and β-particles, γ-rays are electrically neutral and are not affected by magnetic or electric fields.

X-rays are short electromagnetic waves. They are used in medicine to take photographs of bones and in chemistry to study the structure of crystals and big organic molecules.

Radiation is detected by the Geiger-Muller counter, scintillation counter and diffusion cloud chamber.

The nucleus of a radioactive element is unstable and disintegrates by emitting radiation until a stable nucleus results. In this process, the nucleus of a particular radioactive element may pass through a series of radioisotopes of other elements before finally becoming stable. The transformation of one element to another during nuclear disintegration is known as transmutation.

The time required for one-half of the atoms of a radioactive substance to decay is termed the half-life of that substance.

Radioisotopes are used extensively in medicine, industry and scientific research.

The transforming of one element into another by means of particle bombardment is known as artificial transmutation.

The defect of a nucleus is due to the conversion of some parts of the mass to energy. This mass-energy relationship can be explained using Einstein's equation:

$$E = mc^2$$

- The binding energy is the energy released during the formation of a nucleus from its constituents.
- Nuclear fission is the process whereby a heavy nucleus is split into two or more lighter nuclei, with a release of energy and radiation.
- A chain reaction is a succession of nuclear fissions in which excess neutrons produced by each fission cause further fissions in other nuclei.

- Nuclear fusion is the process whereby two or more light nuclei unite to form a heavier nucleus, with release of energy and radiation.
- Nuclear reactors use fission reactions to produce energy.

EXERCISES

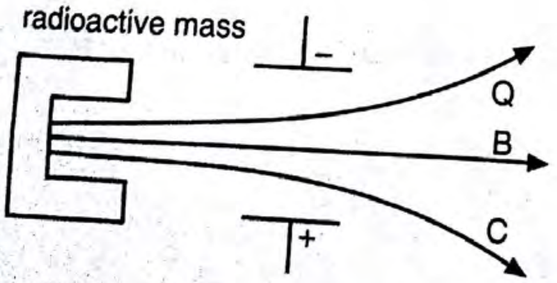
1. A factor affecting rate of nuclear reactions is
A pressure.
B temperature.
C catalyst.
D charge on the bombarding particles.

2. The following characteristics belong to one of the basic nuclear particles.
(i) Low penetrating.
(ii) Powerful ionizing power on gases.
(iii) Particulate.

A Alpha particles B Beta particles
C Gamma rays D X-ray

3. Radiation is detected by the following except
A diffusion cloud chamber.
B scintillation counter.
C Geiger-Muller counter.
D pulse current.

4. Radioactive mass



Q represents
A Beta particles. B Alpha particles.
C Gamma rays. D X-rays.

5. Basic nuclear radiation was discovered by
A Becquerel.
B Marie Curie.
C Geiger Muller.
D Marsden.

6. The equation, $^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He$ represent
A gamma bombardment.
B beta decay.
C alpha decay.
D artificial radioactivity.

7. What is the value of Z in the equation
$^{234}_{90}Th \rightarrow ^{234}_{91}Pa + Z$
A Alpha particle.
B Beta particle.
C X-ray.
D Gamma ray.

8. Radioactivity sets in a nucleus when the atomi number is
A 10 B 30
C 50 D 80 and above

9. Radioactive decay is expressed in terms of
A rate of radioactive absorption.
B rate of radioactive stabililty.
C position of element in the periodic table.
D half life.

10. Workers in radioactive laboratories are shielded from the harmful effects of radiation by using
A thick lab coats.
B thick blocks of lead.
C cosmic rays in the lab.
D non-radioactive pills daily after work.

11. Radioisotopes have wide application in
A medicine.
B industries.
C agriculture.
D weather forecast.

12. A large quantum of nuclear energy is derivable from
A nuclear fusion using positions.
B nuclear fusion using neutrons.
C nuclear fission using neutrons.
D nuclear fission using positions.

13. The equation, $^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}P$ represents
A nuclear fusion.
B nuclear fission.
C artificial radioactivity.
D natural radioactivity.

14. Common nuclear energy is traced back to the conversion of
A binding energy to nuclear energy.
B mass defect to energy.
C nucleons into energy.
D Einstein's equation into energy.

15. 100 g of radioactive mass has a half-life of 5 days. Calculate the mass decayed off after 15 days.
A 25 g
B 50 g
C 12.5 g
D 6.25 g

16. Copper with an atomic number of 29 has isotopes ^{63}Cu and ^{65}Cu. Give the composition of their atomic particles.

17. Determine the relative atomic mass of each element from the data given below.

	Isotope	Mass	% abundance
(a)	^{79}Br	79	50.54
	^{81}Br	81	49.46
(b)	^{24}Mg	24	78.70
	^{25}Mg	25	10.13
	^{26}Mg	26	11.17

18. What are the three main types of radiations? Give the properties of each.

19. (a) Complete the following equation.

$$^{14}_{6}C \rightarrow ^{14}_{7}N +$$

(b) The half-life of an element X is 5 days. If we have 5 g of X initially, what is the mass of X after
(i) 5 days,
(ii) 20 days,
(ii) 40 days?

20. Explain the term radioisotopes. Give an account of the uses of radioisotopes.

21. Explain the following terms using examples.

(a) Nuclear fission

(b) Nuclear fusion

(c) Artificial transmutation.

22. How much energy is released when 0.002 g of mass is annihilated in a nuclear reaction?

23. (a) What is meant by *the binding energy of the nucleus* of an atom?

(b) The atomic mass of ${}^{16}_{8}O$ is 15.995 amu. If the individual masses of a proton and a neutron are 1.0078 and 1.0087 amu respectively, calculate the binding energy of the oxygen nucleus in joules. (1 amu = 1.6 × 10^{-27} kg)

24. Identify *A*, *B* and *C* in the following equatio

$${}^{238}_{92}U \rightarrow {}^{234}_{90}Th + A$$

$${}^{214}_{82}Pb \rightarrow {}^{214}_{83}Bi + B$$

$${}^{6}_{3}Li + C \rightarrow {}^{3}_{1}H + {}^{4}_{2}He$$

25. (a) What is a chain reaction?

(b) Explain briefly the principle of the operati of a nuclear power plant.

SECTION TWO

NON-METALS

19

HYDROGEN • HYDRIDES

HYDROGEN

Cavendish is regarded as the discoverer of hydrogen because he was the first (in 1766) to prepare it in the pure state, describe its properties and recognize it as an element. He found that the gas was flammable and that it burned in air to produce water. Therefore, Lavoisier named it *hydrogen*, meaning *water-former.*

Occurrence

Hydrogen makes up approximately 1% of the earth's crust. It is found free only in very smal amounts (0.01 %) in the atmosphere and in volcanic gases, although recent spectroscopic studies show that large amounts are present in the sun and the stars.

Hydrogen is widely distributed in combination with other elements. It makes up one ninth by mass of water and is an important constituent of all acids and alkalis. Combined with carbon, hydrogen is found in natural gas, kerosene, gasoline and other petroleum products. It is also a constituent of most other organic substances, including proteins, carbohydrates and fats which are essential components of all living matter.

Laboratory Preparation

Hydrogen is liberated when certain metals react with dilute mineral acids, water or steam. It is also given off when tin, zinc or aluminium reacts with hot concentrated solutions of sodium or potassium hydroxide.

The three methods commonly used for the preparation of hydrogen in the laboratory are as follows:

Action of zinc on an acid Dilute hydrochloric or tetraoxosulphate(VI) acid attacks metallic zinc with the liberation of hydrogen gas. No heating is necessary.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$
$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

Ionically, both these reactions can be represented as follows:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

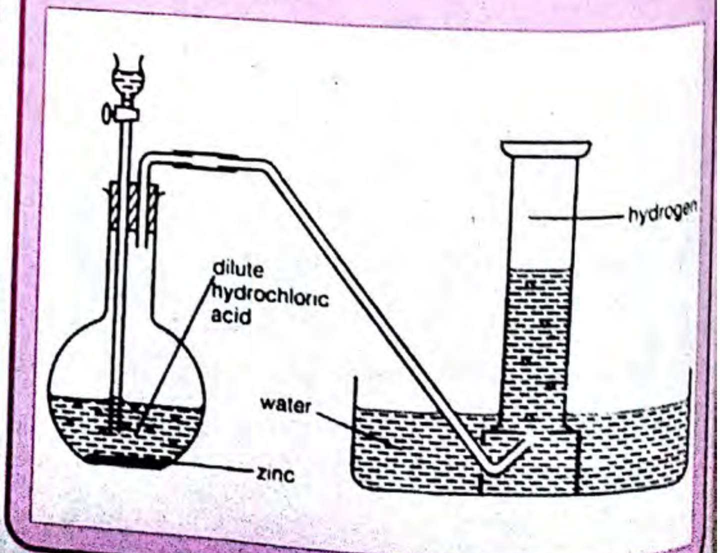
Action of sodium on cold water Sodium liberates hydrogen from cold water. This reaction is very vigorous and should be carried out with extreme care using only a small piece of sodium.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Action of iron on steam Iron, at red heat liberates hydrogen from steam. Iron(II) diiron(III); oxide, Fe_3O_4, is formed at the same time. This reaction is reversible.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Fig. 19.1 Preparing hydrogen by the action of a dilute acid on zinc.



Experiment 19.1 To prepare hydrogen.

Method (a) ***Action of a dilute acid on zinc*** Place some pieces of zinc in a flat-bottomed flask and set up the apparatus as shown in fig. 19.1. Add some dilute hydrochloric acid to cover the pieces of zinc. If the zinc is pure, add a few drops of copper(II) tetraoxosulphate(VI) solution to act as a catalyst. Collect the hydrogen that is given off in a gas-jar over water. If the gas is required dry, pass it through fused calcium chloride or concentrated tetraoxosulphate(VI) acid, and collect it over mercury or by the downward displacment of air.

(b) ***Action of cold water on sodium*** Half fill a trough with tap water coloured red with litmus. Hold a small piece of sodium in the water with a sodium-spoon, or wrap it loosely in a piece of wire gauze and drop it into the water so that it sinks to the bottom of the trough. Fill a test-tube with water and invert it over the piece of sodium in the trough to collect the hydrogen gas formed.

(c) ***Action of steam on iron at red heat*** Partially fill a combustion tube with some iron filings and set up the apparatus as shown in fig. 19.3. Heat the heap of iron filings strongly until it is red-hot. Generate steam by boiling the water in the flask, and pass it over the red-hot iron. Maintain a constant flow of steam and collect the hydrogen gas formed over water.

CAUTION A mixture of hydrogen and air is explosive when heated, so make sure that there are no naked flames near by when doing experiments with hydrogen. Discard the first jar of hydrogen as it is a mixture of hydrogen and air.

Result (a) There is an effervescence of hydrogen gas as the zinc reacts with the dilute acid. Hydrogen is collected in the gas-jar by the downward displacement of water.

(b) Sodium reacts vigorously with water. It melts and gradually dissolves in water which turns red litmus blue due to the formation of sodium hydroxide. Hydrogen gas is given off with effervescence and is collected in the test-tube inverted over the metal.

(c) The hydrogen produced is collected over water. The black residue which is left behind in the combustion tube is iron(II) diiron(III) oxide.

Conclusion Hydrogen gas may be prepared by the action of a dilute acid on zinc, the action of cold water on sodium, or the action of steam on iron at red heat.

19.2 Preparing hydrogen by the action of sodium on cold water.

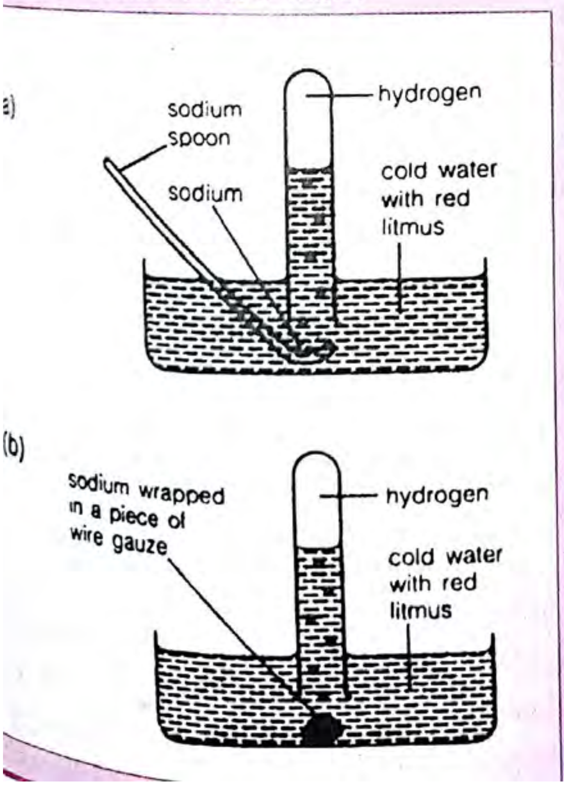
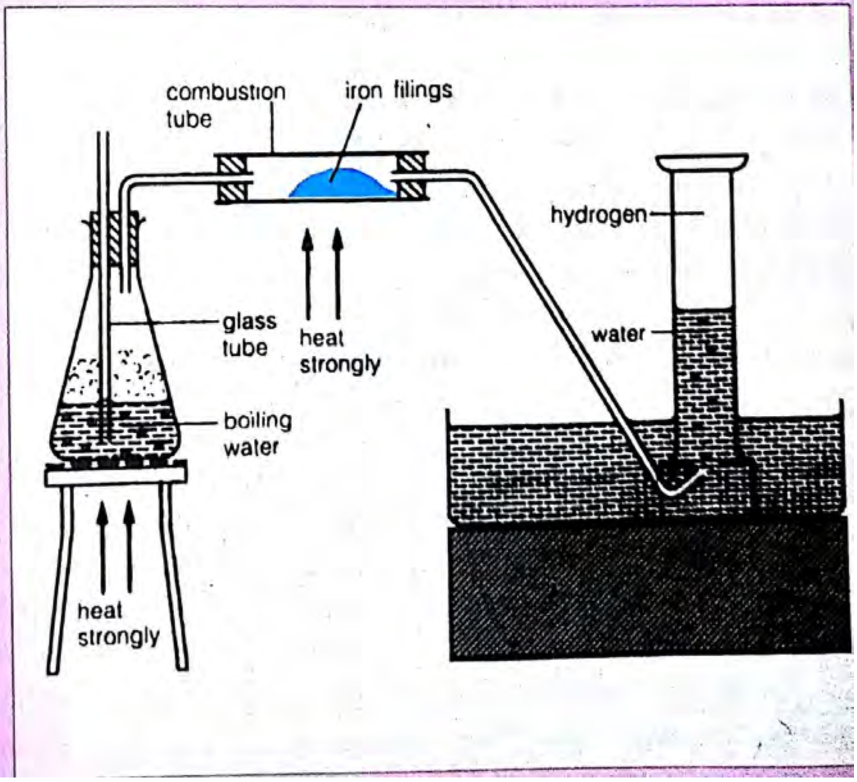


Fig. 19.3 Preparing hydrogen by the action of steam on iron filings.



Industrial Preparation

From water gas (Bosch process) In this process large quantities of hydrogen are produced from cheap raw materials, namely water and coke. When steam is passed over red-hot coke (carbon) at about 1 200 °C, a mixture of carbon(II) oxide and hydrogen known as *water gas* is produced. Excess steam is then mixed with the water gas and passed over a catalyst, iron(III) oxide or chromium(III) oxide, at 450 °C. As a result, the carbon(II) oxide in the water gas is converted to carbon(IV) oxide with a further yield of hydrogen.

The first reaction, i.e.

- the production of water gas, is endothermic, while the second, i.e.
- the reduction of steam to hydrogen by carbon(II) oxide, is exothermic.

Endothermic reaction

$$\underset{\text{steam}}{H_2O(g)} + \underset{\text{coke}}{C(s)} \rightarrow \underbrace{CO(g) + H_2(g)}_{\text{water gas}}$$

Exothermic reaction

$$\underbrace{CO(g) + H_2(g)}_{\text{water gas}} + \underset{\text{steam}}{H_2O(g)} \rightleftharpoons CO_2(g) + 2H_2(g)$$

The carbon(IV) oxide is then removed from the mixture by dissolving it in water (under a pressure of 30 atmospheres) or other solvents such as caustic soda solution. Any unreacted carbon(II) oxide is absorbed in an ammoniacal solution of copper(I) ethanoate.

From methane The Bosch process is now being replaced by a similar process which uses cheap hydrocarbons like methane instead of coke. For example, in the first stage, steam is mixed with methane (obtained as a natural gas) and passed over a nickel catalyst at about 800 °C. The mixture of carbon(II) oxide and hydrogen produced is known as *synthesis gas*.

$$\underset{\text{methane}}{CH_4(g)} + \underset{\text{steam}}{H_2O(g)} \xrightarrow[800°C]{Ni} \underbrace{CO(g) + 3H_2(g)}_{\text{synthesis gas}}$$

The second stage in this process is exactly the same as the water gas-steam reaction in the Bosch process.

By electrolytic methods Very pure hydroge obtained as a by-product in the electrolysis of b for the manufacture of sodium hydroxide and chlori If required, it can also be made by the electrolysis dilute sodium or potassium hydroxide solution.

Hydrogen and the Activity Series

In the laboratory preparation of hydrogen, we sa that some metals could displace hydrogen from water and acids. There are, however, other metals lik copper and silver which cannot displace hydroge from water or acids. We can regard metals whic displace hydrogen from water and acids as being mo active than hydrogen, and those that do not as bein less active.

The metals which can displace hydrogen fro water or acids vary in their degree of activity to Potassium and sodium react vigorously with cold water to displace hydrogen, while calcium reac slowly. Heated magnesium displaces hydrogen fro steam; aluminium, zinc and iron will only do so at re heat; while lead and copper do not react at all.

Decreasing activity with water

K, Na, Ca,	Mg, Al, Zn, Fe,	Sn, Pb, Cu, Hg, Ag, Au
Attack cold water to form alkalis and hydrogen gas	Attack steam to form oxides and hydrogen gas	No reaction with either cold water or steam

With dilute hydrochloric or tetraoxosulphate(VI) acid, potassium and sodium react too violently for the reaction to be carried out safely in the laboratory. Calcium and magnesium react vigorously, while aluminium, zinc and iron react moderately, with the rate of reaction (as measured by the rate of release of hydrogen bubbles) being the fastest with aluminium and the slowest with iron. Lead and copper do not react with dilute acids.

NOTE The pieces of metals should be cleaned to remove oxides before being placed in the dilute acid solution. Lead does not show any reaction with the dilute acids because the lead salts formed are insoluble and form a protective coating over the metal.

We can also determine the relative activity of netals by doing another set of experiments where ne metal displaces another from a solution of its salt. or example, if an iron rod is dipped in a solution of copper(II) salt, reddish-brown deposits of metallic opper are found on the iron rod after some time, howing that iron has displaced copper from a solution f a copper(II) salt. No diplacement occurs if a copper d is dipped in a solution of an iron salt. However, etallic copper can displace silver from a solution of silver salt. Thus, iron is more reactive than copper, hile the latter is more reactive than silver.

From the above experiments, we can arrange the rious metals in an activity series as shown. This ries is very similar to the electrochemical series. ydrogen is placed in the activity series to indicate e position it would occupy. Metals above hydrogen the series liberate hydrogen from acids, while those low hydrogen do not. Generally, metals high up in e series are very electropositive. They are very active emically. Metals low down in the series are less tive. Any metal will displace those metals below it m a solution of their salts. Thus, the activity series a useful guide to the chemical behaviour of metals d their compounds.

ig. 19.4 Activity series of metals.

Increasing electropositivity ↑

Lithium	Li
Potassium	K
Sodium	Na
Calcium	Ca
Magnesium	Mg
Aluminium	Al
Zinc	Zn
Iron	Fe
Tin	Sn
Lead	Pb
Hydrogen	H
Copper	Cu
Mercury	Hg
Silver	Ag
Platinum	Pt
Gold	Au

Decreasing chemical activity ↓

Physical Properties

1 Hydrogen is a colourless, odourless and tasteless gas.
2 It is neutral to moist litmus paper.
3 It is relatively insoluble in water. Only 2 cm^3 of it will dissolve in 100 cm^3 of water at s.t.p.
4 Hydrogen is the lightest known substance. It is 14.4 times less dense than air.
5 It has a very low boiling point of –253 °C.

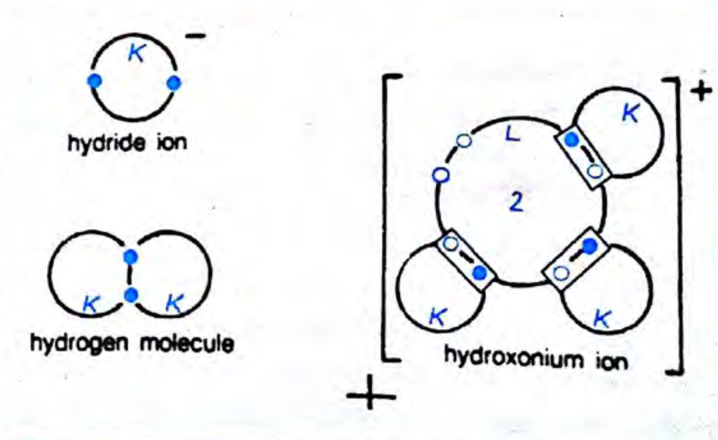
Chemical Properties

Hydrogen is an unusual element. It has a single valence electron like the Group 1 alkali metals, yet it is clearly a gas with non-metallic properties like the Group 7 halogens. In the Periodic Table, hydrogen is usually placed in Group 1 for convenience. However, sometimes it is placed between Groups 1 and 7 to depict its unusual nature.

The chemical behaviour of hydrogen can be explained by its tendency to acquire the stable duplet electronic configuration of helium. Thus, hydrogen

- accepts an electron from another atom to form the negative hydride ion, H^-;
- forms a covalent bond by sharing its lone electron as in the hydrogen molecule, H—H;
- donates its lone electron to form the positive hydrogen ion, H^+, and enters into coordinate bond formation with molecules having lone pairs of electrons. For example, hydrogen ion combines with water to form the hydroxonium ion, H_3O^+, and with ammonia to form the ammonium ion, NH_4^+.

Fig. 19.5 During chemical combinations, hydrogen acquires the duplet electronic configuration.



Experiment 19.2 To demonstrate that hydrogen is lighter than air.

Method Take four test-tubes *A*, *B*, *C* and *D*. Fill test-tubes *A* and *B* with hydrogen and stopper them with corks. Hold test-tube C, containing air, mouth-to-mouth above test-tube *A* and remove the cork. After about 15 seconds, insert a burning splinter into each of the test-tubes to test for the presence of hydrogen. What do you observe?

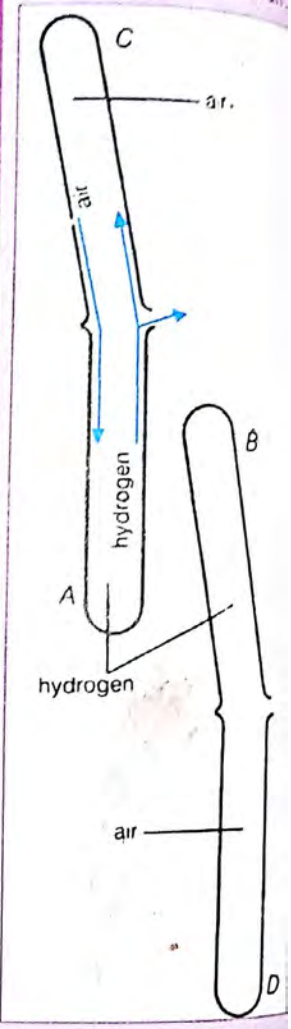
Hold test-tube *D*, containing air, mouth-to-mouth beneath test-tube *B* and remove the cork. After about 15 seconds, insert a burning splinter into each of the test-tubes. What happens?

Result The results are summarized in the following table.

Test-tube	Observation	Inference
C	The splinter burns with a pop sound.	A mixture of hydrogen and air is present. The hydrogen from test-tube *A* has risen to displace the denser air.
A	No pop sound.	Hydrogen has been displaced by air.
B	Hydrogen burns quietly with a pale blue flame around the rim of the test-tube. When a lighted splinter is inserted into the test-tube, the flame is extinguished.	Only pure hydrogen is present. Hydrogen will burn in air but does not support combustion, i.e. it does not allow a splinter to burn in it.
D	The splinter continues to burn but no pop sound is heard.	Only air is present. Air allows the splinter to burn in it.

Conclusion Since hydrogen can be displaced upwards by air, it is lighter than air.

Fig. 19.6 Hydrogen is lighter than air



Combination reactions

Hydrogen combines with certain metals and non-metals to form electrovalent and covalent hydrides respectively. In both instances, the hydrogen atom gains an extra electron to achieve the stable electronic configuration of helium.

With metals Hydrogen combines directly with several of the more active metals to form ionic hydrides, i.e compounds which contain the hydride ion, H^-. For example,

$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$

With oxygen Pure hydrogen burns with a pale bl flame as it combines with oxygen to produce stea

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

With halogens Hydrogen combines directly with t halogens to produce halides. For example,

$$Cl_2(g) + H_2(g) \rightarrow 2HCl(g)$$
$$Br_2(g) + H_2(g) \rightarrow 2HBr(g)$$

The reaction between hydrogen and chlorine is spontaneous in bright sunlight but slower in diffused light. The combination of hydrogen with bromine and with iodine is much less vigorous.

Reducing action

Hydrogen is a strong reducing agent. It reduces the oxides of copper, lead, iron and zinc to the respective metals when they are heated in a stream of the gas. At the same time, the hydrogen itself is oxidized to form water.

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$$
$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$$

Test for hydrogen

Insert a lighted splinter into a test-tube containing the unknown gas. If the gas is hydrogen, it will burn with a pop sound, since it will invariably mix with the air as soon as the test-tube is unstoppered. This test should only be carried out with small quantities of the gas.

Uses

1. Hydrogen is used in the manufacture of ammonia, hydrochloric acid and methanol.
2. Hydrogen under high pressure is passed through vegetable oils (e.g. palm oil, corn oil, cotton seed oil or soybean oil) in the presence of a nickel catalyst to give solid fats, which are used as margarine or as lard substitutes, and in the manufacture of soap and candles.
3. Since hydrogen has a low density, it is used for filling balloons. Its highly flammable nature, however, limits this use to meteorological studies and other scientific purposes.
4. Hydrogen is passed through a mixture of oil and powdered coal at high temperatures and pressures to yield a mixture of hydrocarbons from which synthetic petrol can be extracted by fractional distillation. This petrol is more expensive than ordinary petrol and is used in countries with plenty of coal but no petrol.
5. Hydrogen is a constituent of many gaseous fuels such as water gas and coal gas. Liquid hydrogen is also used as a rocket fuel.
6. Hydrogen gives out a lot of heat when it burns. Thus it is used in oxy-hydrogen flames to produce high temperatures (over 2 000 °C) that can melt metals. Hydrogen is also used in atomic hydrogen flames. When hydrogen is passed through an electric arc, its molecules absorb energy and break up to form atoms. These atoms recombine when they are out of the arc, evolving large amounts of energy in the form of heat.

Isotopes of Hydrogen

Hydrogen exists in three isotopic forms, namely *hydrogen or protium,* ^1_1H, *heavy hydrogen or deuterium,* ^2_1H or D, and *tritium,* ^3_1H or T, with relative atomic masses of 1, 2 and 3 respectively. Deuterium is chemically similar to protium except that it is slightly less reactive. Deuterium also forms an oxide, D_2O, which is similar to water, H_2O. Deuterium oxide is commonly known as heavy water because it is about 1.1 times heavier than water. Tritium is radioactive and is rarely found in ordinary hydrogen.

HYDRIDES

The alkali and alkali-earth metals like sodium and calcium form ionic hydrides with hydrogen. These hydrides are crystalline solids with high melting points that conduct electricity when molten. They readily react with water to form hydroxides and liberate hydrogen gas. For example,

$$CaH_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + 2H_2(g)$$

Ionically,

$$H^-(s) + H_2O(l) \rightarrow OH^-(aq) + H_2(g)$$

Boron and aluminium form complex covalent hydrides which are important reducing agents especially in organic chemistry. The two common complex hydrides are lithium tetrahydridoaluminate(III) and sodium tetrahydridoborate(III).

Most non-metallic elements like chlorine and nitrogen form simple covalent hydrides. These are volatile compounds that are gaseous at room temperature. The exceptions are the hydrides of fluorine, HF, and oxygen, H_2O, which are liquids because of extensive hydrogen bonding. The hydrides of the more electronegative elements like chlorine and sulphur form acidic solutions with water.

SUMMARY

- Hydrogen is prepared in the laboratory by the action of water, steam or dilute mineral acids on meta above copper in the activity series.
- Industrially, hydrogen can be produced from water gas, methane or by electrolytic methods.
- The activity series of metals gives the order of reactivity of the metals, with the most reactive metal the top and the least reactive at the bottom. Metals above hydrogen in the series displace it from dilu acids, while metals below hydrogen cannot do so.
- Hydrogen is neutral to litmus; is the lightest known substance; burns in air but does not support combustio is a strong reducing agent; undergoes direct combination with active metals to form ionic hydrides; reac with oxygen to form oxides; reacts with halogens to form halides; and reduces the metallic oxides to the metals.
- With a lighted wooden splinter, hydrogen gives a *pop* sound and burns with a pale blue flame. This is test for hydrogen.
- Hydrogen has three isotopes, viz. protium, ${}^{1}_{1}H$, deuterium, ${}^{2}_{1}H$, and tritium, ${}^{3}_{1}H$.
- Hydrides of alkali and alkali-earth metals are ionic and react with water to form hydroxides and liberat hydrogen. Hydrides of non-metals are mainly covalent.

EXERCISES

1. An isotope of hydrogen commonly referred to as heavy water is
A protium. B deuterium.
C tritium. D basic water.

2. Hydrogen is manufactured via the following methods except
A action of steam on iron.
B action of steam on red-hot coke.
C action of steam on methane under nickel catalyst.
D electrolytic method.

3. All, except one metal, can displace hydrogen from water or acids.
A Zinc
B Silver
C Potassium
D Heated magnesium

4. Oxidation state of hydrogen in the hydride of nitrogen is
A +1 B +3
C −3 D −1

5. From the reaction;

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$$

hydrogen is behaving as an
A oxidizing agent.
B reducing agent.
C steam donor.
D hydride.

6. Which of the following metals will not give hydrogen with dilute hydrochloric acid?
A Cu C Fe E Mg
B Zn D Ca

7. Sodium hydride reacts with water to
A form an acidic solution.
B liberate hydrogen gas.
C form a salt.
D liberate oxygen.
E form a neutral solution.

8. (a) How would you prepare hydrogen from zinc and a dilute acid?

(b) Describe what happens when a piece of potassium is dropped into a trough of water coloured with red litmus.

(c) Giving the conditions of the reaction, describe in detail how hydrogen may be obtained in large quantity from water gas, starting with coke and other raw materials.

(a) How would you show the following experimentally?
- (i) Hydrogen is a reducing agent.
- (ii) Water is an oxide of hydrogen. Illustrate with diagrams and equations.
- (iii) Hydrogen is lighter than air.

(b) How would you identify hydrogen?

(c) Give four uses of hydrogen.

10. Under what conditions do the following metals react with water?
Sodium, calcium, magnesium, iron, copper

How would you arrange the metals listed in order of their relative reactivities?

11. (a) Hydrogen exists in three isotopic forms. What are the isotopes known as? Give the electronic configuration of these isotopes.

(b) Ordinary hydrogen contains 99.30% of $^{1}_{1}H$ atoms and 0.70% $^{2}_{1}H$ atoms. Calculate the relative atomic mass of hydrogen. Why is tritium not found naturally in the earth's crust?

20 CHLORINE AND ITS COMPOUNDS • HALOGEN FAMILY

CHLORINE

Chlorine is the most important element of a family of very reactive non-metals known as the *halogens.* The halogens are found in Group 7 of the Periodic Table. Each halogen atom has seven valence electrons. This accounts for the similarity in the chemical properties of the halogens.

Chlorine was first discovered by Scheele in 1774 when he heated some concentrated hydrochloric acid with manganese(IV) oxide. In 1810, Davy named the gas *chlorine,* a derivative of the Greek word *chloros,* meaning greenish-yellow.

Chlorine does not occur free in nature because it is too reactive. Instead, it is usually found in the combined state as chlorides. The most abundant of these is sodium chloride or common salt, which is found both in the sea and as salt deposits.

Laboratory Preparation

Chlorine is usually prepared by the oxidation of concentrated hydrochloric acid with a strong oxidizing agent such as manganese(IV) oxide, potassium tetraoxomanganate(VII) or lead(IV) oxide.

Using manganese(IV) oxide Heat a mixture of manganese(IV) oxide and concentrated hydrochloric acid. The acid is oxidized to liberate chlorine.

$$MnO_2(s) + 4HCl(aq) \xrightarrow{heat} MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

Ionically,

$$Mn^{4+}(O^{2-})_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$$

Alternatively, add concentrated tetraoxosulphate(VI) acid to a mixture of sodium chloride and manganese(IV) oxide. On heating, the acid reacts wi the sodium chloride to give hydrogen chloride, whi is then oxidized by the manganese(IV) oxide to libera chlorine.

$$2NaCl(s) + MnO_2(s) + 2H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + MnSO_4(aq) + 2H_2O(l) + Cl$$

Ionically,

$$2Cl^-(s) + Mn^{4+}(O^{2-})_2(s) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl$$

Using tetraoxomanganate(VII) Potassium tetraox manganate(VII) oxidizes concentrated hydrochlori acid to liberate chlorine.

$$2KMnO_4(aq) + 16HCl(aq) \rightarrow 2MnCl_2(aq) + 2KCl(aq) + 8H_2O(l) + 5Cl$$

Ionically,

$$2MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cl$$

Industrial Preparation

Chlorine is manufactured industrially by the electrolysis of

- brine, and
- the chlorides of molten sodium, magnesium or calcium.

The chlorine is then liquefied and stored, under pressure, in steel cylinders.

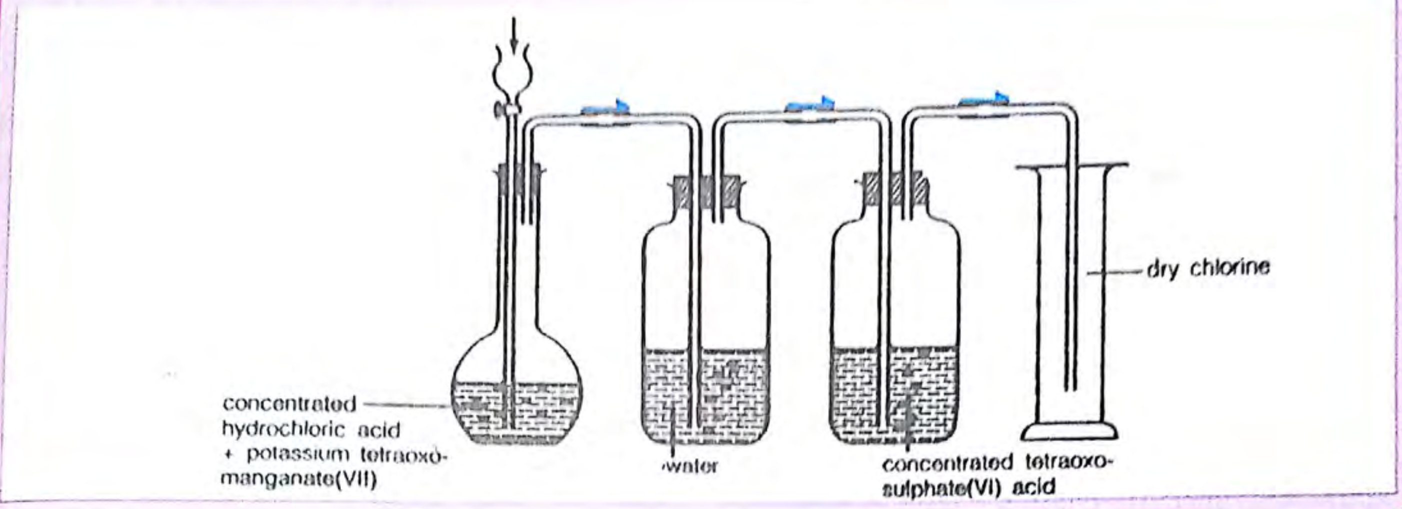
Physical Properties

1 Chlorine is a greenish-yellow gas with an unpleasant choking smell.

Experiment 20.1 To prepare chlorine by the oxidation of concentrated hydrochloric acid with potassium tetraoxomanganate(VII).

Method Place some potassium tetraoxomanganate(VII) in a flat-bottomed flask and set up the apparatus as shown. Add concentrated hydrochloric acid gradually into the flask through the thistle funnel. Pass the gas produced through water and concentrated tetraoxosulphate(VI) acid and collect it by downward delivery.

Fig. 20.1 Preparation of chlorine.



Result Chlorine is evolved as soon as the drops of acid touch the tetraoxomanganate(VII). A small amount of hydrogen chloride is also evolved from the concentrated acid. As this mixture of gases passes through the water, the hydrogen chloride dissolves, and so is removed. The pure chlorine gas is then dried as it passes through the concentrated tetraoxosulphate(VI) acid.

Conclusion Chlorine can be prepared by the action of concentrated hydrochloric acid on potassium tetraoxomanganate(VII)

2 It is moderately soluble in water. About 2.3 cm^3 of it will dissolve in 1 cm^3 of water at s.t.p.

3 It is about 2.5 times denser than air.

4 It can easily be liquefied under a pressure of about 6 atmospheres.

5 It is poisonous. As little as 20 parts per million of it in the air can damage the mucous lining of our lungs.

Chemical Properties

chlorine atom has seven valence electrons. It is ery reactive as it tries to achieve a stable electron ctet either

by gaining an electron, usually from the metals of Groups 1 and 2, to form a negative ion, Cl^- as in electrovalent compounds like sodiun chloride, NaCl, and calcium chloride, $CaCl_2$, or

by sharing a pair of electrons in a single covalent bond with another atom, having a fairly similar electronegative value, as in gaseous chlorine, Cl–Cl, and hydrogen chloride, H–Cl.

Displacement of other halogens

With the exception of fluorine, chlorine can displace any of the other halogens from solutions of their respective acids and salts. This is because it is more reactive than the halogen it replaces as indicated by its electrode potential value.

Half-cell reduction reaction

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^\ominus = +1.36$ V

Half-cell oxidation reaction

$2Br^- \rightarrow Br_2 + 2^{e-}$ $E^\ominus = -1.06$ V

Overall redox reaction

$Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(l) + 2Cl^-(aq)$

Displacement occurs when chlorine gas is bubbled into the appropriate solutions, e.g.

$$Cl_2(g) + 2NaBr(aq) \rightarrow 2NaCl(aq) + Br_2(l)$$
$$Cl_2(g) + 2HI(aq) \rightarrow 2HCl(aq) + I_2(s)$$
$$Cl_2(g) + 2NaI(aq) \rightarrow 2NaCl(aq) + I_2(s)$$

Direct combination with other elements

Chlorine is a very reactive gas. It combines directly with most other elements to form chlorides.

With metals Metals react readily with chlorine, especially when heated, to form the corresponding chlorides.

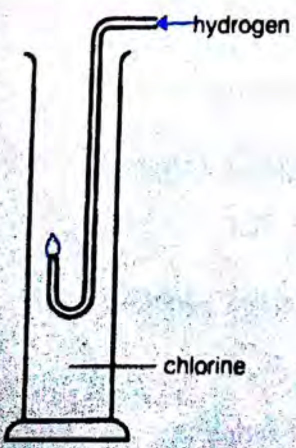
$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$
$$Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s)$$
$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

Anhydrous metallic chlorides such as iron(III), aluminium and tin(IV) chlorides are prepared by direct combination.

NOTE Where a metal forms more than one chloride, the higher chloride is usually formed, e.g. in the case of iron, iron(III) chloride is formed and not iron(II) chloride. This is due to the oxidizing nature of chlorine.

With non-metals With the exception of the noble gases, oxygen, nitrogen and carbon, all the other non-metals burn in chlorine to produce the corresponding chlorides.

Fig. 20.2 Burning hydrogen in chlorine.



Hydrogen and chlorine combine explosively in bright sunlight, although the reaction is slower in diffused light. The combination reaction between these gases can be shown by introducing a jet of burning hydrogen into a gas jar of chlorine. As the reaction proceeds, the greenisn-yellow colour of chlorine diminishes in intensity as misty fumes of hydrogen chloride appear.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Reactions with hydrogen

Chlorine has a very strong affinity for hydrogen. Besides combining readily with free molecular hydrogen, it also readily removes hydrogen from its compounds to form hydrogen chloride.

With hydrocarbons A piece of filter paper saturated with warm turpentine ($C_{10}H_{16}$) will rapidly catch fire in a jar of chlorine, forming soot (a black deposit of carbon) and misty fumes of hydrogen chloride.

$$C_{10}H_{16}(l) + 8Cl_2(g) \rightarrow 10C(s) + 16HCl(g)$$

Chlorine also removes hydrogen from burning hydrocarbons like wax, candle, petrol or methane to form hydrogen chloride fumes and soot.

Under controlled conditions, substitution reactions occur. In such reactions, chlorine reacts with saturated hydrocarbons to produce chlorinated hydrocarbons and hydrogen chloride.

$$\underset{\text{methane}}{CH_4(g)} + Cl_2(g) \rightarrow \underset{\text{chloromethane}}{CH_3Cl(g)} + HCl(g)$$

With ammonia Chlorine will remove hydrogen from ammonia with the formation of nitrogen and hydrogen chloride. The latter then combines with excess ammonia to form ammonium chloride.

$$2NH_3(g) + 3Cl_2(g) \rightarrow N_2(g) + 6HCl(g)$$
$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

With hydrogen sulphide When chlorine and hydrogen sulphide are mixed, a yellow deposit of sulphur is formed as a result of the oxidation of the sulphide by chlorine.

$$H_2S(g) + Cl_2(g) \rightarrow 2HCl(g) + S(s)$$

With water Chlorine water (made by bubbling chlorine through water) gives off oxygen when exposed to sunlight. This is due to the formation of oxochlorate(I) acid which decomposes slowly to hydrogen chloride and oxygen.

$$Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$$

$$2HOCl(aq) \xrightarrow{\text{sunlight}} 2HCl(aq) + O_2(g)$$

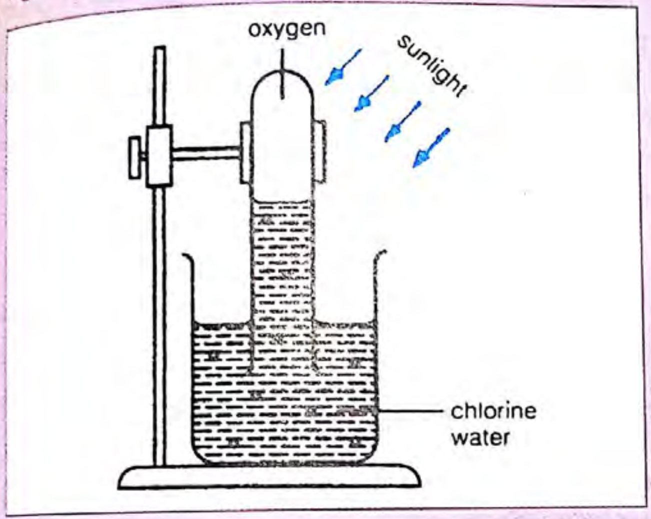


Fig. 20.3 Effect of sunlight on chlorine water.

As an oxidizing agent

Chlorine is a powerful oxidizing agent because of its ability to remove hydrogen and its readiness to accept electrons from reducing agents to form chloride ions. All the reactions discussed above are basically redox reactions in which chlorine is the oxidizing agent.

Typical examples of the oxidizing behaviour of chlorine are as follows:

With iron(II) salts Chlorine oxidizes a solution of green iron(II) chloride to yellow iron(III) chloride.

$$2FeCl_2(aq) + Cl_2(g) \rightarrow 2FeCl_3(aq)$$

Ionically,

$$2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$

With trioxosulphate(IV) ion When bubbled through a freshly prepared solution of trioxosulphate(IV) acid, chlorine oxidizes the trioxosulphate(IV) ion to tetraoxosulphate(VI) acid.

$$H_2SO_3(aq) + H_2O(l) + Cl_2(g) \rightarrow H_2SO_4(aq) + 2HCl(aq)$$

Ionically,

$$SO_3^{2-}(aq) + H_2O(l) + Cl_2(g) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2Cl^-(aq)$$

As a bleaching agent

Chlorine is a common bleaching agent. In the presence of water, it bleaches most dyes and inks, except those containing carbon, e.g. printer's ink.

The bleaching action of chlorine is due to its ability to react with water to form oxochlorate(I) acid. The latter is unstable and decomposes to release oxygen which oxidizes the dye to form a colourless compound.

$$HOCl(aq) \rightarrow HCl(aq) + [O]$$

$$\underset{\text{coloured}}{\text{Dye}} + [O] \rightarrow \underset{\text{colourless}}{(\text{Dye} + O)}$$

Reaction with alkalis

With dilute alkali solutions When chlorine is bubbled through a cold dilute solution of sodium hydroxide, a pale-yellowish mixture of the oxochlorate(I) and chloride of the metal is formed.

$$Cl_2(g) + 2NaOH(aq) \rightarrow \underset{\substack{\text{sodium}\\ \text{oxochlorate(I)}}}{NaOCl(aq)} + NaCl(aq) + H_2O(l)$$

Ionically,

$$Cl_2(g) + 2OH^-(aq) \rightarrow OCl^-(aq) + Cl^-(aq) + H_2O(l)$$

Bleaching powder is produced by bubbling chlorine through a freshly prepared solution of slaked lime.

$$Cl_2(g) + \underset{\text{slaked lime}}{Ca(OH)_2(s)} \rightarrow \underset{\text{bleaching powder}}{CaOCl_2.H_2O(s)}$$

With concentrated alkali solutions If chlorine is bubbled through a ***hot concentrated*** solution of sodium hydroxide, a mixture of the trioxochlorate(V) and chloride of the metal is formed.

$$3Cl_2(g) + 6NaOH(aq) \rightarrow \underset{\text{sodium trioxochlorate(V)}}{NaClO_3(aq)} + 5NaCl(aq) + 3H_2O(l)$$

Ionically,

$$3Cl_2(g) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$$

Tests for chlorine

Chlorine is a greenish-yellow gas, with an irritating smell. Its presence can be confirmed by its action on damp litmus paper and starch-iodide paper.

Damp litmus paper test Drop a piece of damp blue litmus paper into a gas jar of the unknown gas. If the litmus paper turns pink and then becomes bleached, the gas is chlorine.

Starch-iodide paper test Drop a piece of damp starch-iodide paper into the unknown gas. If the paper turns dark blue, then the gas is chlorine.

Chlorine turns starch-iodide paper blue because it displaces iodine from the iodide. The iodine liberated then turns the starch blue.

$$2KI(aq) + Cl_2(g) \rightarrow 2KCl(aq) + I_2(s)$$

Uses

1 Chlorine is a powerful germicide because of its oxidizing nature. It is used in the sterilization of water for domestic and industrial use and in the treatment of sewage.
2 Chlorine is used as a bleaching agent for cotton, linen and wood-pulp. It is too strong for bleaching animal fibres like silk and wool.
3 Chlorine is used in the manufacture of:
   - Important organic solvents such as trichloromethane, $CHCl_3$, tetrachloromethane, CCl_4, trichloroethene, C_2HCl_3, and trichloroethanal (chloral), $CCl_3.CHO$. Trichloroethanal is also used for the manufacture of the insecticide D.D.T.
   - The widely used plastic, poly(chloroethene), known commonly as polyvinyl chloride or PVC, and synthetic rubber.
   - Hydrochloric acid.
   - Potassium trioxochlorate(V) which is used in making matches and fireworks, and sodium trioxochlorate(V), a weed-killer.
   - Bleaching agents such as bleaching powder and sodium oxochlorate(I) which are widely used in dye works and laundries.
   - Domestic antiseptics, e.g. acidified sodium oxochlorate(I) solution.

HYDROGEN CHLORIDE

Hydrogen chloride exists as a gas at s.t.p. When it dissolves in water, it forms hydrochloric acid. Pure hydrogen chloride was first prepared in 1772 by Priestley, who called it *marine-acid gas* because it was made from sea salt.

Hydrogen chloride occurs in traces in the air as an industrial by-product. It is considered as an air pollutant, but can readily be washed down by the rain because of its solubility in water.

Laboratory Preparation

Hydrogen chloride is prepared by the action of hot concentrated tetraoxosulphate(VI) acid on any soluble chloride, e.g. sodium chloride. Initially, when the temperature is low, sodium hydrogentetraoxosulphate(VI), $NaHSO_4$, is formed together with some hydrogen chloride. Later at higher temperatures, the reaction goes to completion, forming sodium tetraoxosulphate(VI) and more hydrogen chloride.

$$NaCl(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g)$$
$$NaCl(s) + NaHSO_4(aq) \rightarrow Na_2SO_4(aq) + HCl(g)$$

The overall equation for the reaction can be represented as follows:

$$2NaCl(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2HCl(g)$$

Ionically,

$$Cl^-(s) + H^+(aq) \rightarrow HCl(g)$$

Industrial Preparation

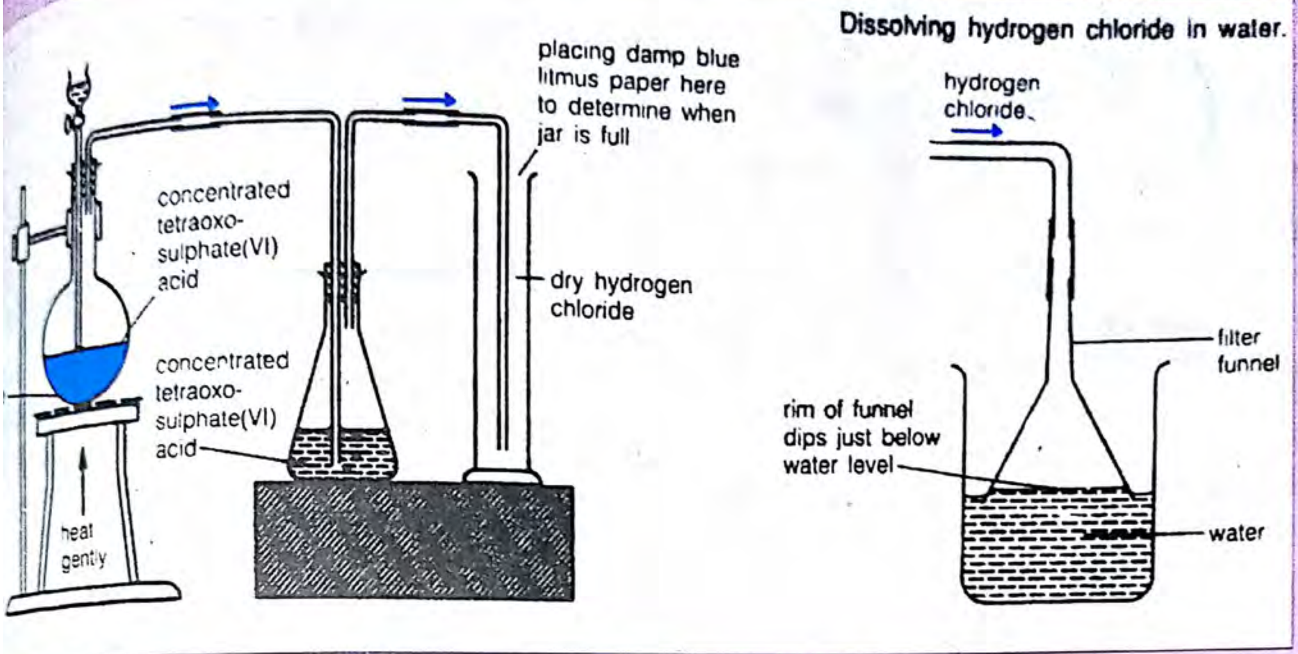
Hydrogen chloride is made in large amounts by the direct combination of hydrogen and chlorine gases obtained from the electrolysis of brine. This hydrogen chloride, which is obtained by burning a jet of hydrogen in chlorine, is very pure. It is dissolved in water to form hydrochloric acid.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

iment 20.2 To prepare hydrogen chloride.

Method Place some sodium chloride in the round-bottomed flask and set up the apparatus as shown. Add concentrated tetraoxosulphate(VI) acid through the thistle funnel and heat the mixture gently. Dry the gas formed by passing it through concentrated tetraoxosulphate(VI) acid and collect it in a gas jar.

.4 Preparation of hydrogen chloride.


Dissolving hydrogen chloride in water.

Result The acid reacts with the chloride to produce misty fumes of hydrogen chloride, which turns the damp blue litmus paper red.

Conclusion Hydrogen chloride is an acidic gas which can be prepared by the action of concentrated tetraoxosulphate(VI) acid on a soluble chloride.

NOTE To prepare hydrochloric acid, attach an inverted filter funnel to the delivery tube. Let the rim of the funnel just dip into a beaker of water. This prevents the water in the beaker from being sucked into the reaction flask as hydrogen chloride may dissolve faster than it is being generated, thereby reducing the pressure inside the reaction system.

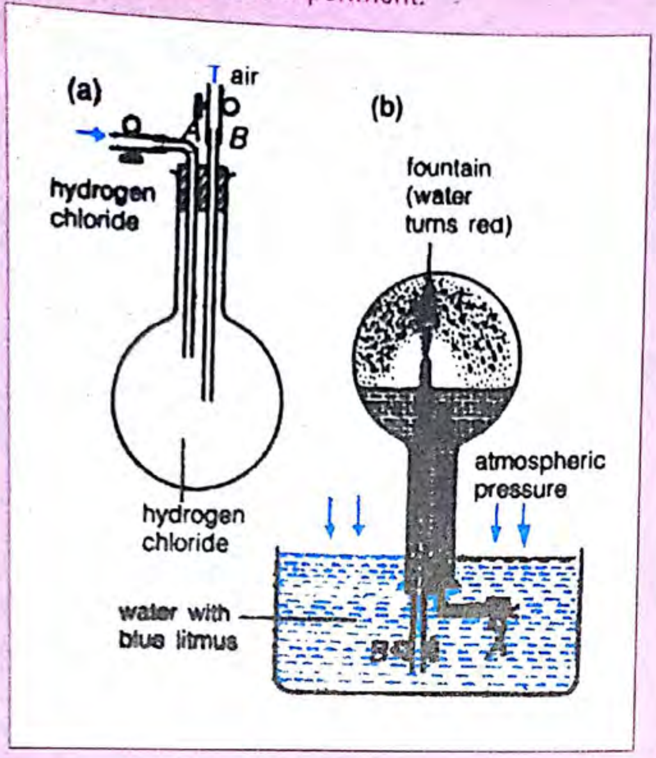
periment 20.3 To show that hydrogen chloride is extremely soluble in water.

Method Fit a dry round-bottomed flask with a rubber bung carrying two delivery tubes *A* and *B* as shown in fig. 20.5a. Fill the flask with dry hydrogen chloride through tube *A*. At the same time, open the clip on tube *B* to allow the air inside the flask to be displaced. When the flask is full of gas, add a few drops of water through tube *B* and immediately close the clips at *A* and *B*. Allow the water to run down into the flask. Then invert the flask into a trough of water containing a few drops of blue litmus solution. Open the clip at tube *B* as shown in fig. 20.5b. What happens?

Result The first few drops of water which were added into the flask dissolve nearly 400 times their own volume of hydrogen chloride, creating a reduced pressure inside the flask. As soon as the clip at tube *B* is opened the water in the trough is forced into the flask by the greater atmospheric pressure outside. The water then rises up the delivery tube *B* and splashes into the flask as a fountain, dissolving the remaining gas. The water turns red immediately on entering the flask, showing that the gas is acidic in aqueous solution.

Conclusion This experiment shows that hydrogen chloride is extremely soluble in water.

Fig. 20.5 Fountain experiment.



Physical Properties of Hydrogen Chloride Gas

1. Pure hydrogen chloride is a colourless gas with a sharp, irritating smell.
2. It turns damp blue litmus paper red, showing that it is acidic in aqueous solution.
3. It is about 1.25 times denser than air.
4. It is very soluble in water, forming an aqueous solution of hydrochloric acid.
5. It forms misty fumes in moist air because it dissolves in the moisture to form tiny droplets of hydrochloric acid.
6. Dry hydrogen chloride readily dissolves in non-polar solvents like chloroform and toluene. Such a solution does not conduct electricity and has no acidic properties. This is because hydrogen chloride, which is a covalent molecule, does not ionize when it dissolves in non-polar solvents. In aqueous solution, it reacts with the polar water molecules and ionizes to form chloride and oxonium ions. The latter ions are responsible for the acidic properties of an aqueous solution of the gas.

$$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

7. Hydrogen chloride neither burns nor supports combustion. Hence, it extinguishes a burning splinter.

CHEMICAL PROPERTIES OF HYDROGEN CHLORIDE GAS

Direct Combination with ammonia

When a gas jar of hydrogen chloride is inverted over a gas jar full of ammonia, dense white fumes are formed. These fumes are particles of solid ammonium chloride suspended in air.

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

Reaction with metals

Hydrogen chloride reacts with many metals, especially when they are heated, to form the respective chlorides and hydrogen.

$$Zn(s) + 2HCl(g) \rightarrow ZnCl_2(s) + H_2(g)$$

If the metal can form two chlorides, usually the lower chloride is formed.

$$Fe(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2(g)$$

PROPERTIES OF HYDROCHLORIC ACID

Action of heat

When concentrated hyrochloric acid is heated, it boils to liberate hydrogen chloride fumes, making the solution more dilute. When dilute hydrochloric acid is heated, water is lost, making the residual solution more concentrated. In both cases, the solutions will boil until they contain about 20.24% hydrochloric acid. This solution is known as a *constant boiling mixture* or an *azeotropic mixture* because any further heating will not affect its concentration.

As an acid

Hydrogen chloride gas dissolves in water to form hydrochloric acid whicn exhibits all the usual properties of acids.

With metals Metals which are more electropositive than hydrogen will liberate hydrogen gas from the acid. For example,

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Ionically,

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

A mixture of zinc and copper dust can be separated by adding dilute hydrochloric acid to it. Zinc which is more electropositive than hydrogen reacts with the acid, leaving behind the copper dust.

With bases It reacts with a base or an alkali to produce a salt and water only.

$$ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l)$$
$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Ionically, the last reaction can be represented as follows:

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

With trioxocarbonates(IV) It reacts with trioxocarbonates(IV) and hydrogentrioxocarbonates(IV) to liberate carbon(IV) oxide.

$$2HCl(aq) + Na_2CO_3(s) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$
$$HCl(aq) + NaHCO_3(s) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

Ionically,

$$2H^+(aq) + CO_3^{2-}(s) \rightarrow H_2O(l) + CO_2(g)$$
$$H^+(aq) + HCO_3^-(s) \rightarrow H_2O(l) + CO_2(g)$$

As a precipitating agent

When hydrochloric acid is added to silver trioxonitrate(V) or lead(II) trioxonitrate(V) solution, a white precipitate of silver or lead(II) chloride is formed.

$$AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$$
$$Pb(NO_3)_2(aq) + 2HCl(aq) \rightarrow PbCl_2(s) + 2HNO_3(aq)$$

Ionically,

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

Reactions with strong oxidizing agents

Concentrated hydrochloric acid is easily oxidized by strong oxidizing agents, such as potassium tetraoxomanganate(VII), to liberate chlorine. This is why hydrochloric acid is never used for acidifying solutions of oxidizing agents. Instead, tetraoxosulphate(VI) acid is used.

Tests for hydrogen chloride

If the unknown gas is colourless, has an irritating smell, fumes in moist air and turns blue litmus paper red, then it is probably hydrogen chloride. The following two tests confirm its presence.

With ammonia Place a glass rod dipped with ammonia solution at the mouth of a gas jar containing the unknown gas. If the gas is hydrogen chloride, dense white fumes composed of suspended particles of ammonium chloride are produced.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

With silver trioxonitrate(V) Add a few drops of silver trioxonitrate(V) solution to a gas jar containing the unknown gas and shake. If the gas is hydrogen chloride, a white precipitate of silver chloride will be formed.

Instead of silver trioxonitrate(V), lead(II) trioxonitrate(V) can also be used.

Uses

1 Hydrogen chloride gas is used in the synthesis of chloroethene, an important component of some plastics.
2 Hydrochloric acid is used in the manufacture of gelatin and glue from the tendons of animals, and in the production of glucose from starch. It is also used in the manufacture of textiles and dyes.
3 Hydrochloric acid is used to remove oxides from metals prior to electroplating. This process is known as *pickling* and is used in the steel-making industry.
4 In the laboratory, hydrochloric acid is used for the testing, analysis and preparation of other compounds.

CHLORIDES

The chlorides are normal salts formed when metallic ions replace the hydrogen ions in hydrochloric acid. Chlorides are soluble in water, except

copper(I) chloride, CuCl,
mercury(I) chloride, Hg_2Cl_2, and
silver chloride, AgCl.

Lead(II) chloride, $PbCl_2$, is insoluble in cold water but dissolves gradually when warmed.

Laboratory Preparation

Chlorides can be prepared in the laboratory by various methods. The specific method which is used for the preparation of a given chloride depends on the activity of the metal and the nature of the given chloride.

Action of hydrochloric acid or hydrogen chloride on metals The chlorides of magnesium and zinc are prepared by the action of dilute hydrochloric acid on the corresponding metals.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$
$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Anhydrous aluminium chloride and iron(II) chloride are formed by passing dry hydrogen chloride gas over the heated metals.

$$2Al(s) + 6HCl(g) \rightarrow 2AlCl_3(s) + 3H_2(g)$$
$$Fe(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2(g)$$

Action of the acid on the oxides, hydroxides or trioxocarbonates(IV) of metals The chlorides of potassium, sodium and calcium are prepared by neutralizing their hydroxides with dilute hydrochloric acid or by adding the acid to their oxides or trioxocarbonates(IV).

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
$$2HCl(aq) + K_2CO_3(aq) \rightarrow 2KCl(aq) + H_2O(l) + CO_2(g)$$
$$2HCl(aq) + CaO(s) \rightarrow CaCl_2(aq) + H_2O(l)$$

Copper is too inactive to react with dilute hydrochloric acid. Instead, copper(II) chloride is prepared by the action of the acid on copper(II) oxide or trioxocarbonate(IV).

$$2HCl(aq) + CuO(s) \rightarrow CuCl_2(aq) + H_2O(l)$$
$$2HCl(aq) + CuCO_3(s) \rightarrow CuCl_2(aq) + H_2O(l) + CO_2(g)$$

Double decomposition Metallic lead, silver and mercury are also too inactive to react with dilute hydrochloric acid. Since their chlorides are insoluble, they are usually prepared by double decomposition. Mercury(II) chloride, however, cannot be prepared by this method.

$$Pb(NO_3)_2(aq) + 2KCl(aq) \rightarrow PbCl_2(s) + 2KNO_3(aq)$$
$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$
$$Hg_2(NO_3)_2(aq) + 2NaCl(aq) \rightarrow Hg_2Cl_2(s) + 2NaNO_3(aq)$$

Direct combination of the metal with chlorine Under appropriate conditions, chlorine can react with any metal to produce the respective chlorides. For example, iron(III) chloride and mercury(II) chloride can be prepared by passing a stream of dry chlorine over a heated iron wire and mercury respectively.

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$
$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Table 20.1 Methods of preparing chlorides.

Metal	Method	Property of metal
K Na Ca	Action of dilute hydrochloric acid on their oxides, hydroxides and trioxocarbonates(IV).	Attacked by dilute hydrochloric acid and chlorine.
Mg Al Zn Fe	Action of dilute hydrochloric acid on the metals, their oxides and trioxocarbonates(IV). Action of chlorine on the metal for iron(III) chloride.	
Pb	By double decomposition.	
Cu	Action of dilute hydrochloric acid on the oxide, trioxocarbonate(IV).	
Hg	By double decomposition for mercury(I) chloride, and by the action of chlorine on metal for mercury(II)	Attacked by chlorine but not by dilute hydrochloric acid.
Ag	By double decomposition.	
Au	By the action of chlorine on the metal.	

Recovery of chlorides from their solutions

Chlorides are not decomposed by heat. Hence, they can be recovered by evaporating their solutions to dryness. Sometimes, they are also separated from their solutions by crystallization.

Properties

Action of heat Chlorides are not decomposed by heat. They are used in flame tests where the metals are identified by the colours of their flames.

With tetraoxosulphate(VI)acid All chlorides react with hot concentrated tetraoxosulphate(VI) acid to produce hydrogen chloride.

$$2Cl^-(s) + (H^+)_2SO_4^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2HCl(g)$$

When a metallic chloride is heated with concentrated tetraoxosulphate(VI) acid and a strong oxidizing agent, chlorine is produced.

$$2Cl^-(s) + Mn^{4+}(O^{2-})_2(s) + 4H^+(aq) \\ \rightarrow Mn^{2+}(aq) + 2H_2O(l) + Cl_2(g)$$

Test for soluble chlorides

Acidify the test solution with excess dilute trioxonitrate(V) acid (to prevent the precipitation of other salts) and then add a few drops of silver trioxonitrate(V). A white precipitate of silver chloride, which readily dissolves in aqueous ammonia indicates the presence of a chloride.

$$Ag^+NO_3^-(aq) + Cl^-(aq) \rightarrow AgCl(s) + NO_3^-(aq)$$

This test can also be carried out with lead(II) trioxonitrate(V). A white precipitate of lead(II) chloride which dissolves when heated and reappears when cooled indicates the presence of a chloride.

$$Pb^{2+}(NO_3^-)_2(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s) + 2NO_3^-(aq)$$

THE HALOGEN FAMILY

Besides chlorine, the halogen family includes fluorine, bromine, iodine and astatine. Fluorine is the most reactive element among the halogens and is in many ways unique. Thus, it is usually studied separately. Astatine, which is radioactive, has been made artificially and does not occur naturally. Bromine and iodine are chemically very similar to chlorine.

Fluorine

Fluorine does not occur in the free state in nature because of its high reactivity. Instead, it is found mainly in minerals like *cryolite*, $3NaF.AlF_3$, and *fluorspar*, CaF_2.

Preparation

The only method of preparing fluorine is by electrolysis. The electrolyte used is a solution of potassium fluoride in anhydrous hydrogen fluoride. In order to resist attack by the fluorine produced, carbon is used as the anode and a steel vessel as the cathode. Water must not be present because it will react with the fluorine formed.

Properties

Fluorine is a poisonous yellow gas with an irritating smell. It is the most reactive element found on earth. Most metals catch fire in fluorine, and even inactive metals like gold and platinum are attacked if heated in a stream of the gas. Usually the highest fluoride of the metal is formed. It combines directly with all other non-metals except nitrogen, oxygen, helium, neon and argon to form fluorides like PF_5 and SF_6. Hydrogen and fluorine combine explosively to form hydrogen fluoride. Because of its great affinity for hydrogen, it will also react vigorously with any compound containing hydrogen, e.g. water. The hydrogen fluoride produced is a fuming colourless liquid with a very low boiling point (19.5 °C). This boiling point, however, is much higher than that of hydrogen chloride (−84 °C). This is because the hydrogen fluoride molecules are linked together by hydrogen bonding. It dissolves readily in water to form hydrofluoric acid, which unlike the other hydrohalic acids, is only mildly acidic.

$$2H_2O(l) + 2F_2(g) \rightarrow 4HF(l) + O_2(g)$$

Fluorine is the most electronegative element known, and so is the strongest oxidizing agent. It can displace all the other halogens from aqueous solutions of their compounds. It can also react with most reducing agents and elements, even the noble gases like krypton and xenon.

$$Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$$

Uses

1 Fluorine and hydrogen fluoride are used to make uranium hexafluoride which is used in separating the isotopes of uranium.

2 In minute quantities, sodium fluoride is used for the fluoridation of drinking water, while tin(II) fluoride is used in many toothpastes to prevent tooth decay.

3 Hydrofluoric acid is used in etching glass and in cleaning steel.

4 Some fluorides and other fluorine compounds also have a wide variety of uses, e.g. as a refrigerant, anaesthetic, non-stick agent, insulator, and so on.

Bromine, Iodine and Their Salts

Bromine and iodine were discovered by Courtois (1812) and Balard (1826) respectively. Like chlorine, they usually occur naturally in the combined state.

Bromides such as those of potassium, sodium and magnesium occur in sea water and in salt deposits, but they are not as abundant as the chlorides.

Iodides occur in minute concentration in sea water. They are also found as organic compounds in some sea weeds, and as deposits of sodium and calcium trioxoiodate(V) in association with sodium trioxonitrate(V).

Preparation

Some bromine is obtained from salt wells but most of the world's supply is obtained from sea water. The water is first acidified and the chlorides which are less soluble are crystallized out. Chlorine is then used to displace bromine from the bromide solution.

$$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$$

Some iodine is extracted from sea weeds but most of it is obtained from sodium or calcium trioxoiodate(V) by treatment with sodium hydrogentrioxosulphate(IV).

In the laboratory, bromine and iodine are prep in a similar manner as chlorine, i.e. by the oxida of the appropriate halides. The gases are evolved wh the halides are heated with manganese(IV) oxide a concentrated tetraoxosulphate(VI) acid.

$$2KBr(s) + 3H_2SO_4(aq) + MnO_2(s)$$
$$\rightarrow 2KHSO_4(aq) + MnSO_4(aq) + 2H_2O(l) + Br_2(g$$

$$2KI(s) + 3H_2SO_4(aq) + MnO_2(s)$$
$$\rightarrow 2KHSO_4(aq) + MnSO_4(aq) + 2H_2O(l) + I_2(g$$

Properties

Bromine and iodine show marked resemblance t chlorine. For example,

- they are all non-metals,
- they form poisonous vapours which exist a diatomic molecules,
- they combine with hydrogen to form very soluble gases which dissolve in water to yield acidic solutions, and
- they form constant boiling mixtures when distilled.

Tests for bromide and iodide ions

With tetraoxosulphate(VI) acid Heat some of the unknown solid with a little concentrated tetraoxosulphate(VI) acid.

If a bromide is present, white fumes of hydrogen bromide and brown fumes of bromine will be evolved. If an iodide is present, purple fumes of iodine will be evolved.

With silver trioxonitrate(V) Add some dilute trioxonitrate(V) acid and silver trioxonitrate(V) solution to the unknown solution.

If a bromide is present, a pale-yellow precipitate of silver bromide will be formed. If an iodide is present, a yellow precipitate of silver iodide will be formed.

Displacement reaction Add chlorine water followed by a small quantity of tetrachloromethane to the unknown solution. If a bromide is present, it will be oxidized to free bromine which will dissolve in the organic layer to give it a brown colour. If an iodid is present, a similar reaction produces a purple colour, due to the presence of free iodine, in the organic layer.

Test for iodine

Add a drop of the unknown solution to some starch solution. If iodine is present, a dark blue colouration appears due to the formation of an iodine-starch complex. This test is sensitive even when only a few parts per million of iodine is present.

Uses of bromine and iodine

- Bromine is used in the manufacture of 1,2-dibromoethane, a petrol additive. It is added to convert the lead in petrol to lead(II) bromide which is then removed through the exhaust. This prevents lead from being deposited in the engines of motor vehicles.
- Bromine is also used in making dyestuffs, silver bromide (used on photographic film) and fire retardants.
- Iodine is used in making dyes for colour photography and pharmaceutical chemicals.
- A dilute solution of iodine in ethanol, which is known as tincture of iodine, is widely used as an antiseptic.
- Iodine is used in the treatment of simple goitre, a condition which is caused by a deficiency of iodine in our diet.

Comparing the Properties of the Halogens

Each halogen atom has seven electrons in its outermost orbit. As a result, the halogens exhibit the following features.

1 Electronegative nature.
2 Oxidizing ability.
3 Tendency to enter into chemical combinations and attain stable octets by
   - gaining an electron to form a univalent ion, e.g. F^-, Cl^-, Br^-; or
   - forming single covalent bonds as in F_2.

The halogens also show a gradation in their properties. This is due to the increasing complexity of the atoms as their atomic numbers increase from fluorine to iodine.

Table 20.2 Increasing complexity of the atoms from fluorine to iodine

Halogen	Atomic number	Electronic configuration
Fluorine	9	2, 7
Chlorine	17	2, 8, 7
Bromine	35	2, 8, 18, 7
Iodine	53	2, 8, 18, 18, 7

As the atomic number increases, the atoms increase in size too. The fluorine atom with its two electron shells is the smallest halogen atom while the iodine atom with its five shells is the largest halogen atom. The nucleus of the fluorine atom can easily attract an additional electron to achieve an octet structure, while the ability to do this is less easy in the case of the iodine atom. Therefore, the ease with which the halogen atoms ionize by gaining an electron decreases from fluorine to iodine. This makes fluorine the most powerful oxidizing agent among the halogens, and iodine the least. This is also reflected by the standard electrode potential values, E$^\ominus$, of the halogens (see page 181). Thus, the reactivity of the halogens decreases down the group as shown:

$$\underrightarrow{F_2 \;>\; Cl_2 \;>\; Br_2 \;>\; I^2}$$

Decreasing order of reactivity

This reactivity series of the halogens also gives the order in which halogens displace one another from solutions of their salts.

The properties of chlorine, bromine and iodine are given in table 20.3. We can make the following observations from this table.

1 The molecules of chlorine, bromine and iodine which are diatomic and covalent show a decrease in volatility down the group — chlorine is a gas, bromine is a liquid and iodine is a solid. This decrease in volatility is due to the increasing strength of the van der Waals' forces. This in turn results in
   - increasing relative density;
   - increasing boiling and melting points;
   - decreasing solubility;
   - progressive darkening of colour.
2 The chemical reactivity and oxidizing power decrease from chlorine to iodine.
3 The stability of the hydrogen halides also decrease from chlorine to iodine.

	Chlorine(Cl_2)	Bromine(Br_2)	Iodine(I_2)
Physical state, colour, smell and nature	Greenish-yellow poisonous gas; irritating smell.	Dark-red poisonous liquid; volatile with irritating smell.	Black crystalline solid; on heating, sublimes to form purple fumes; poisonous.
Relative density (of solid)/g cm^{-3}	1.9	3.2	4.9
Melting point/°C	−102	−7	114
Boiling point/°C	−34	59	184
Solubility	Moderately soluble in water to yield acidic solution of HCl and HClO.	Slightly soluble in water to yield acidic solution of HBr and HBrO.	Sparingly soluble in water but soluble in ether, ethan and potassium iodide.
Electronegativity and reactivity		Decreasing electronegativity → Decreasing reactivity	
Affinity for hydrogen	Combines explosively in sunlight.	Combines on heating or in the presence of a platinum catalyst.	Combines reversibly at 400 °C in the presence of a platinum catalyst.
Reaction with metals and non-metals	Vigorous	Moderately vigorous	Least vigorous
Reaction with dilute acids	Yields chlorides and oxochlorates(I).	Yields bromides and oxobromates(I).	Yields iodides and oxoiodides(I).
Reaction with concentrated alkalis	Yields chlorides and trioxochlorates(V).	Yields bromides and trioxobromates(V).	Yields iodides and trioxoiodides(V).
Bleaching action	Strong	Weak	—
Oxidizing action	Strong	Moderate	Weak
Displacement reaction	Displaces bromine and iodine from bromides and iodides respectively.	Displaces iodine from iodides.	—
Hydrogen halide	Colourless gas; denser than air; dissolves to give an acidic constant boiling mixture.	Colourless gas; denser than air; dissolves to give an acidic constant boiling mixture.	Colourless gas; denser than air; dissolves to give an acidic constant boiling mixture.
		Decreasing thermal stability → Increasing reducing power	
Silver halide	White solid; soluble in aqueous ammonia; reduced to silver by light.	Pale-yellow solid; sparingly soluble in aqueous ammonia; reduced to silver by light.	Yellow solid; insoluble in aqueous ammonia; reduced to silver by light.

NOTE Silver halides have different degrees of solubility in ammonia. Silver chloride is soluble in aqueous ammonia while silver bromide and silver iodide are not. In order to differentiate the latter two, some chlorine water is added to both the halides, followed by a little tetrachloromethane. Free bromine and iodine will go into the organic layers to give a brown and a purple colour respectively.

SUMMARY

orine

Chlorine is prepared in the laboratory by the oxidation of concentrated hydrochloric acid with an oxidizing agent. Commercially, it is manufactured by the electrolysis of brine.

Chlorine is a very reactive gas. It can combine directly with metals and non-metals to form chlorides; it can displace bromine and iodine from solutions of their salts; it has a very strong affinity for water and hydrogen sulphide; it is a powerful oxidizing agent; in the presence of water, it is a strong bleaching agent, which bleaches by oxidation; and it reacts with alkalis to form trioxochlorates(V) or oxochlorates(I).

Test for chlorine (a) Chlorine has an irritating smell and is greenish-yellow in colour; (b) it turns blue litmus paper red and then bleaches it; and (c) it turns starch-iodide paper dark-blue.

rogen chloride

Hydrogen chloride is usually prepared in the laboratory by the action of hot concentrated tetraoxosulphate(VI) acid on sodium chloride. Industrially, it is prepared by the direct combination of hydrogen and chlorine. It is a very soluble gas which dissolves readily in water to form hydrochloric acid; it combines directly with ammonia to form ammonium chloride; and it reacts with many metals to form chlorides.

ochloric acid

Dilute hydrochloric acid behaves like a typical acid—it reacts with metals to liberate hydrogen; it neutralizes bases; it liberates carbon(IV) oxide from hydrogentrioxocarbonates(IV) and trioxocarbonates(IV). It forms insoluble chlorides with silver or lead salts.

Concentrated hydrochloric acid is oxidized to chlorine by a strong oxidizing agent.

lorides

Chlorides are prepared by (a) the action of hydrogen chloride or hydrochloric acid on metals; (b) the action of hydrochloric acid on the oxides, hydroxides and trioxocarbonates(IV); (c) double decomposition; and (d) direct combination of metals with chlorine.

Chlorides react with hot concentrated tetraoxosulphate(VI) acid to liberate hydrogen chloride; if a strong oxidizing agent is also present, they liberate chlorine.

Test for soluble chlorides (a) With silver trioxonitrate(V) solution, a white precipitate of silver chloride is formed which is soluble in excess aqueous ammonia; (b) with lead(II) trioxonitrate(V), a white precipitate of lead(II) chloride is formed which dissolves on heating and reappears on cooling.

logen family

The halogens show similarity in properties because each of the atoms has seven valence electrons. In chemical combination, the halogen atom (X) attains its octet structure by gaining an electron to form a halide ion, X^-, or by sharing its electrons in covalent bond formation, X-X.

The halogens also show a progressive gradation in properties down the group as a result of the increasing complexity of the atoms from fluorine to iodine. Fluorine is the most chemically reactive halogen followed by chlorine, bromine and iodine.

EXERCISES

1. These are following methods of preparing chlorine gas. Which one involves heating?
   - A $MnO_2(s) + HCl(aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$
   - B $KMnO_4(aq) + HCl(aq) \rightarrow 2\,KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$
   - C $CaOCl_2(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + Cl_2(g)$
   - D Electrolysis of brine.

2. The following are physical properties of chlorine except
   - A it cannot be liquefied.
   - B it is denser than air.
   - C it is sparingly soluble in water.
   - D it is poisonous.

3. Which of these is correct?
   - A $Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$
   - B $Br_2 + Cl^- \rightarrow Cl_2 + 2Br^-$
   - C $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$
   - D $Cl_2 + 2F^- \rightarrow F_2 + 2Cl^-$

4. Chlorine reacts with metals to form chlorides except
   - A $Cl_2 + Fe \rightarrow FeCl_2$
   - B $3Cl_2 + 2Al \rightarrow 2AlCl_3$
   - C $2Cl_2 + Sn \rightarrow SnCl_4$
   - D $Cl_2 + 2Na \rightarrow 2NaCl$

5. Chlorine reacts with hydrogen to form hydrogen chloride. Under what condition does this reaction occur without explosion?
   - A Under bright sunlight.
   - B Under diffused sunlight.
   - C In the presence of nickel catalyst.
   - D Under strong heating.

6. Chlorine is a common bleaching agent. This is not true with
   - A wet litmus paper.
   - B printer's ink.
   - C wet pawpaw leaf.
   - D most wet fabric dyes.

7. From the equation; give the conditions of reactio
   $3Cl_2(g) + 6NaOH(aq) \rightarrow NaClO_3(aq) + 5NaCl(aq) + 3H_2O(l$
   - A Cold dilute NaOH.
   - B Hot concentrated NaOH.
   - C Warm dilute NaOH.
   - D Hot dilute NaOH.

8. One of these equations stands for the manufactur of hydrogen chloride.
   - A $2NaCl(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2HCl(g$
   - B $H_2(g) + Cl_2(q) \rightarrow 2HCl(g)$
   - C $NaCl(aq) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g$
   - D $NaCl(s) + NaHSO_4(aq) \rightarrow Na_2SO_4(aq) + HCl(g$

9. Apart from HCl, which other common gas i used in the demonstration of fountai experiment?
   - A H_2S
   - B SO_2
   - C NH_3
   - D C_2H_2

10. Which of the products of these mixtures i acidic?
    - A HCl(g) + chloroform
    - B HCl(g) + water
    - C $HCl(aq)^2$ + Zn
    - D HCl(aq) + Mg

11. Fluorine is prepared by
    - A reacting fluorides with chlorine gas.
    - B reacting fluorides with hydrogen chlorid
    - C electrolysis.
    - D reacting fluorine with concentrated H_2SO

12. Bromine was discovered by
    - A Balard.
    - B Scheele.
    - C Courtois.
    - D Cavendish.

13. The bleaching action of chlorine in water i because
    - A of its reducing property.
    - B of its oxidizing power.

D it is a weak acid.
E it is an oxygen acceptor.

14. The reaction between common salt and concentrated tetraoxosulphate(VI) acid liberates
A sulphur(IV) oxide.
B oxygen and chloride.
C hydrogen chloride gas.
D hydrogen sulphide gas.
E hydrogen gas.

15. When chlorine water is exposed to sunlight, the products formed are
A hydrochloric acid and oxygen.
B chlorine gas and oxochlorate(I) acid.
C oxygen and oxochlorate(I) acid.
D hydrogen and oxygen.
E oxochlorate(I) acid and hydrogen.

6. (a) With the aid of a labelled diagram and equation of reaction, describe how you would prepare a gas-jar of dry hydrogen chloride gas.
(b) How would you adapt the apparatus to prepare hydrochloric acid? Describe and explain your method.
(c) How would you demonstrate that hydrogen chloride is a very soluble gas?

7. (a) A solution of hydrogen chloride in water is said to be different from a solution of the gas in the solvent toluene. Show the various ways in which these solutions differ and explain.
(b) Describe and explain what happens when hydrogen chloride gas is passed continuously into a dilute aqueous solution of sodium hydroxide, coloured with a little blue litmus and contained in a cup made of iron.

18. (a) Why is hydrochloric acid described as a typical acid? Give the equations of the reactions.
(b) Why does bleaching powder smell of chlorine in damp air?

19. (a) Describe what happens when a glass rod is dipped into concentrated hydrochloric acid and then held at the mouth of a jar of ammonia. Give the equation of the reaction.
(b) Describe the effects of heat on dilute and concentrated hydrochloric acid respectively.
(c) How does hydrochloric acid react with a solution of
(i) lead(II) trioxonitrate(V);
(ii) potassium tetraoxomanganate(VII)?

20. (a) How would you prepare a few dry samples of the following chlorides? Give the equations of the reactions.
(i) Potassium chloride.
(ii) Copper(II) chloride.
(b) Give four uses of chlorine.

21. (a) How would you obtain a few gas jars of dry chlorine starting with common salt?
(b) How would you distinguish between the solutions of chlorine in water and hydrogen chloride in water? Explain the procedure that you would follow, giving reasons.

22. (a) What happens when chlorine is passed into a solution of sulphur(IV) oxide in water? How would you identify all the products formed? Give the equation for the reaction and the identification tests.
(b) How does chlorine react with alkalis? Give the conditions, the products and the equations of the reactions.

23. (a) Comment on the relative reactivities and oxidizing powers of fluorine, chlorine, bromine and iodine.
(b) Compare the abilities of the halogens to displace one another from aqueous solutions of their compounds.
(c) Give four uses of fluorine and its compounds.
(d) Name three deliquescent chlorides. How would you test for soluble chlorides?

21

OXYGEN • OXIDES • HYDROGEN PEROXIDE • OZO

OXYGEN

Oxygen was discovered independently by Scheele in 1772 and Priestley in 1774. However, it was Lavoisier who first described the major properties of this newly discovered gas and arrived at the conclusion that the gas was essential for the combustion of substances. He erroneously thought that this gas was a major constituent of all acids and named it oxygen, which meant acid-producer.

Occurrence

Oxygen is the most abundant element on earth. It occurs in nature in both the free and combined states. Free oxygen constitutes about 21% by volume of atmospheric air and about 33% by volume of dissolved air. In the combined form, oxygen accounts for nearly 50% by mass of the earth's crust, the oceans and the air. It is present in the trioxosilicates(IV), trioxocarbonates(IV) and oxides of both metals and non-metals which make up the rocks and clays. Water, one of the most abundant compounds on earth, is made up of 88.9% oxygen by mass. The human body is made up of about two-thirds by mass of oxygen in the combined state.

Laboratory Preparation

Oxygen is usually prepared in the laboratory by

- the decomposition of potassium trioxochlorate(V) and hydrogen peroxide, and
- the oxidation of hydrogen peroxide.

Other methods include the thermal decomposition of mercury(II) oxide and lead(IV) oxide, and the reaction of sodium peroxide with water.

From trioxochlorate(V) Potassium trioxochlorate(V) decomposes slowly to release all its oxygen when heated above its melting point (368 °C). In the presence of manganese(IV) oxide, which acts as a catalyst, the reaction occurs at a lower temperature and at a much faster rate.

$$2KClO_3(s) \xrightarrow{\text{heat}} 2KCl(s) + 3O_2(g)$$

From hydrogen peroxide In the presence of the catalyst, manganese(IV) oxide, hydrogen peroxide readily decomposes to liberate oxygen without any heating.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Hydrogen peroxide also reacts with acidified potassium tetraoxomanganate(VII) solution in the cold to produce oxygen. This is a redox reaction in which the tetraoxomanganate(VII) is the oxidizing agent and the hydrogen peroxide, the reducing agent.

$$5H_2O_2(aq) + 2KMnO_4(aq) + 3H_2SO_4(aq)$$
$$\rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(l) + 5O_2(g)$$

Ionically,

$$5H_2O_2(aq) + 2MnO_4^-(aq) + 6H^+(aq)$$
$$\rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

Industrial Preparation

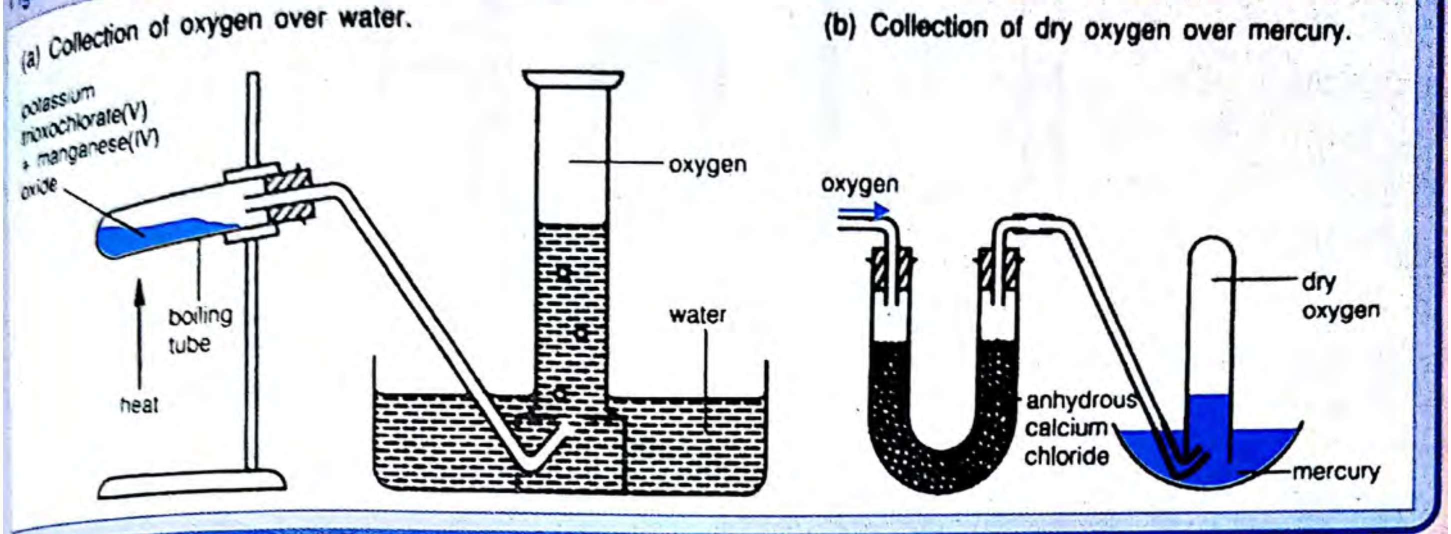
In places where a cheap source of electricity is available, oxygen may be prepared industrially by the electrolysis of water. However, in most places, it is prepared by the fractional distillation of liquid air. This preparation involves two main processes,

- the liquefaction of air, and
- the fractional distillation of the resultant liquid air

Experiment 21.1 To prepare oxygen from potassium trioxochlorate(V).

Method Grind a mixture of potassium trioxochlorate(V) and manganese(IV) oxide in the ratio of about 4:1 by mass. Place the mixture in a boiling tube and set up the apparatus as shown. Heat gently and collect the gas liberated over water. If the gas is required dry, pass it through concentrated tetraoxosulphate(VI) acid or anhydrous calcium chloride, and then collect it over mercury.

Fig. 21.1 Preparation of oxygen from potassium trioxochlorate(V).


(a) Collection of oxygen over water.

(b) Collection of dry oxygen over mercury.

Result On heating, oxygen is given off as colourless gas. It cannot be collected by the displacement of air because its density is nearly the same as that of air.

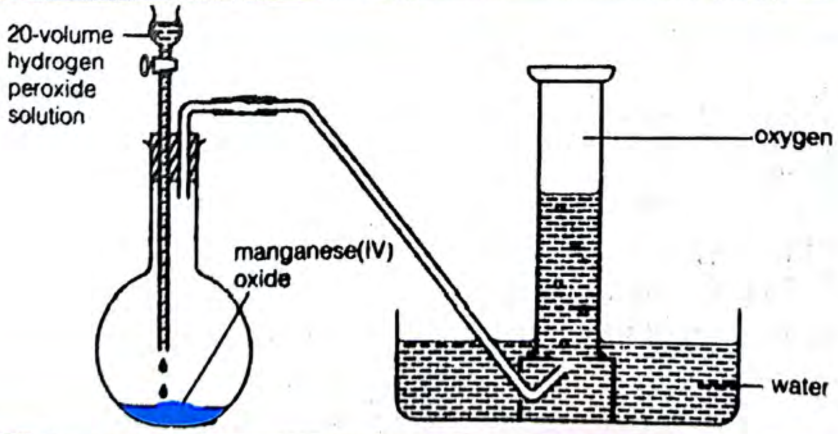
Conclusion Oxygen can be prepared by heating a mixture of potassium trioxochlorate(V) and manganese(IV) oxide.

Experiment 21.2 To prepare oxygen from hydrogen peroxide by (a) catalytic decomposition, (b) oxidation using potassium tetraoxomanganate(VII).

Method (a) Place some black manganese(IV) oxide in a flask and set up the apparatus as shown in fig. 21.2. Add hydrogen peroxide (20-volume), drop by drop, to the manganese(IV) oxide.

(b) The same apparatus is used as for method (a). Instead of the manganese(IV) oxide, place some potassium tetraoxomanganate(VII) solution in the flask and acidify it with dilute tetraoxosulphate(VI) acid solution. Add the hydrogen peroxide, drop by drop, to the tetraoxomanganate(VII) solution.

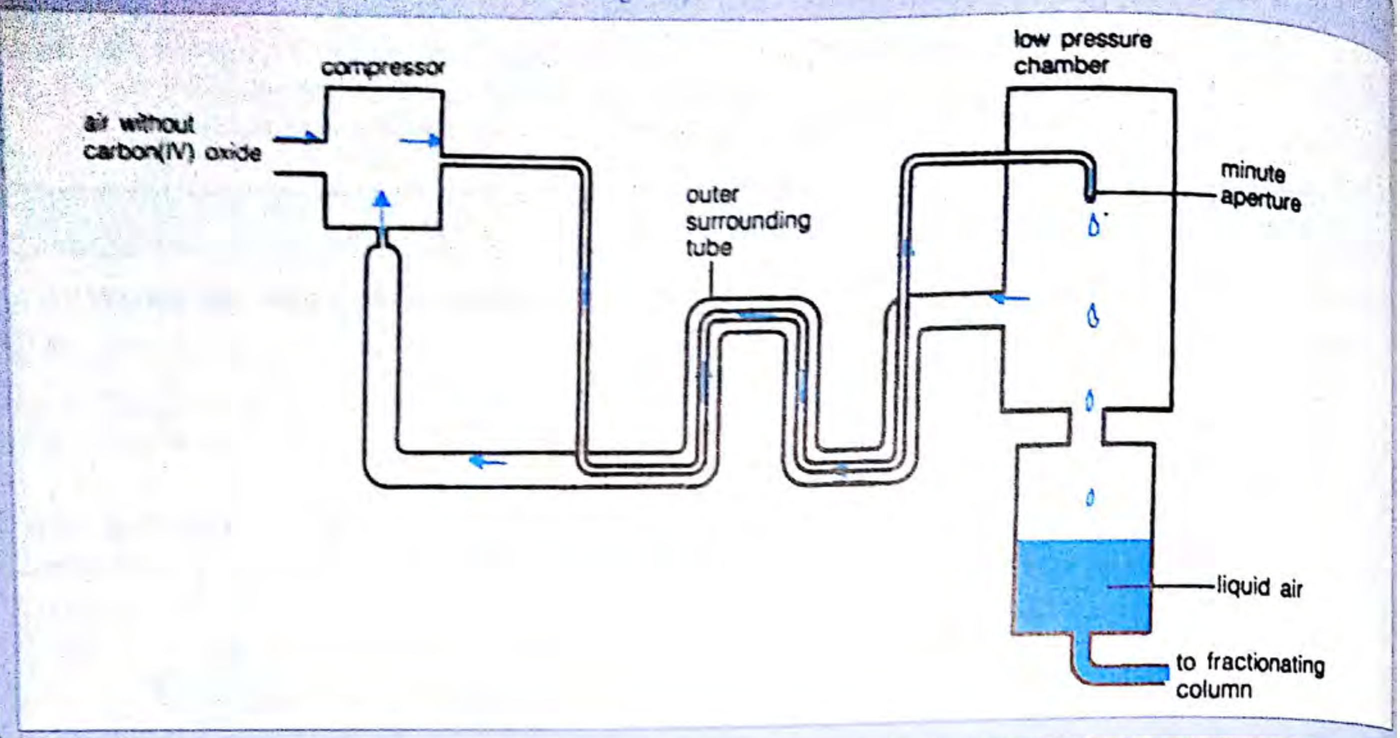
Fig. 21.2 Preparation of oxygen from hydrogen peroxide solution.



Result In both the reactions, oxygen is readily produced as colourless gas and collected in a gas jar over water.

Conclusion Oxygen can be prepared from hydrogen peroxide by **(a)** the catalytic decomposition, **(b)** reduction using a powerful oxidizing agent.

Fig. 21.3 Liquefaction of air (simplified flow diagram).



Liquefaction of air

Air, in the gaseous form, is first passed through caustic soda to remove carbon(IV) oxide. It is then compressed to a pressure of about 200 atm, cooled and allowed to escape rapidly through a minute aperture. The sudden expansion of the air into a region of lower pressure causes it to cool even further (since heat energy is used up in separating the molecules). The cooled air will cool the incoming stream of air. This process is repeated until the gaseous air becomes a liquid at –200 °C.

Fractional distillation of liquid air

The liquid air is then led to a fractionating column. On distillation, nitrogen, which has a lower boiling point of –196 °C, is evolved first, leaving behind a liquid very rich in oxygen. Further heating converts the liquid oxygen to a gas at –183 °C. The oxygen gas is dried, compressed and stored in steel cylinders under a pressure of about 100 atm.

Physical Properties

1 Oxygen is a diatomic gas which is colourless, odourless and tasteless.

2 It is neutral to moist litmus paper.

3 It is slightly soluble in water, i.e. only about 2% by volume of it will dissolve in water at roo temperature and standard pressure. This solubilit of the gas, however, is of vital importance aquatic life.

4 Gaseous oxygen is approximately 1.1 time denser than air.

5 Gaseous oxygen liquefies at –183 °C an solidifies at –225 °C.

Chemical Properties

Oxygen is a non-metallic element belonging to Grou 6 of the Periodic Table. The oxygen atom has si valence electrons and can acquire a stable octe electronic configuration by

- accepting two electrons from electropositiv elements like metals to form the negative oxid ion, O^{2-}. Oxygen is thus strongly electro-negativ and chemically reactive.
- entering into covalent bond formation, usuall with non-metal. It forms single covalent bond with two hydrogen atoms to give the wate molecule, H–O–H. In the oxygen molecule, double covalent bond unites the two oxyge atoms.

Note Oxygen is the only element in this grou which can form multiple bonds with itself.

Direct combination with other elements

Oxygen combines readily with all other elements (except the rare gases, some holagens and some unreactive metals) to form oxides.

With metals Most metals react with oxygen to form basic oxides. The oxides of very electro-positive metals like potassium, sodium and calcium dissolve in water to form alkalis.

$$K(s) + \underset{\text{limited supply}}{O_2(g)} \rightarrow 2K_2O(s) + \xrightarrow{+2H_2O} 4KOH(aq)$$

nically,

$$4K(s) + O_2(g) \rightarrow 2(K^+)_2O^{2-}(s)$$
$$O^{2-}(s) + H_2O(l) \rightarrow 2OH^-(aq)$$

However, the basic oxide is not formed when dium is heated in a plentiful supply of oxygen. stead, it burns with a bright yellow flame to form dium peroxide, Na_2O_2. Similarly, potassium burns excess oxygen with a lilac flame to form a higher ide, KO_2, instead of the basic oxide, K_2O.

With non-metals Non-metals like sulphur, carbon and phosphorus burn in oxygen to form acidic oxides. These are also known as *acid anhydrides*, as they dissolve in water to form acids.

$$S(s) + O_2(g) \rightarrow \underset{\text{acid anhydride}}{SO_2(g)} \xrightarrow{+H_2O} \underset{\text{acid}}{H_2SO_3(aq)}$$

$$P_4(s) + 3O_2(g) \rightarrow \underset{\text{acid anhydride}}{P_4O_6(g)} \xrightarrow{+6H_2O} \underset{\text{acid}}{4H_3PO_3(aq)}$$

$$P_4(s) + 5O_2(g) \rightarrow \underset{\text{acid anhydride}}{P_4O_{10}(g)} \xrightarrow{+6H_2O} \underset{\text{acid}}{4H_3PO_4(aq)}$$

$$C(s) + O_2(g) \rightarrow \underset{\text{acid anhydride}}{CO_2(g)} \xrightarrow{+H_2O} \underset{\text{acid}}{H_2CO_3(aq)}$$

Reactions with compounds

Many compounds react with oxygen. Most hydrocarbons and compounds of carbon, hydrogen and oxygen burn in oxygen to form carbon(IV) oxide and water. Sulphides burn in oxygen to give sulphur(IV) oxide and another oxide. Ammonia does not form an oxide of nitrogen when it burns in oxygen. Instead, nitrogen and water are formed. In the presence

Experiment 21.3 To investigate what is formed when (a) sulphur (b) phosphorus burn in oxygen.

Method (a)Heat a piece of yellow sulphur in a deflagrating spoon until it begins to burn. Then lower it into a gas jar containing oxygen. When it stops burning, remove the spoon and cover the jar. Add some distilled water into the jar and shake well. Add a piece of blue litmus paper to the resulting solution.

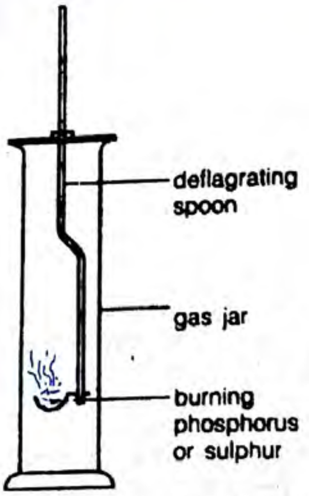
(b)Repeat the above experiment, but use a piece of yellow phosphorus instead of sulphur.

Result (a)The sulphur burns brightly with a blue flame, giving off misty fumes of sulphur(IV) oxide. The gas obtained dissolves readily in water to form trioxosulphate(IV) acid, which changes blue litmus paper red.

(b)The phosphorus burns with a very bright yellow flame, giving off dense white fumes of phosphorus(III) and phosphorus(V) oxides. The two gases dissolve readily in water to form acids which change blue litmus paper red.

Conclusion Sulphur and phosphorus burn in oxygen to yield oxides which dissolve in water to form acids.

Fig. 21.4 Burning of phosphorus or sulphur in oxygen.



of a catalyst, ammonia is oxidized to nitrogen(II) oxide and water at room temperature.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

The reactions of oxygen with elements and compounds are examples of oxidation reactions. Oxidation may take place at varying speeds. The formation of iron rust, for example, is normally a slow oxidation, but when iron is burned in pure oxygen, the reaction takes place more rapidly, accompanied by the production of heat and light. An oxidation process in which heat and light are produced is called *combustion.* Examples are the burning of fuels, like wood, coal and petrol. For a given oxidation reaction, the same quantity of heat is evolved irrespective of whether the reaction takes place rapidly or slowly. A relatively higher temperature is reached in a rapid reaction because the heat is generated in a brief period of time. Some important examples of slow combustion include the oxidation of food in the body, the drying of paint and the rotting of vegetation.

Test for oxygen

Insert a glowing splinter into a test-tube containing the unknown gas. The rekindling of the glowing splinter indicates the presence of oxygen. Nitrogen(I) oxide, N_2O, also does this but it can be distinguished from oxygen as given in table 21.1.

Table 21.1 Differences between oxygen and nitrogen(I) oxide.

Property	Nitrogen(I) oxide	Oxygen
Smell	Pleasant smell	Odourless
Solubility in water	Fairly soluble	Slightly soluble
Reaction with nitrogen(II) oxide	No reaction	Produces reddish brown fumes of nitrogen(IV) oxide
Reaction with heated copper	Residual gas, N_2	No residual gas

Uses

1 Oxygen is required for respiration. It is used in breathing apparatus by people who have to be in surroundings which do not contain any air or contain too little air for breathing, e.g. divers i the sea, astronauts in space, and mountaineers and pilots at high altitudes. People with lung diseases and injuries, who have difficulty i breathing in ordinary air, are placed in oxygen tents. During surgical operations, a mixture o anaesthetic and oxygen is given to the patient. The anaesthetic makes the patient unconscious, while the oxygen keeps him alive.

2 Oxygen combines with ethyne to produce oxy-ethyne flame which has a temperature of over 2 000 °C. The flame is used to cut through metals like steel. The flame is first used to heat the metal to a very high temperature before more oxygen is supplied to oxidize the hot metal. The oxide layer then falls off in small pieces, leaving behind a clean cut. Oxygen is also used in oxy-hydrogen flame. This flame is not as hot as the oxy-ethyne flame. It is frequently used in welding pieces of metal together.

3 Liquid oxygen and fuels are used as propellants for space rockets.

4 Oxygen is used in the steel industry for the removal of carbon, sulphur and phosphorus impurities from pig iron. It is sometimes called tonnage oxygen because it is produced on a large scale by a special plant in the steel-works.

5 Oxygen is also used in the manufacture of important chemical compounds like tetraoxosulphate(VI) acid, trioxonitrate(V) acid and ethanoic acid.

OXIDES

Oxides are formed when elements combine with oxygen. They can be classified into several groups, namely basic oxides, acidic oxides, amphoteric oxides, neutral oxides, peroxides and other higher oxides.

Basic oxides

Basic oxides are oxides of metals. They react with acids to form a salt and water only. For example,

$$Na_2O(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l)$$
$$PbO(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l)$$

Ionically, both the above reactions can be represented as follows:

$$O^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l)$$

Most basic oxides do not dissolve in water, but those that do form alkalis.

Acidic oxides

Acidic oxides are oxides of non-metals. Thev react with water to form acids. They react with alkalis to form a salt and water only.

$$CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$$
$$SO_3(g) + 2KOH(aq) \rightarrow K_2SO_4(aq) + H_2O(l)$$

Ionically,

$$CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$$
$$SO_3(g) + 2OH^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l)$$

Nitrogen(IV)) oxide forms two salts with sodium hydroxide since it is a mixed anhydride.

$$2NO_2(g) + 2NaOH(aq) \rightarrow NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$$

Amphoteric oxides

Amphoteric oxides are metallic oxides which can behave both as basic oxides and as acidic oxides, i.e. they can react with both acids and alkalis to form salts and water only. They include the oxides of aluminium, zinc, lead and tin. The behaviour of amphoteric oxides is determined by the conditions of the reaction.

1 With acids, amphoteric oxides behave as bases, forming a salt and water only.

$$ZnO(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2O(l)$$
$$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$

2 With alkalis, they exhibit acidic properties by forming complex salts.

$$ZnO(s) + 2NaOH(aq) + H_2O(l) \rightarrow Na_2Zn(OH)_4(aq)$$
$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$$

Ionically,

$$ZnO(s) + 2OH^-(aq) + H_2O(l) \rightarrow \underset{\text{zincate(II) ion}}{[Zn(OH)_4]^{2}(aq)}$$
$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow \underset{\text{aluminium(II) ion}}{2[Al(OH)_4]^-(aq)}$$

Neutral oxides

Neutral oxides are neither acidic nor basic. Hence they are neutral to litmus. They include water, carbon(II) oxide and nitrogen(I) oxide.

Peroxides

Peroxides are oxides containing a higher proportion of oxygen than the ordinary oxides. They contain the peroxide ion, $(O–O)^2$, and yield hydrogen peroxide, when treated with dilute acids. Examples of H_2O_2, when treated with dilute acids. Examples of peroxides include sodium peroxide, Na_2O_2, calcium peroxide, CaO_2, and barium peroxide, BaO_2.

$$BaO_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq)$$

Experiment 21.4 To prepare hydrogen peroxide.

Method Put some dilute tetraoxosulphate(VI) acid in a beaker. Cool it in a freezing mixture of ice and salt. Mix some finely powdered hydrated barium peroxide with a little water to form a paste, and add this gradually to the acid, stirring continuosly. When the solution is just acidic to litmus, allow the white barium tetraoxosulphat(VI) to settle and then filter the solution.

NOTE The temperature of the reaction mixture must be kept low in order to minimize the decomposition of the hydrogen peroxide.

Result The resultant filtrate obtained is an aqueous solution of hydrogen peroxide.

Conclusion Dilute tetraoxosulphate(VI) acid reacts with barium peroxide to yield hydrogen peroxide.

Other higher oxides

Other higher oxides resemble the peroxides in that they contain a higher proportion of oxygen than the ordinary oxides. However, they do not produce hydrogen peroxide with acids but show a tendency to release oxygen on heating, and hence, are oxidizing agents. Examples are

- lead(IV) oxide, PbO_2, and
- manganese(IV) oxide, MnO_2.

Another group of higher oxides include

- dilead(II) lead(IV) oxide, Pb_3O_4, also known as red lead oxide, and
- iron(II) diiron(III) oxide, Fe_3O_4.

HYDROGEN PEROXIDE

Oxygen combines with hydrogen to form two major hydrides, water and hydrogen peroxide. Thenard was the first person to prepare hydrogen peroxide by the action of dilute tetraoxosulphate(VI) acid on barium peroxide. He discovered that hydrogen peroxide, H_2O_2, contained one more oxygen atom in its molecule than water, H_2O, and he thus described it as oxygenated water.

In nature, hydrogen peroxide occurs only in traces in snow and dew as well as in air and in water that has been exposed to brilliant sunshine.

Laboratory Preparation

Hydrogen peroxide is usually prepared by the action of a dilute acid on certain metallic peroxides

acid + metallic peroxide
→ salt + hydrogen peroxide

Usually, barium peroxide and dilute tetraoxosulphate(VI) acid are used because the barium tetraoxosulphate(VI) produced is insoluble and can be easily filtered off.

$$H_2SO_4(aq) + BaO_2(s) \rightarrow BaSO_4(s) + H_2O_2(aq)$$

Industrial Preparation

Hydrogen peroxide is produced industrially by

- the oxidation of propan-2-ol with oxygen under slight pressure;

$$(CH_3)_2CHOH(l) + O_2(g) \rightarrow (CH_3)_2C{=}O(l) + H_2O_2(l)$$

- the oxidation of substituted anthracene-9, 10-diones. The solution of hydrogen peroxide obtained can be concentrated by distillation under reduced pressure. Hydrogen peroxide is easily decomposed by light. So, it is stored in dark glass bottles or in aluminium containers. The solution must also be kept pure to prevent its catalytic decomposition.

Hydrogen peroxide is sold commercially in various concentrations. The concentration of a hydrogen peroxide solution is usually expressed as its volume-strength which is the number of volumes of oxygen, measured at s.t.p., liberated by one volume of hydrogen peroxide on heating. Thus, 1 cm^3 of a 10-volume solution will liberate 10 cm^3 of oxygen (at s.t.p.) when it decomposes completely. The concentrations at which hydrogen peroxide is usually sold are 10-volume. 20-volume and 30-volume.

Physical Properties

1 Pure hydrogen peroxide is a pale blue syrupy liquid.
2 It dissolves in water to give a very weak acidic solution.
3 It boils, with decomposition, at 150 °C, and freezes at about –0.9 °C.

Chemical Properties

Decomposition

When hydrogen peroxide is exposed to air, it decomposes to form water and oxygen. The decomposition is exothermic and is accelerated by

- heating,
- the addition of alkalis,
- the introduction of finely divided metals, such as gold and platinum, and manganese(IV) oxide which act as catalysts.

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

Mineral acids and propane-1.2,3-triol retard the decompositn of hydrogen peroxide. They are usually its decomposition.

Hydrogen peroxide as an oxidizing agent

Hydrogen peroxide is a strong oxidizing agent as it can readily donate oxygen or accept electrons. During the process, the hydrogen peroxide itself is reduced to water.

Donate oxygen $H_2O_2(l) \rightarrow H_2O(l) + [O]$

Accept electrons $H_2O_2(l) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

With potassium iodide Hydrogen peroxide reacts with potassium iodide solution, acidified with tetraoxosulphate(VI) acid, to liberate iodine. The tetraoxosulphate(VI) acid first reacts with the iodide to form iodic acid, HI, which is then oxidized by the peroxide to liberate iodine. Here, the hydrogen peroxide oxidizes by accepting electrons from the iodide ion, and is itself reduced to water.

$$2KI(aq) + H_2SO_4(aq) + H_2O_2(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l) + I_2(aq)$$

Ionically,

$$2I^-(aq) + H_2O_2(aq) + 2H^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

Hydrogen peroxide as a reducing agent

Although hydrogen peroxide is a strong oxidizing agent, it can also behave as a reducing agent when it reacts with more powerful oxidizing agents, either by accepting oxygen or by donating electrons. During the process, the hydrogen peroxide itself is converted to gaseous oxygen.

Accept oxygen $H_2O_2(l) + [O] \rightarrow H_2O(l) + O_2(g)$

Donate electrons $H_2O_2(l) \rightarrow 2H^+(aq) + O_2(g) + 2e^-$

With tetraoxomanganate(VII) Hydrogen peroxide reduces acidified potassium tetraoxomanganate(VII) solution. As a result, the solution becomes decolourized because the purple tetraoxamanganate(VII) ion is changed to the pale pink manganese(II) ion.

$$2KMnO_4(aq) + 3H_2SO_4(aq) + 5H_2O_2(aq) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(l) + 5O_2(g)$$

Ionically,

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

With chlorine and silver oxide Hydrogen peroxide reduces chlorine to hydrochloric acid and silver oxide to the metal.

$$Cl_2(g) + H_2O_2(aq) \rightarrow 2HCl(aq) + O_2(g)$$

$$Ag_2O(s) + H_2O_2(aq) \rightarrow 2Ag(s) + H_2O(l) + O_2(g)$$

Uses

1. Hydrogen peroxide is used as an antiseptic.
2. Hydrogen peroxide is used in bleaching delicate materials such as silk, wool, wood pulp (for paper making), feathers and human hair which would easily be damaged by chlorine or sulphur(IV) oxide.
3. White lead(II) paints containing lead(II) trioxocarbonate(IV) blacken when exposed to atmospheric hydrogen sulphide because the lead(II) compounds present are converted to lead(II) sulphide. Treatment with hydrogen peroxide oxidizes the lead(II) sulphide to lead(II) tetraoxosulphate(VI), thus restoring the white colour.

   $$PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(l)$$

4. Liquid hydrogen peroxide provides oxygen for the burning of fuel in space rockets. It is also used for the burning of diesel oil in the engines of submerged submarines.
5. Hydrogen peroxide is used in the making of compounds like sodium dioxochlorate(III) and some organic peroxides which are used for initiating polymerization reactions.

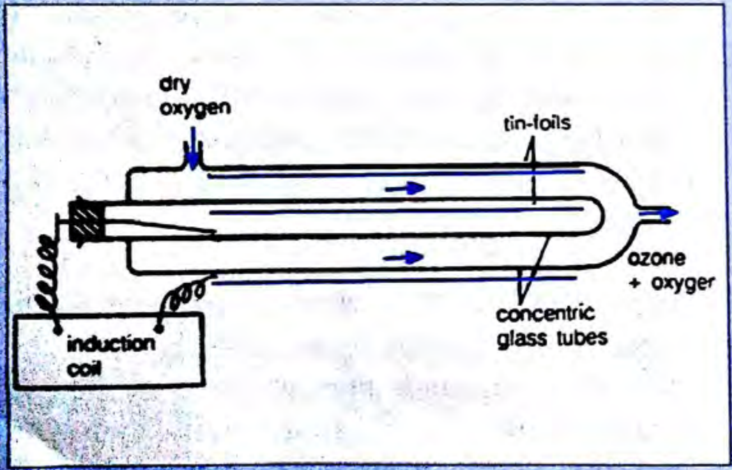
OZONE

Gaseous oxygen normally exists as diatomic molecules, but it can also exist as an unstable triatomic molecule, called ozone, O_3. Ozone was first discovered by Schonbein in 1839. However, it was not until 1866 that J. Soret was able to demonstrate that ozone was an allotrope of oxygen, O_2. *Allotropy is the ability of an element to exist in more than one form in the same physical state.*

Occurrence

In nature, ozone is formed from atmospheric oxygen by lightning flashes. Ozone is too reactive to remain for long in the atmosphere, but it exists in a layer at a height of about 20 km above earth where it is believed to protect the earth's surface from receiving too much ultra-violet radiation. Small amounts of ozone are also formed around electrical machinery when they are in operation.

Fig. 21.5 Ozonizer.



Preparation

Ozone can be prepared from oxygen by passing an electric discharge through it. It is necessary to use a silent discharge because sparking would generate heat which decomposes the ozone. An ozonizer is used for ozonizing oxygen.

Properties

Ozone is a pale-blue gas (at s.t.p.) with a characteristic smell like that of dilute chlorine. It is poisonous at concentrations above 100 parts per million. Pure ozone can be obtained as a blue liquid by cooling ozonized oxygen to −112 °C. Ozone is only slightly soluble in water but it dissolves in turpentine.

Ozone has the same chemical properties as oxygen except that it is more reactive. It decomposes into ordinary oxygen on heating or even just on standing.

$$2O_3(g) \rightarrow 3O_2(g)$$

Ozone is also a more powerful oxidizing agent than oxygen. Oxygen is formed as a by-product in these reactions, for example,

$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$
$$SO_2(g) + O_3(g) \rightarrow SO_3(g) + O_2(g)$$

Uses

Ozone is a good bleaching agent. In low concentrations, it is used for ventilating areas which get very little fresh air such as underground railway premises. It is also used as a disinfectant in water and sewage purification, and in airconditioning plants.

SUMMARY

- Oxygen is the most abundant element on earth.
- In the laboratory, oxygen is prepared by the catalytic decomposition of potassium trioxochlorate(V) or hydrogen peroxide. Industrially, it is prepared by the liquefaction of air followed by fractional distillation of the liquefied air.
- Oxygen, being strongly electronegative, is chemically very reactive. It reacts with
  (a) most metals to form basic oxides which are ionic,
  (b) most non-metals to form acidic oxides which are covalent molecules,
  (c) hydrocarbons (fuels) to form carbon(IV) oxide and water.
- Oxygen will rekindle a glowing splinter. This is a common test for oxygen.
- Oxides can be classified into basic, acidic, amphoteric and neutral oxides. Peroxides contain the $(O—O)^{2-}$ ions.
- Hydrogen peroxide is prepared by the action of a dilute acid on the peroxides of certain metals. It is a strong oxidizing agent. However, in the presence of more powerful oxidizing agents like chlorine, it behaves as a reducing agent.
- Ozone, O_3, is an unstable allotrope of oxygen. The ozone layer in the atmosphere acts as a protective shield by preventing too much ultra-violet radiation from falling on earth and harming living organisms.

EXERCISES

1. The most abundant element on earth is
   A nitrogen. B helium.
   C silicon. D oxygen.

2. These are various methods of preparing oxygen except
   A $KI(aq) + H_2O_2(aq) + H_2SO_4(aq) \rightarrow$
   B $KMnO_4(aq) + H_2SO_4(aq) + H_2O_2 \rightarrow$
   C $H_2O_2(aq) \rightarrow$
   D $MnO_2 + H_2O_2 \rightarrow$

3. Which of these gases has the following physical properties?
   (i) Diatomic gas.
   (ii) Colourless, tasteless and odourless.
   (iii) Slightly soluble in water.
   (iv) Liquefies easily.
   A CO B N_2
   C O_2 D H_2

4. Which of these gases has the following chemical characteristics?
   (i) Combines with other elements except rare gases.
   (ii) Combines with some halogens.
   (iii) Forms multiple bonds with itself.
   A CO B N_2
   C O_2 D H_2

5. Name the gas with the following characteristics.
   (i) A good bleaching agent.
   (ii) Used in ventilating stuffy chambers.
   (iii) Used as a disinfectant in water and sewage.
   A CO B CL_2
   C O_3 D N_2O

6. Which of these reactions with oxygen is slowest?
   A Rusting B $Fe + O_2$
   C $Petrol + O_2$ D $Coal + O_2$

7. Most acid anhydrides react with water to form acids. Which of these is a mixed anhydride?

A N_2O B NO
C NO_2 D SO_2

8. Which of these is not an amphoteric oxide?

A ZnO B Al_2O_3
C SnO_2 D Na_2O_2

9. Which of these oxides occurs in snow, dew, air and water when exposed to brilliant sunlight?

A K_2O B H_2O_2
C Pb_3O_4 D Fe_3O_4

10. The decomposition of hydrogen peroxide is accelerated by these treatments except

A $H_2O_2(aq) \xrightarrow{\text{heat}}$

B $H_2O_2(aq) + \xrightarrow[\text{catalyst}]{MnO_2}$

C $H_2O_2(aq) + NaOH \rightarrow$

D $H_2O_2(aq)$ + Propan-1, 2, 3 triol $\rightarrow$

11. Which one is an amphoteric oxide?

A SiO_2 D CaO
B Al_2O_3 E K_2O
C CuO

12. Oxygen in air can be absorbed by passing it through

A caustic soda.
B fused calcium chloride.
C alkaline pyrogallol.
D 95% ethanol.
E washing soda.

13. (a) Using a labelled diagram, describe preparation of oxygen. Give the condit of the experiment and the equation reaction.

(b) What happens if a piece of phosphoru burnt on a deflagrating spoon in a gas and the products shaken with water?

(c) How is oxygen produced industrially?

14. (a) How would you prepare hydrogen perox in the laboratory?

(b) Using equations, explain what happe when hydrogen peroxide is added to:

(i) lead(II) sulphide
(ii) manganese(IV) oxide
(iii) acidified potassium iodide
(iv) ozone
(v) silver oxide.

15. (a) Explain the term *allotropy* and why ozone may be defined as an allotrope of oxygen

(b) Compare the chemical properties of ozone with those of diatomic oxygen.

(c) Give the uses of ozone and oxygen.

16. (a) Explain the term *amphoteric*. Give two examples of oxides which are amphoteric.

(b) Why are acidic oxides also known as acid anhydrides? Give an example.

SULPHUR AND ITS COMPOUNDS

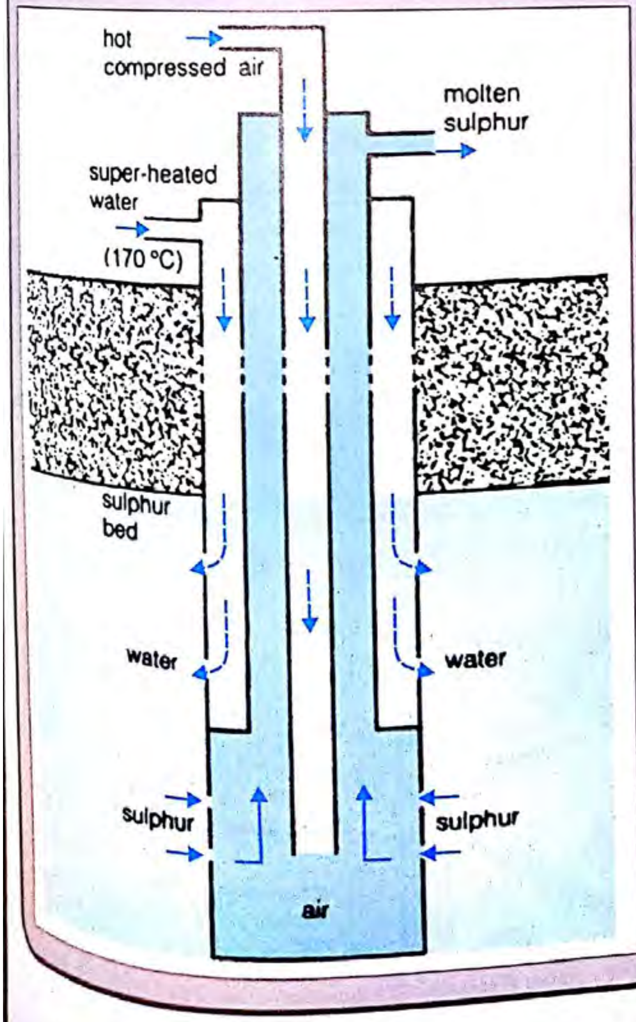
22

SULPHUR

Sulphur has been known for its medicinal value and its germicidal effect since 1000 B.C. However, its chemical nature remained unknown until 1787 when Lavoisier recognized it as an element.

Sulphur makes up about 0.1% of the earth's crust. It occurs freely as deposits in U.S.A., Poland, Japan, New Zealand and Sicily. It is also widely found in the combined state as sulphides of iron, zinc, lead, copper and mercury, and as the tetraoxosulphate(VI) salts of calcium, magnesium and barium. Sulphur is also present in some proteins.

Fig. 22.1 Extraction of sulphur (the Frasch process).



Extraction of Sulphur

Most of the world's sulphur is obtained from underground deposits which may be more than 200 m below the surface of earth. Extraction of sulphur from these deposits is based on the *Frasch process*. A hole, about 30 cm in diameter, is drilled through the soil layers to the sulphur bed. A sulphur pump made up of three concentric steel pipes is then driven down the hole. Super-heated water at about 170 °C and 10 atm pressure is forced through the outermost tube to the sulphur bed to melt the sulphur (melting point: 115 °C). Hot compressed air at a pressure of 15 atm is then blown down the innermost tube to force the molten sulphur up through the middle tube. The molten sulphur is continuously pumped into a receptacle at the surface where it is allowed to solidify in large tanks. The sulphur obtained is about 99.5% pure.

Natural gas contains a small amount of hydrogen sulphide. The hydrogen sulphide is first separated out from the natural gas and then oxidized to sulphur by mixing it with air and passing it over a heated aluminium oxide (Al_2O_3) catalyst.

$$2H_2S(g) + O_2(g) \rightarrow 2H_2O(l) + 2S(s)$$

Allotropes of Sulphur

The main allotropes of sulphur are *rhombic sulphur* (α-sulphur) and *monoclinic* or *prismatic sulphur* (β-sulphur), which are crystalline, and *amorphous sulphur* (δ-sulphur). There is also another form known as *plastic sulphur.*

Rhombic sulphur Free sulphur exists as rhombic sulphur in nature because it is the only stable allotrope at temperatures below 96 °C. Crystals of rhombic sulphur are bright yellow and octahedral. They are made up of S_8 molecules. Each S_8 molecule consists of a ring of eight atoms.

Rhombic sulphur is prepared by allowing a saturated solution of sulphur in carbon(IV) sulphide to evaporate slowly. Octahedral crystals will gradually be deposited.

CAUTION As carbon(IV) sulphide is poisonous and highly inflammable, this preparation should be done in a fume cupboard.

Monoclintc sulphur Monoclinic sulphur is the only stable allotrope at temperatures between 96 °C and 119 °C. The crystals are long, thin and needle-shaped, and consist of S_8 molecules. At room temperature, they slowly revert to rhombic sulphur crystals.

Monoclinic sulphur is less dense than rhombic sulphur. This is because the S_8 molecules are more tightly packed in rhombic sulphur than in monoclinic sulphur.

Monoclinic sulphur is obtained by cooling molten sulphur. Heat some powdered sulphur in a crucible till it melts. Add more sulphur and continue heating and stirring it at the same time. Repeat this process until the crucible is almost filled with molten sulphur. Then allow the molten sulphur to cool. After some time, a hard crust will be formed at the top. Pierce two holes through the crust and pour off the remaining molten sulphur from inside before removing the crust. Needle-shaped crystals of monoclinic sulphur can be found as deposits on the sides of the crucible.

The following relationship exists between rhombic and monoclinic sulphur.

$$\textbf{rhombic sulphur} \underset{\text{below 96 °C}}{\overset{\text{between 96 °C and 119 °C}}{\rightleftharpoons}} \textbf{monoclinic sulphur}$$

Table 22.1 *Comparing the physical properties of rhombic and monoclinic sulphur.*

	Rhombic sulphur	Monoclinic sulphur
Colour	Bright yellow	Amber
Shape	Octahedral	Needle-shaped
Density ($g\ cm^{-3}$)	2.08	1.98
Melting point	113 °C	119 °C
Stability	Stable below 96 °C	Stable between 96 °C and 119 °C

We see that the two allotropes change from one form to the other at 96 °C. This is known as the transition temperature for the two allotropes.

Amorphous sulphur Amorphous sulphur has no regular crystalline shape. It is prepared as a pale yellow, almost white deposit when hydrogen sulphide is bubbled through water for a long time and the saturated solution is exposed to air. It is also deposited in chemical reactions, e.g. by the action of dilute hydrochloric acid on a trioxothiosulphate(VI) solution.

$$2H_2S(g) + O_2(g) \rightarrow 2H_2O(l) + 2S(s)$$
$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g) + S(s)$$

Plastic sulphur Plastic sulphur is a supercooled form of sulphur. If yellow sulphur is heated and poured into cold water, it will roll up into yellow ribbons which look as if they are made of plastic material. It is soft and elastic and will not dissolve in carbon(IV) sulphide. Plastic sulphur is generally not considered to be a true allotrope of sulphur because it is unstable and reverts to rhombic sulphur on standing.

Fig. 22.2 Rhombic and monoclinic sulphur crystals.

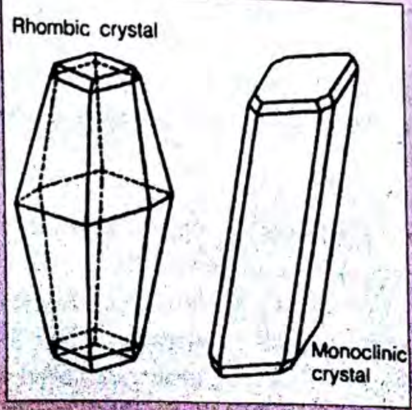


Fig. 22.3 Preparing monoclinic sulphur.

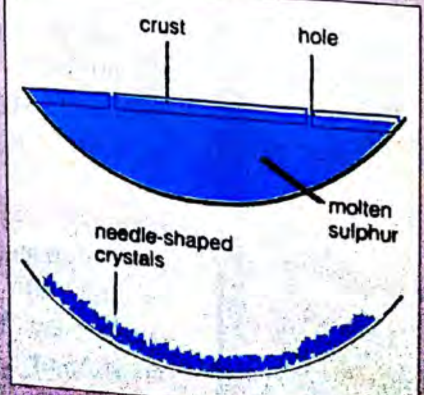
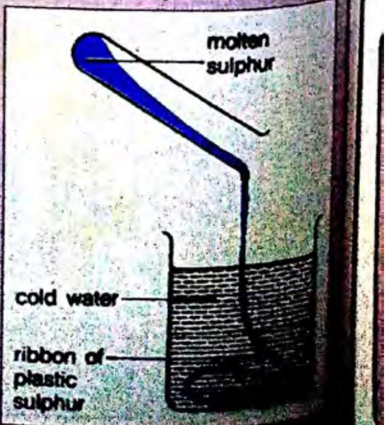


Fig. 22.4 Preparing plastic sulphur.



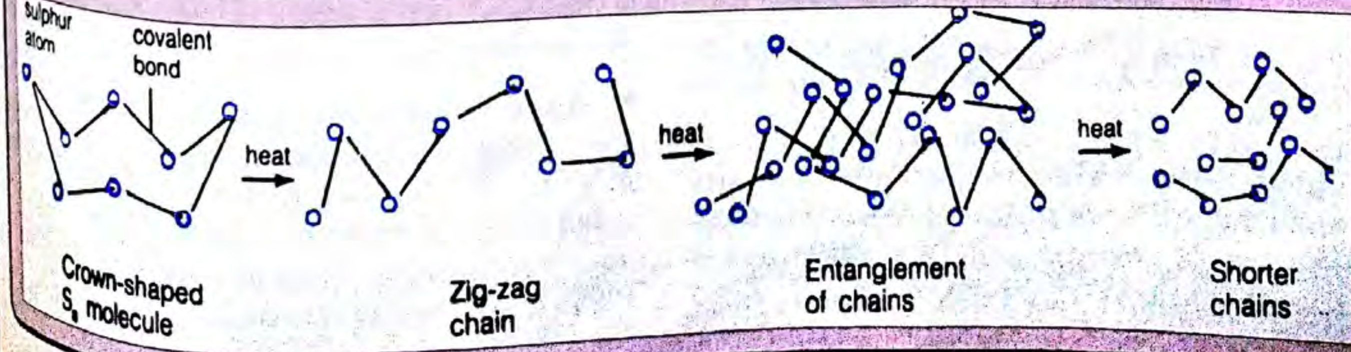
Physical Properties

1. Sulphur is a yellow solid. It exists in two forms – amorphous and crystalline.
2. It is insoluble in water but soluble in carbon(IV) sulphide and methyl benzene (toluene).
3. Being a non-metal, sulphur is a bad conductor of heat and electricity.
4. Density depends on allotropic form.
5. It has a melting point of 119 °C and a boiling point of 444 °C.

Effect of heat When sulphur is heated in a limited amount of air, it melts at temperatures between 115 °C and 119 °C into an amber-coloured liquid. The colour darkens as the temperature increases. At about 160 °C, the liquid becomes very dark and starts to turn viscous, reaching its maximum viscosity at 200 °C. On further heating, it begins to flow again, and boils to give off a light brown sulphur vapour at its boiling point of 444 °C. When this vapour is condensed on a cold surface, a fine powder which forms a floral pattern is obtained. This is *flowers of sulphur*. Molten sulphur is often poured into tubular moulds to form *roll sulphur*.

We can explain the effect of heat on sulphur in terms of its molecular structure. The crystalline forms of sulphur exist as S_8 molecules. The eight sulphur atoms in each molecule are arranged in the shape of a crown or ring with strong covalent bonds linking the atoms together. When sulphur is heated in limited air, the atoms in the molecule start to vibrate. This puts a strain on the covalent bonds and, at about 160 °C, the rings break up to form zig-zag chains. These zig-zag chains tangle with one another making the liquid viscous. At 200 °C, when all the S_8 molecules have opened up, the liquid sulphur reaches its maximum viscosity. At increasingly high temperatures, the zig-zag chains tend to break into even shorter chains. Hence, the viscosity decreases and the liquid sulphur flows more easily. At 800 °C, gaseous S_2 molecules exist which dissociate into monoatomic sulphur on further heating.

Fig. 22.5 Effect of heat on the molecular structure.



Chemical Properties

Sulphur, like oxygen, belongs to Group 6 of the Periodic Table. The sulphur atom has six valence electrons like the oxygen atom. In order to achieve an octet structure, it gains two electrons, usually from Groups 1 and 2 metals, to form the divalent sulphide ion, S^{2-}. With non-metals, sulphur attains the octet structure by sharing electrons to form covalent compounds such as hydrogen sulphide, H–S–H. The oxidation states of sulphur can range from –2 to +6.

Table 22.2 Oxidation states of sulphur in its compounds.

Name of compound	Formula	Oxidation state
Tetraoxosulphate(VI) acid	H_2SO_4	+6
Sulphur(IV) oxide	SO_2	+4
Sulphur	S_8	0
Hydrogen sulphide	H_2S	–2

Direct combination with other elements

Nearly all metals and most non-metals combine directly with sulphur.

With metals Sulphur combines directly with many metals to form sulphides when heated in the absence of air. Reactive metals like sodium and potassium may even react with sulphur spontaneously without heating, if both the metal and the sulphur are in a finely divided form.

$$Fe(s) + S(s) \rightarrow FeS(s)$$
$$2Cu(s) + S(s) \rightarrow Cu_2S(s)$$

With oxygen When sulphur is heated in a plentiful supply of air, it burns with a bright blue flame to form sulphur(IV) oxide and a small amount of sulphur(VI) oxide.

$$O_2(g) + S(s) \rightarrow SO_2(g)$$

With hydrogen At high temperatures, sulphur combines slowly with hydrogen to form hydrogen sulphide. The reaction is more rapid if hydrogen is bubbled through boiling sulphur.

$$H_2(g) + S(s) \rightarrow H_2S(g)$$

With carbon Sulphur combines with coke in an electric furnace to form a colourless liquid known as carbon(IV) sulphide, which vapourizes readily, forming poisonous and highly flammable fumes.

$$C(s) + 2S(s) \rightarrow CS_2(l)$$

With other non-metals Sulphur combines with other non-metals to form various sulphides, e.g. tetraphosphorus trisulphide, P_4S_3, disulphur dichloride, S_2Cl_2, and sulphur hexafluoride, SF_6.

Action of oxidizing acids

Sulphur is readily oxidized when warmed with concentrated tetraoxosulphate(VI) acid to form sulphur(IV) oxide. The acid itself is reduced to sulphur(IV) oxide. When warmed with concentrated trioxonitrate(V) acid, using bromine as a catalyst, sulphur is oxidized to tetraoxosulphate(VI) acid.

$$2H_2SO_4(aq) + S(s) \rightarrow 2H_2O(l) + 3SO_2(g)$$
$$6HNO_3(aq) + S(s) \rightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$$

Action of hot concentrated alkalis

Sulphur will react with hot concentrated alkaline solutions to form a mixture of sulphides and trioxosulphates(IV), which, in the presence of excess sulphur, react to form a polysulphide and a trioxothiosulphate(VI) respectively.

$$3S + 6OH^- \rightarrow 2S^{2-} + SO_3^{2-} + 3H_2O$$
$$S^{2-} + nS \rightarrow S_{n+1}^{2-} \quad \text{where } n = 1 \text{ to } 8$$
$$SO_3^{2-} + S \rightarrow S_2O_3^{2-}$$

Uses

1 Sulphur is used to produce sulphur(IV) oxide for manufacturing tetraoxosulphate(VI) acid.
2 Sulphur is used in the vulcanization of rubber.
3 Sulphur and some of its products are used as fungicides.and insecticides for spraying crops.
4 Sulphur is used to manufacture the bleaching agent used in the pulp and paper industry. It is also used for the production of carbon(IV) sulphide, skin ointments and dyes, and as sulphides in manufacturing matches, fireworks and gunpowder.

HYDROGEN SULPHIDE

Hydrogen sulphide is found in volcanic gases, sulphur springs, coal gas, and gases formed during the decay of organic matter containing sulphur.

Preparation

Hydrogen sulphide is prepared both in the laboratory and commercially by the action of a dilute acid on a metallic sulphide, like iron(II) sulphide.

$$2HCl(aq) + FeS(s) \rightarrow FeCl_2(aq) + H_2S(g)$$
$$H_2SO_4(aq) + FeS(s) \rightarrow FeSO_4(aq) + H_2S(g)$$

Ionically,

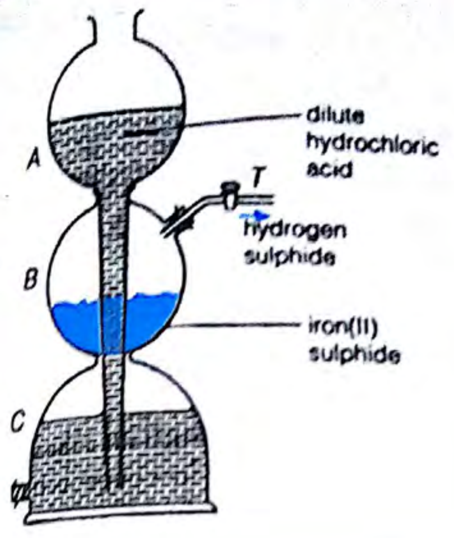
$$2H^+(aq) + FeS(s) \rightarrow Fe^{2+}(aq) + H_2S(g)$$

The gas is easily liquefied, and may be purchased in this form in steel cylinders.

Kipp's apparatus

Kipp's apparatus allows a gas to be supplied any time it is required. The apparatus consists of three chambers, *A*, *B* and *C*. The solid reactant is packed in *B* while *A* and *C* contain the liquid reactant. The apparatus is used to produce frequently used gases like hydrogen sulphide and carbon(IV) oxide.

Fig 22.6 Kipp's apparatus.



To produce hydrogen sulphide, *B* is packed with n(II) sulphide and *C* is filled with dilute rochloric acid via *A*. When tap *T* is opened, the ssure inside *B* drops. The acid from *C* rises into *B* reacts with the iron(II) sulphide in it to produce rogen sulphide which is delivered through the tap mmediately.

Tap *T* is turned off when the gas is no longer uired. The gas which is still being produced raises pressure inside *B* and pushes the acid back into *C* t of contact with the sulphide). This stops the duction of the gas.

hysical Properties

Hydrogen sulphide is a colourless gas with a repulsive smell like that of a rotten egg.

It is very poisonous.

It is about 1.18 times denser than air.

It is moderately soluble in water. Three volumes of the gas dissolve in every volume of water to form a very weak acidic solution.

It burns with a pale blue flame.

Chemical Properties

As an acid

Hydrogen sulphide ionizes slightly in water to form a weak, dibasic acid, which exhibits typical acidic properties.

$$H_2S(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$
$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$$

When it is bubbled through an alkali, a normal salt and water are formed. However, when present in excess, hydrogen sulphide can react with sodium or potassium hydroxide to form the corresponding acid salt, namely sodium or potassium hydrogensulphide respectively.

$$2NaOH(aq) + H_2S(g) \rightarrow Na_2S(aq) + 2H_2O(l)$$
$$NaOH(aq) + \underset{\text{excess}}{H_2S(g)} \rightarrow \underset{\text{acid salt}}{NaHS(aq)} + H_2O(l)$$

As a precipitating agent

Many metals form insoluble sulphides which are usually coloured. When hydrogen sulphide is bubbled through solutions of salts of such metals, the coloured sulphides are precipitated. This reaction is used, in qualitative analysis, to identify the metal ions present in an unknown substance.

$$Pb(CH_3COO)_2(aq) + H_2S(g) \rightarrow \underset{\text{black}}{PbS(s)} + 2CH_3COOH(aq)$$

$$ZnSO_4(aq) + H_2S(g) \rightarrow \underset{\text{white}}{ZnS(s)} + H_2SO_4(aq)$$

Paints often change colour because of the reaction of a metallic pigment with the hydrogen sulphide in the surrounding air.

Reaction with oxygen

Hydrogen sulphide does not support combustion but it burns in a plentiful supply of air with a bright blue flame to produce sulphur(IV) oxide. If the supply of oxygen is limited, a deposit of sulphur may form.

$$2H_2S(g) + \underset{\text{excess supply}}{3O_2(g)} \rightarrow 2H_2O(l) + 2SO_2(g)$$

$$2H_2S(g) + \underset{\text{limited supply}}{O_2(g)} \rightarrow 2H_2O(l) + 2S(s)$$

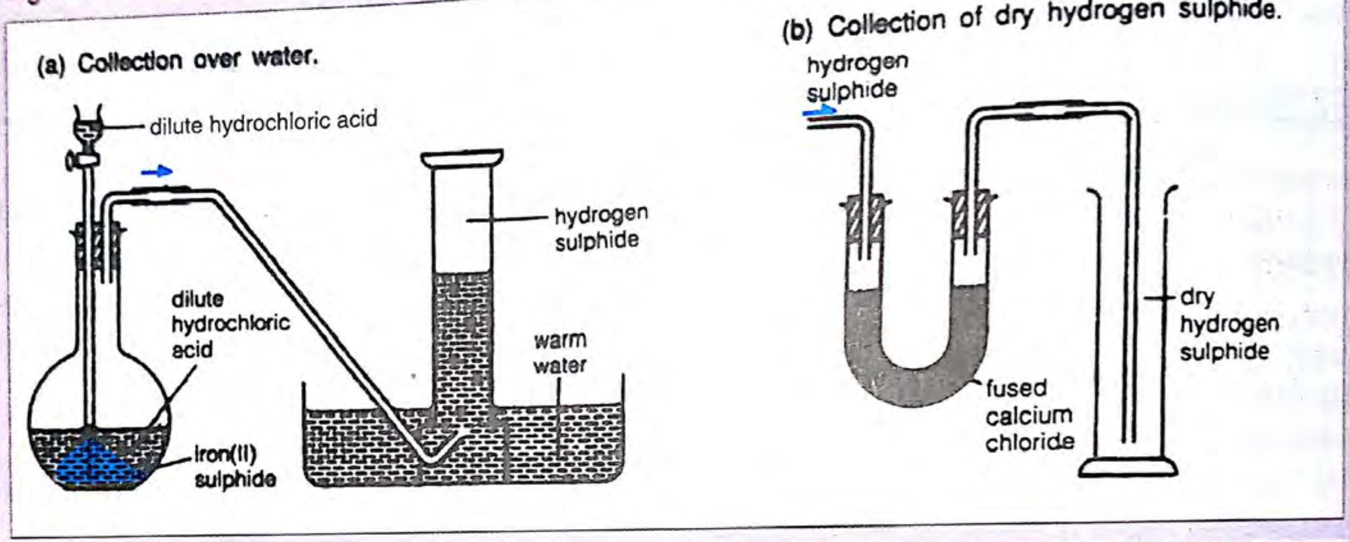
If traces of hydrogen sulphide are present in air, finely divided sulphur will form, causing some metals,

Experiment 22.1 To prepare hydrogen sulphide.

Method Put some iron(II) sulphide in a flat-bottomed flask and cover it with water. Then set up the apparatus as shown. Add some concentrated tetraoxosulphate(VI) or hydrochloric acid through a thistle funnel. Collect the gas produced over warm water as it is less soluble in warm water than in cold. If the gas is required dry, pass it through a U-tube containing fused calcium chloride and collect it.

NOTE Concentrated tetraoxosulphate(VI) acid cannot be used to dry hydrogen sulphide because it oxidizes the gas to sulphur.

Fig. 22.7 Preparation of hydrogen sulphide.


(a) Collection over water.

(b) Collection of dry hydrogen sulphide.

Result As soon as the acid reaches the iron(II) sulphide, there is effervescence and hydrogen sulphide is produced. It is easily recognized by its smell which resembles that of a rotten egg.

Conclusion Hydrogen sulphide can be prepared by the action of a dilute acid on a metallic sulphide.

e.g. silver and copper, to tarnish by forming sulphides with the metals. This can be prevented by coating these metallic objects with silicone

$$\underset{\text{}}{2Ag(s) + S(s) \rightarrow} \underset{\text{black}}{Ag_2S(s)}$$

As a reducing agent

Hydrogen sulphide is a strong reducing agent because the oxidation number of sulphur in this compound is –2, the lowest exhibited by sulphur. It is frequently used in qualitative analysis to test for oxidizing agents. During the redox process, hydrogen sulphide itself is usually oxidized to sulphur, while the electrons released in the process are accepted by the oxidizing agent.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
$$S^{2-} \rightleftharpoons S + 2^{e-}$$

With tetraoxomanganate(VII) When hydrogen sulphide is bubbled through a solution of acidified potassium tetraoxomanganate(VII), the purple colour of the tetraoxomanganate(VII) solution disappears and sulphur is deposited. The colour change is due to the reduction of the purple tetraoxomanganate(VII) ion to the very pale pink manganese(II) ion.

$$2KMnO_4(aq) + 3H_2SO_4(aq) + 5H_2S(g) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(l) + 5S(s)$$

Ionically,

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2S(g) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5S(s)$$

With heptaoxochromate(VI) When hydrogen sulphide is bubbled through a solution of acidified potassium heptaoxochromate(VI), the solution changes from orange to green. Sulphur is also deposited at the same time. The colour change is due to the reduction of the orange heptaoxochromate(VI) ion to the green chromium(III) ion.

$$K_2Cr_2O_7(aq) + 4H_2SO_4(aq) + 3H_2S(g) \rightarrow K_2SO_4(aq) + Cr_2(SO_4)_3(aq) + 7H_2O(l) + 3S(s)$$

Ionically,

$$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2S(g) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3S(s)$$

With the halogens Hydrogen sulphide is oxidized by the halogens to sulphur. Moisture must be present for the reactions to occur.

$$Cl_2(g) + H_2S(g) \rightarrow 2HCl(g) + S(s)$$

With iron(III) chloride Hydrogen sulphide reduces a brownish-yellow solution of iron(III) chloride to a green solution of iron(II) chloride. The hydrogen sulphide itself is oxidized to sulphur and hydrogen chloride.

$$2FeCl_3(aq) + H_2S(g) \rightarrow 2FeCl_2(aq) + 2HCl(aq) + S(s)$$

Ionically,

$$2Fe^{3+}(aq) + H_2S(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq) + S(s)$$

With sulphur(IV) oxide Hydrogen sulphide is a stronger reducing agent than sulphur(IV) oxide. It reduces sulphur(IV) oxide to sulphur in the presence of moisture.

$$SO_2(g) + 2H_2S(g) \rightarrow 2H_2O(l) + 3S(s)$$

With oxidizing acids Hydrogen sulphide is readily oxidized by the oxidizing acids to sulphur. Since concentrated trioxonitrate(V) acid is a very strong oxidizing agent, it oxidizes the sulphide t tetraoxosulphate.(VI) acid to a certain extent.

$$H_2SO_4(aq) + H_2S(g) \rightarrow 2H_2O(l) + SO_2(g) + S(s)$$

$$2HNO_3(aq) + H_2S(g) \rightarrow 2H_2O(l) + 2NO_2(g) + S(s)$$

$$8HNO_3(aq) + H_2S(g) \rightarrow 4H_2O(l) + 8NO_2(g) + H_2SO_4(aq)$$

Test for hydrogen sulphide

A gas with a repulsive smell, like that of rotten eggs, is probably hydrogen sulphide. Confirm this by doing the following test.

With lead(II) trioxonitrate(V) Moisten a piece of filter paper with lead(II) trioxonitrate(V) solution and drop it into a gas jar of the unknown gas. If the gas is hydrogen sulphide, the paper turns black due to the fornation of black lead(II) sulphide. Lead(II) ethanoate too gives the same reaction.

$$Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2HNO_3(aq)$$

Uses

Hydroygen sulphide is used in the analysis of ores and metals. It is possible to separate groups of metals from one another because their sulphides have different solubilities in acids and alkalis. The presence of a certain metal is also often indicated by the colour of its sulphide.

Table 22.3 Colours of some metallic sulphides.

Sulphide	Colour
PbS, CuS, FeS, Ag_2S, HgS, NiS, CoS	Black
ZnS	White
SnS_2, CdS	Yellow
As_2S_3	Orange-yellow
Sb_2S_3	Reddish-orange
MnS	Pink

SULPHIDES

Hydrogen sulphide forms two series of salts, namely the sulphides and the hydrogen sulphides. Almost all sulphides, other than potassium, sodium and ammonium sulphides, are insoluble in water. Some of these insoluble sulphides will not precipitate in the presence of dilute hydrochloric acid while others will.

Table 22.4 *Solubility of metallic sulphides.*

Metallic sulphide	Solubility in water	Solubility in acidified solutions
K_2S, Na_2S, $(NH_4)_2S$	Soluble	Soluble
CaS, MgS, ZnS, NiS, CoS, MnS, FeS	Insoluble (form coloured precipitates)	
SnS_2, CdS, CuS, PbS, HgS, Sb_2S_3, Bi_2S_3, As_2S_3		Insoluble (form coloured precipitates)

Preparation

By neutralization The three soluble sulphides, namely sodium, potassium and ammonium sulphides are prepared by bubbling hydrogen sulphide through the corresponding alkalis.

To prepare ammonium sulphide, take two test-tubes, *A* and *B*, and fill them with equal amounts of aqueous ammonia. Then, bubble hydrogen sulphide through the solution in tube *A*, until no more of the gas can be absorbed. This solution now contains ammonium hydrogen sulphide. Next, pour the aqueous ammonia from tube *B* into tube *A*, to convert the ammonium hydrogensulphide to ammonium sulphide.

$$NH4^+(aq) + OH^-(aq) + H_2S(g) \rightarrow NH_4HS(aq) + H_2O(l)$$

$$NH_4HS(aq) + NH_4^+(aq) + OH^-(aq) \rightarrow (NH_4)_2S(aq) + H_2O(l)$$

By direct combination Some sulphides, e.g. iron(II) and zinc sulphides, can be prepared by heating a mixture of the metal and sulphur.

$$Fe(s) + S(s) \rightarrow FeS(s)$$

By precipitation Insoluble sulphides can be obtained by bubbling hydrogen sulphide through a solution of the corresponding salts.

$$SnCl_2(aq) + H_2S(g) \rightarrow \underset{\text{dark brown}}{SnS(s)} + 2HCl(aq)$$

NOTE Tin(II) sulphide, SnS, is readily oxidized to the yellow tin(IV) sulphide, SnS_2, by ammonium polysulphide. The tin(IV) sulphide then dissolves in the ammonium sulphide to give a complex salt.

Properties

Reaction with oxygen

When most metallic sulphides are heated in air or oxygen, they produce the corresponding metallic oxides and sulphur(IV) oxide. An exception is mercury(II) sulphide which yields the metal itself instead of the oxide.

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$
$$HgS(s) + O_2(g) \rightarrow Hg(l) + SO_2(g)$$

This chemical reaction is used in the extraction of metals from their naturally occurring sulphide.

Reaction with hydrochloric acid

Most sulphides react with hydrochloric acid upon heating to yield hydrogen sulphide. This reaction is used as a test for sulphides. However, those sulphides which are insoluble in hydrochloric acid must first be fused with sodium trioxocarbonate(IV) before the test is carried out.

$$PbS(s) + 2HCl(aq) \rightarrow PbCl_2(s) + H_2S(g)$$

Uses

1 Iron(II) sulphide is reacted with dilute hydrochloric acid in the Kipp's apparatus to obtain a supply of hydrogen sulphide when needed in the laboratory.

2 Zinc sulphide is used to coat the inside of television screens as it fluoresces or becomes luminescent on being exposed to light.

3 Tin(IV) sulphide is used in paints.

SULPHUR(IV) OXIDE

Sulphur(IV) oxide is usually present in volcanic gases and in the waters of certain sulphur springs. Coal, which contains sulphur in the combined form, produces sulphur(IV) oxide when burned. The presence of substantial amounts of sulphur(IV) oxide in the atmosphere is one of the major causes of acid rain.

Preparation

Sulphur(IV) oxide is produced indrustrially by burning sulphur or metallic sulphides in air or oxygen. The gas is usually sold in the liquid form under pressure.

In the laboratory, it is readily generated by heating sodium or potassium trioxosulphate(IV) with tetraoxosulphate(VI) or hydrochloric acid. The trioxosulphate(IV) acid formed breaks down to yield water and sulphur(IV) oxide.

$$Na_2SO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + SO_2(g)$$

Ionically,

$$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$$

The gas is also obtained by heating concentrated tetraoxosulphate(VI) acid with copper.

$$Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

Physical properties

1 Sulphur(IV) oxide is a colourless and poisonous gas with a very irritating smell like that of burning matches.
2 It is very soluble in water, one volume of water dissolving about 70 volumes of the gas. The resultant solution is trioxosulphate(IV) acid. Hence, sulphur(IV) oxide is the anhydride of trioxosulphate(IV) acid.
3 It is about 2.5 times denser than air
4 It can be easily liquefied under pressure (about 3 atm) at room temperature.

Chemical Properties

As an acid

The gas reacts with alkalis to form a normal salt, i.e. a trioxosulphate(IV), and water only.

$$2NaOH(aq) + SO_2(g) \rightarrow Na_2SO_3(aq) + H_2O(l)$$

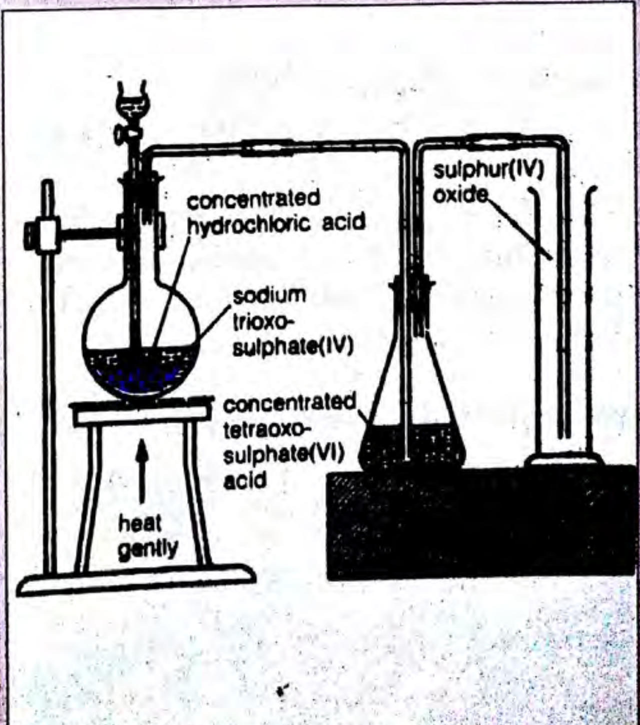
Experiment 22.2 To prepare sulphur(IV) oxide.

Method Place some sodium trioxosulphate(IV) crystals in a round-bottomed flask and set up the apparatus as shown in a fume cupboard. Pour in some concentrated hydrochloric acid through the thistle funnel. Heat the mixture gently. Dry the gas evolved by passing it through concentrated hydrogen teraoxosulphate(VI) acid and collect it in a gas-jar by downward delivery. Hold a moist blue litmus paper at the mouth of the jar.

Result Sulphur(IV) oxide is readily evolved when the mixture is heated, leaving a solution of sodium chloride in the flask. The moist blue litmus paper turns pink when the gas jar is full of the gas, showing that the gas is acidic.

Conclusion Sodium trioxosulphate(IV) reacts with concentrated hydrochloric acid to yield sulphur(IV) oxide when heated.

Fig. 22.8 Preparation of sulphur(IV) oxide.



In the presence of an excess of the gas, the acid salt, hydrogentrioxosulphate(IV), is formed.

$$NaOH(aq) + \underset{\text{excess}}{SO_2(g)} \rightarrow NaHSO_3(aq)$$

As a reducing agent

Sulphur(IV) oxide is a strong reducing agent, in the presence of water. This is due to the formation of the trioxosulphate(IV) ion, SO_3^{2-}, which readily donates electrons to an oxidizing agent.

$$H_2O(l) + SO_2(g) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$$

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

With tetraoxomanganate(VII) Sulphur(IV) oxide decolourizes an acidified potassium tetraoxomanganate(VII) solution by reducing it to manganese(II) tetraoxosulphate(VI). At the same time, sulphur(IV) oxide is itself oxidized to tetraoxosulphate(VI) acid.

$$2KMnO_4(aq) + 5SO_2(g) + 2H_2O(l) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 2H_2SO_4(aq)$$

Ionically,

$$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(l) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 4H^+(aq)$$

With heptaoxochromate(VI) Sulphur(IV) oxide changes the colour of acidified potassium heptaoxochromate(VI) solution from orange to green by reducing it to chromium(III) tetraoxo-sulphate(VI).

$$K_2Cr_2O_7(aq) + 3SO_2(g) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + Cr_2(SO_4)_3(aq) + H_2O(l)$$

Ionically,

$$Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$$

With iron(III) chloride Sulphur(IV) oxide reduces brown iron(III) chloride solution to green iron(II) chloride solution while it is itself oxidized to tetraoxosulphate(VI) acid.

$$2FeCl_3(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2FeCl_2(aq) + H_2SO_4(aq) + 2HCl(aq)$$

Ionically,

$$2Fe^{3+}(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + SO_4^{2-}(aq) + 4H^+(aq)$$

With trioxonitrate(V) acid Sulphur(IV) oxide reduces concentrated trioxonitrate(V) acid to liberate reddish-brown nitrogen(IV) oxide.

$$2HNO_3(aq) + SO_2(g) \rightarrow H_2SO_4(aq) + 2NO_2(g)$$

Ionically,

$$2NO_3^-(aq) + SO_2(g) \rightarrow SO_4^{2-}(aq) + 2NO_2(g)$$

With the halogens Sulphur(IV) oxide reduces the coloured solutions of chlorine, bromine and iodine to the colourless solutions of their hydrogen compounds.

$$Cl_2(g) + SO_2(g) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 2Cl^-(aq) + 4H^+(aq)$$

As a bleaching agent

A solution of sulphur(IV) oxide in water bleaches both natural and artificial dyes. Sulphur(IV) oxide is a good bleaching agent because of its reducing powers. In the presence of water, it dissolves to form trioxosulphate(IV) acid which then donates electrons to the dye and becomes oxidized to tetraoxosulphate(VI) acid. In the process, the dye is reduced to a colourless compound.

$$\underset{\text{R.A.}}{H_2SO_3(aq)} + \underset{\substack{\text{O.A.}\\\text{coloured}}}{Dye(aq)} \rightarrow H_2SO_4(aq) + \underset{\text{colourless}}{\text{Bleached dye}(aq)}$$

The bleaching action of sulphur(IV) oxide is similar to that of chlorine in that water must be present for bleaching to occur. However, chlorine bleaches by oxidizing the dye whereas sulphur(IV) oxide bleaches by reducing it. Bleaching by sulphur(IV) oxide is usually not as lasting as that by chlorine because the bleached dye may become reoxidized by atmospheric oxygen to form the original coloured compound. This is why a white straw hat often turns yellow after some time.

Direct combination reactions

With certain metallic oxides When lead(IV) oxide is heated and lowered into a gas jar of sulphur(IV) oxide, the two compounds combine to form white deposits of lead(II) tetraoxosulphate(VI). Sodium peroxide also reacts in a similar manner with sulphur(IV) oxide. These reactions are exothermic.

$$PbO_2(s) + SO_2(g) \rightarrow PbSO_4(s)$$
$$Na_2O_2(s) + SO_2(g) \rightarrow Na_2SO_4(s)$$

With oxygen In the presence of a catalyst, sulphur(IV) oxide combines reversibly with oxygen to form sulphur(VI) oxide. The forward reaction is exothermic.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

As an oxidizing agent

Sulphur(IV) oxide can act as an oxidizing agent in the presence of a stronger reducing agent. For instance, it oxidizes hydrogen sulphide to sulphur in the presence of moisture. At 1 000 °C, it also oxidizes carbon while itself being reduced to sulphur. This reaction is used for recovering sulphur from industrial fuel gases.

$$2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$$
$$C(s) + SO_2(g) \rightarrow CO_2(g) + S(s)$$

Tests for sulphur(IV) oxide

Sulphur(IV) oxide may be recognized by its irritating smell and confirmed by these tests.

Bleaching action Place some moist coloured flowers into a jar of the unknown gas. If the flowers are bleached, the presence of sulphur(IV) oxide can be suspected. Confirm this by testing for its reducing effect on oxidizing agents.

Action on oxidizing agents Bubble the unknown gas through solutions of either acidified potassium heptaoxochromate(VI) or potassium tetraoxomanganate(VII). If the unknown gas is sulphur(IV) oxide,

- the acidified potassium heptaoxodichromate(VI) solution will change from orange to green colour, while
- the purple potassium tetraoxomanganate(VII) solution will become colourless.

NOTE Both sulphur(IV) oxide and hydrogen sulphide produce similar colour changes with acidified potassium heptaoxodichromate(VI) and potassium tetraoxomanganate(VII). However, hydrogen sulphide also produces a yellow precipitate of sulphur, while sulphur(IV) oxide does not.

Uses

1. The most important use of sulphur(IV) oxide is in the making of tetraoxosulphate(VI) acid.
2. It is used as a germicide and a fumigant. It is often used for destroying termites.
3. It is used as a bleaching agent for straw, sponges, silk, wool and other fabrics which would be damaged by chlorine, the more commonly used bleach. It is also used in the manufacture of calcium hydrogentrioxosulphate(IV), a bleaching agent used for bleaching wood pulp and artificial silk.
4. Liquid sulphur(IV) oxide is sometimes used as a refrigerant because of its easy liquefaction and high latent heat of vaporization.
5. The gas is sometimes used as a preservative in some liquids, e.g. orange juice. It kills bacteria and fungi, and prevents the oxidation of the liquid, by reacting with the oxygen. It is also used in preserving fruits and grains.

SULPHUR(VI) OXIDE

Under normal conditions, sulphur(IV) oxide, SO_2, does not readily combine with oxygen to form sulphur(VI) oxide, SO_3. To get a good yield of sulphur(VI) oxide,

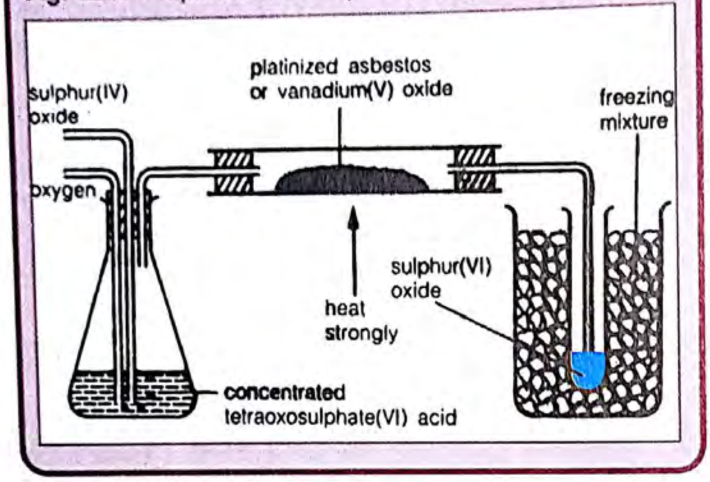
- a catalyst like platinized asbestos or vanadium(V) oxide,
- a slight pressure and
- a temperature of 400–450 °C

are required.

Preparation

In the laboratory, a mixture of sulphur(IV) oxide and oxygen is first dried by passing it through concentrated tetraoxosulphate(VI) acid. Then the gaseous mixture is passed over a strongly heated catalyst. The sulphur(VI) oxide formed is seen as dense white fumes. It solidifies when cooled in a freezing mixture of ice and salt.

Fig. 22.9 Preparation of sulphur(VI) oxide.



This above reaction is carried out in the *Contact process*, the industrial manufacture of tetraoxosulphate(VI) acid.

Sulphur(VI) oxide can also be obtained by dehydrating tetraoxosulphate(VI) acid with phosphorus(V) oxide, or by heating some tetraoxosulphates(VI) or hydrogentetraoxo sulphates(VI).

Properties

At room temperature, sulphur(VI) oxide exists as white needle-shaped crystals. It has a low boiling point (45 °C) and hence readily vaporizes on gentle heating.

It is an acidic oxide. It reacts exothermically with water to form tetraoxosulphate(VI) acid, and neutralizes bases to form tetraoxosulphates(VI). Hence, it is also known as the tetraoxosulphate(VI) anhydride.

$$H_2O(l) + SO_3(g) \rightleftharpoons H_2SO_4(aq)$$

It also dissolves in concentrated tetraoxosulphate(VI) acid to form *oleum* or fuming tetraoxosulphate(VI) acid.

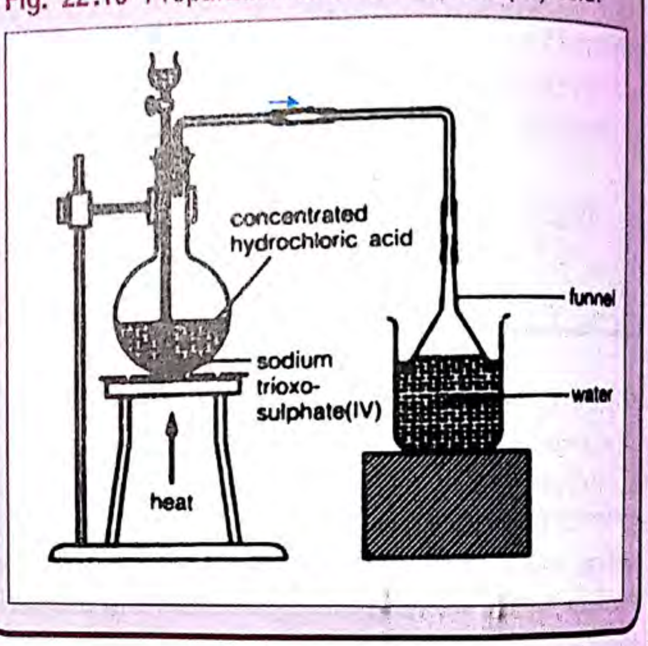
$$SO_3(s) + H_2SO_4(aq) \rightleftharpoons \underset{\text{oleum}}{H_2S_2O_7(aq)}$$

TRIOXOSULPHATE(IV) ACID

Trioxosulphate(IV) acid, H_2SO_3, is an unstable acid formed when sulphur(IV) oxide dissolves in water. The reaction is easily reversible, and the acid decomposes into sulphur(IV) oxide and water even at room temperature. Hence, the acid has never been obtained pure (i.e. free from water) because any attempt to do so would result in its decomposition.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

Fig. 22.10 Preparation of trioxosulphate(VI) acid.



The acid is dibasic and ionizes as follows:

$$H_2SO_3(aq) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$$
$$HSO_3^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H^+(aq)$$

Preparation

Trioxosulphate(IV) acid is prepared by adding concentrated hydrochloric acid to sodium trioxosulphate(IV) and heating the mixture gently. The sulphur(IV) oxide liberated is dissolved in water as shown in fig. 22.10 to form trioxosulphate(IV) acid.

Physical Properties

1 Trioxosulphate(IV) acid is a colourless and unstable acid.
2 It smells strongly of sulphur(IV) oxide, which is a product of its decomposition.
3 It turns blue litmus red.

Chemical Properties

Action of air

When trioxosulphate(IV) acid is exposed to air for some time, it becomes oxidized by atmospheric oxygen to tetraoxosulphate(VI) acid.

$$2H_2SO_3(aq) + O_2(g) \rightarrow 2H_2SO_4(aq)$$

As a reducing and bleaching agent

Trioxosulphate(IV) acid is responslble for all the reducing and bleaching actions of sulphur(IV) oxide.

As an acid

Trioxosulphate(IV) acid is a weak dibasic acid. It forms both acid and normal salts with alkalis. For example, when a limited amount of sodium hydroxide is present, the acid salt, sodium hydrogentrioxosulphate(IV) is produced.

$$\underset{\text{limited}}{NaOH(aq)} + H_2SO_3(aq) \rightarrow \underset{\text{acid salt}}{NaHSO_3(aq)} + H_2O(l)$$

In the presence of excess alkali, the normal salt, sodium trioxosulphate(IV), Na_2SO_3, is produced.

$$\underset{\text{excess}}{2NaOH(aq)} + H_2SO_3(aq) \rightarrow \underset{\text{normal salt}}{Na_2SO_3(aq)} + 2H_2O(l)$$

Uses

1 Trioxosulphate(IV) acid is used for bleaching straw and other fabrics.
2 It is also used as a germicide.

TRIOXOSULPHATES(IV)

The trioxosulphates(IV) are the normal salts formed when sulphur(IV) oxide or trioxosulphate(IV) acid reacts with an excess of alkalis.

Preparation

By neutralization Sulphur(IV) oxide dissolves in excess sodium and potassium hydroxides to form sodium and potassium trioxosulphates(IV) respectively. Trioxosulphate(IV) acid can also be used to react with the alkalis in place of sulphur(IV) oxide.

$$SO_2(g) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + H_2O(l)$$
$$H_2SO_3(aq) + 2KOH(aq) \rightarrow K_2SO_3(aq) + 2H_2O(l)$$

By precipitation Insoluble trioxosulphates(IV) are precipitated out of solution when sulphur(IV) oxide is bubbled through a solution of a corresponding metallic salt.

Properties

Solubility The trioxosulphates(IV) of ammonium, potassium, sodium and calcium are soluble while the other metallic trioxosulphates(IV) are insoluble in water.

Reaction with acids When trioxosulphates(IV) are heated with concentrated or dilute acids, sulphur(IV) oxide is evolved.

$$CaSO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + SO_2(g)$$

Reaction with air A trioxosulphate(IV) is converted to the tetraoxosulphate(VI) slowly by air, and more rapidly by many oxidizing agents.

As a reducing agent Trioxosulphates(IV) in dilute acidified solution have the same reducing powers as trioxosulphate(IV) acid.

Tests for trioxosulphates(IV)

On warming with an acid Warm the unknown substance with a dilute acid. If sulphur(IV) oxide is evolved, then a trioxosulphate(IV) is present.

$$2H^+(aq) + SO_3^{2-}(aq) \rightarrow SO_2(g) + H_2O(l)$$

With barium trioxonitrate(V) Add some barium trioxonitrate(V) solution, $Ba(NO_3)_2$, to a solution of the unknown substance. A white precipitate of barium trioxosulphate(IV) will be formed in the presence of a trioxosulphate(IV). This precipitate will dissolve in dilute trioxonitrate(V) acid with the evolution of sulphur(IV) oxide.

$$Ba^{2+}(aq) + SO_3^{2-}(aq) \rightarrow BaSO_3(s)$$

$$BaSO_3(s) + 2HNO_3(aq) \rightarrow SO_2(g) + Ba(NO_3)_2(aq) + H_2O(l)$$

TETRAOXOSULPHATE(IV) ACID

Tetraoxosulphate(VI) acid, H_2SO_4, is one of the most important chemical compounds known. It is very commonly used in the laboratory, and almost every manufacturing process makes use of this acid directly or indirectly at some stage.

Industrial Preparation

Most of the world's supply of tetraoxosulphate(VI) acid is now manufactured by the Contact process. The main reaction in this process is the catalytic combination of sulphur(IV) oxide and oxygen to form sulphur(VI) oxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{heat}$$

Sulphur(IV) oxide is obtained by burning sulphur in dry air or by roasting sulphide ores.

$$S(s) + O_2(g) \rightleftharpoons SO_2(g)$$

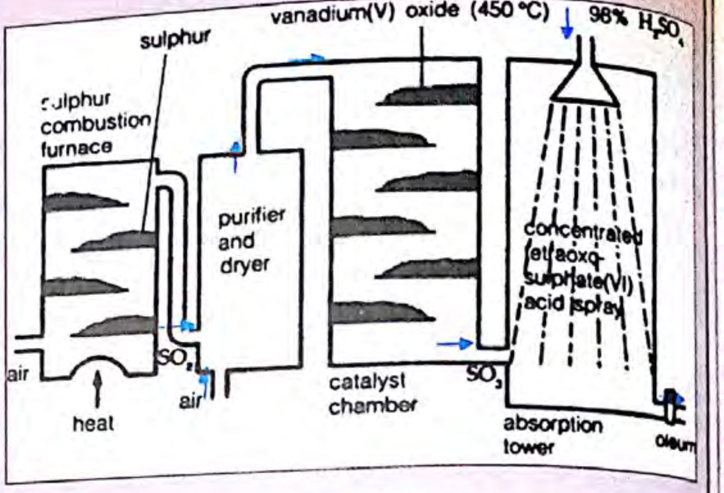
The sulphur(IV) oxide is then mixed with excess air and passed through an electric chamber to remove impurities and dust which might poison the catalyst. The gaseous mixture is then passed through concentrated tetraoxosulphate(VI) acid to be dried before it is delivered to the reaction chamber or contact tower. In this chamber, the sulphur(IV) oxide combines with oxygen in the presence of pellets of the catalyst, vanadium(V) oxide, to yield sulphur(VI) oxide.

The process is operated at atmospheric pressure and a temperature of about 450–500 °C, with an excess of air or oxygen to ensure that all the sulphur(IV) oxide has reacted. About 98% of the possible yield of sulphur(VI) oxide is obtained.

The sulphur(VI) oxide is cooled and passed into an absorption tower where it dissolves in concentrated tetraoxosulphate(VI) acid to produce a very thick liquid called *oleum*. The oxide is not dissolved directly in water because the heat evolved during the process would cause the acid solution to boil, producing a mist of acid droplets which would spread throughout the factory.

$$SO_3(g) + H_2SO_4(aq) \rightarrow \underset{\text{oleum}}{H_2S_2O_7(aq)}$$

Fig. 22.11 Industrial preparation of sulphur(VI) oxide by the Contact process.



The oleum is then diluted with appropriate amounts of water to produce the 98% tetraoxosulphate(VI) acid used in the laboratory, and other desired concentrations.

$$H_2S_2O_7(aq) + H_2O(l) \rightarrow 2H_2SO_4(aq)$$

Scheme of the Contact process

$$S + O_2 \rightarrow \underset{\substack{|\\ O_2\\ \text{(excess}\\ \text{air)}}}{SO_2 \rightarrow} \underset{\substack{|\\ \text{concentrated}\\ H_2SO_4}}{SO_3 \rightarrow} \underset{\text{oleum}}{H_2S_2O_7} \underset{\substack{|\\ H_2O}}{\rightarrow} H_2SO_4$$

Physical Properties

1 Concentrated tetraoxosulphate(VI) acid, often called the oil of *vitriol* is a colourless, viscous liquid with a density of 1.84 g cm^{-3}.

2 It is corrosive and causes severe burns if it comes into contact with the skin.

3 Concentrated tetraoxosulphate(VI) acid has a great affinity for water, evolving a large amount of heat as it dissolves. This heat evolved is a result of the hydration of the tetraoxosulphate(VI) ions. The concentrated acid is also hygroscopic, absorbing water vapour from the surroundings and becoming more dilute in the process.

Chemical Properties

As an acid

Dilute tetraoxosulphate(VI) acid is a strong dibasic acid which ionizes in two stages. It is a typical acid as shown by its reactions with metals, bases and trioxocarbonates(IV).

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + \underset{\text{hydrogentetraoxosulphate(VI) ion}}{HSO_4^-(aq)}$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + \underset{\text{tetraoxo sulphate(VI) ion}}{SO_4^{2-}(aq)}$$

With metals Dilute tetraoxosulphate(VI) acid reacts with metals which are above hydrogen in the electrochemical series to liberate hydrogen.

$$H_2SO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + H_2(g)$$

With bases Dilute tetraoxosulphate(VI) acid reacts with bases or alkalis to form salts and water.

$$H_2SO_4(aq) + MgO(s) \rightarrow MgSO_4(aq) + H_2O(l)$$

Since it is a dibasic acid, tetraoxosulphate(VI) acid forms two series of salts, namely

- the tetraoxosulphates which are the normal salts, and
- the hydrogentetraoxosulphates(VI) which are the acid salts.

$$H_2SO_4(aq) + NaOH(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$$

$$H_2SO_4(aq) + \underset{\text{excess}}{2NaOH(aq)} \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

With trioxocarbonates(IV) Dilute tetraoxosulphate(VI) acid reacts with trioxocarbonates(IV) to liberate carbon(IV) oxide.

$$H_2SO_4(aq) + CuCO_3(aq) \rightarrow CuSO_4(aq) + H_2O(l) + CO_2(g)$$

Ionically,

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$$

As an oxidizing agent

Hot concentrated tetraoxosulphate(VI) acid exhibits oxidizing properties by accepting electrons from reducing agents. The acid itself is usually reduced to trioxosulphate(IV) acid or sulphur(IV) oxide. In these reactions, the oxidation number of sulphur decreases from +6 to +4.

$$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow 2H_2O(l) + SO_2(g)$$

With metals The concentrated acid oxidizes metals to produce the corresponding metallic tetraoxosulphates(VI) and sulphur(IV) oxide. In these reactions, the metals supply the electrons and become oxidized to the metallic ions.

$$Zn(s) + 2H_2SO_4(aq) \rightarrow ZnSO_4(aq) + 2H_2O(l) + SO_2(g)$$

Ionically,

$$Zn(s) + 4H^+(aq) + SO_4^{2-}(aq) \rightarrow Zn^{2-}(aq) + 2H_2O(l) + SO_2(g)$$

With non-metals The concentrated acid oxidizes non-metals to produce their corresponding oxides and sulphur(IV) oxide. For example, when powdered carbon is heated with the concentrated acid, carbon(IV) oxide is formed.

$$C(s) + 2H_2SO_4(aq) \rightarrow CO_2(g) + 2H_2O(l) + 2SO_2(g)$$

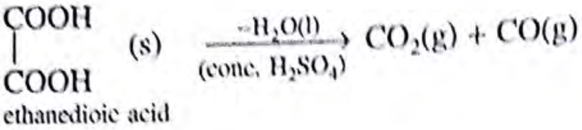
With hydrogen sulphide Tetraoxosulphate(VI) acid oxidizes hydrogen sulphide to sulphur. The reaction takes place readily when hydrogen sulphide is bubbled into hot or cold concentrated tetraoxosulphate(VI) acid.

$$H_2S(g) + H_2SO_4(aq) \rightarrow SO_2(g) + 2H_2O(l) + S(s)$$

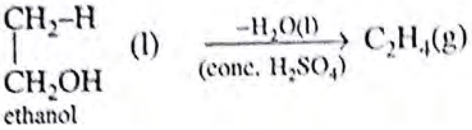
As a dehydrating agent

Concentrated tetraoxosulphate(VI) acid is able to remove the elements hydrogen and oxygen in the form of water from compounds like sugar, ethanol, methanoic acid and ethanedioic acid.

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}(s)} \xrightarrow[\text{(conc. } H_2SO_4)]{-11H_2O(l)} \underset{\text{sugar charcoal}}{12C(s)}$$



$$\underset{\text{ethanedioic acid}}{\begin{matrix}COOH\\ |\\ COOH\end{matrix}}(s) \xrightarrow[\text{(conc. } H_2SO_4)]{-H_2O(l)} CO_2(g) + CO(g)$$



$$\underset{\text{ethanol}}{\begin{matrix}CH_2{-}H\\ |\\ CH_2OH\end{matrix}}(l) \xrightarrow[\text{(conc. } H_2SO_4)]{-H_2O(l)} C_2H_4(g)$$

The removal of water from a compound as seen in these processes is known as *dehydration* and the concentrated acid is said to behave as a *dehydrating agent.*

NOTE Dehydration affects the chemical composition of a compound while drying does not.

Dehydration reactions account for

- the corrosive action of the concentrated acid on cloth, paper, wood, and even the skin;
- the removal of water of crystallization from hydrated compounds so that they become anhydrous, e.g.

$$\underset{\substack{\text{blue}\\ \text{(hydrated form)}}}{CuSO_4.5H_2O(s)} \xrightarrow[\text{(conc. } H_2SO_4)]{-5H_2O(l)} \underset{\substack{\text{white}\\ \text{(anhydrous form)}}}{CuSO_4(s)}$$

The acid itself remains chemically unchanged at the end of these reactions although it may be diluted by the water formed.

Displacement of other acids from their salts

Concentrated tetraoxosulphate(VI) acid is able to displace volatile acids from their corresponding salts. When a chloride or a trioxonitrate(V) is heated with concentrated tetraoxosulphate(VI) acid, hydrochloric or trioxonitrate(V) acid distils over as a vapour because of its lower boiling point. In some instances, the acids displaced are unstable and break down to give volatile products.

$$KCl(s) + H_2SO_4(aq) \rightarrow KHSO_4(aq) + HCl(g)$$

$$NaNO_3(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HNO_3(g)$$

$$Na_2SO_3(s) + 2H_2SO_4(aq) \rightarrow 2NaHSO_4(aq) + H_2O(l) + SO_2(g)$$

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

These reactions, which depend on the high boiling point of concentrated tetraoxosulphate(VI) acid, are used in qualitative analysis to detect the presence of many acid radicals.

Uses

1 About one quarter of the tetraoxosulphate(VI) acid produced in the world is used for the production of the two fertilizers,
  - calcium hydrogentetraoxophosphate(V),
  - ammonium tetraoxosulphate(VI).

2 Large amounts of the acid are used in the manufacture of pigments, e.g. titanium(IV) oxide and barium tetraoxosulphate(VI), for use in paints and dyes.

3 It is used for making cellulose film, natural and artificial fabrics, and plastics.

4 The acid is used in the purification of crude oil and also in the manufacture of artificial silk.

5 The acid is used to clean or pickle metals before electroplating or enamelling.

6 It is used as a dehydrating agent in the nitration of compounds used for making explosives.

7 It is used as an electrolyte in lead accumulators and batteries, and in the refining of metals by electrolysis.

8 In the refining of petroleum, the acid is used to remove waxes, gums and many dark-coloured compounds.

9 It is used in the preparation of many important chemical compounds, e.g. hydrochloric and trioxonitrate(V) acids, metallic tetraoxosulphates(VI), and many others.

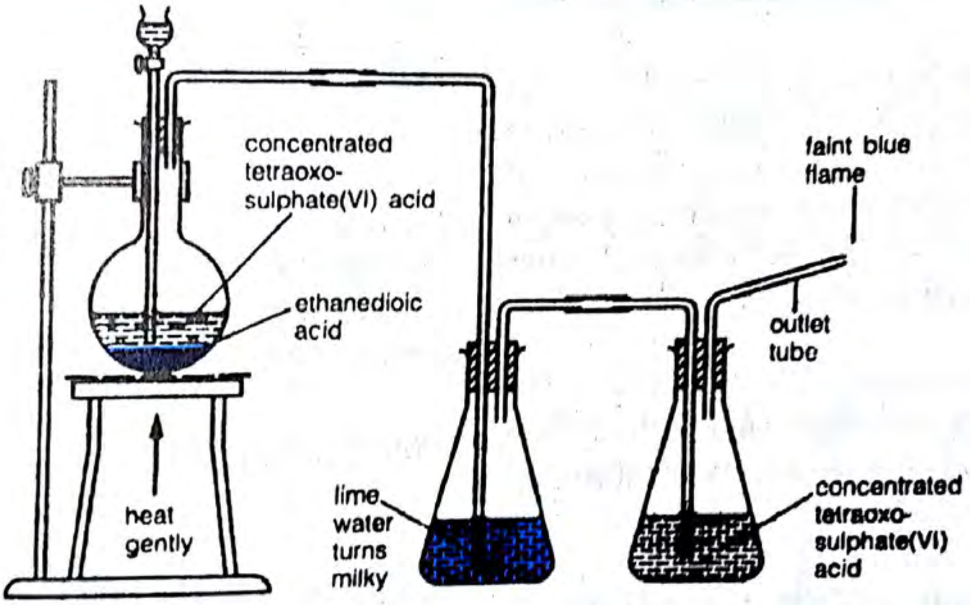
10 When acidic conditions are necessary in industrial processes tetraoxosulphate(VI) acid is usually used, since it is relatively cheaper compared to the other mineral acids.

11 It is used as a drying agent for many gases, except alkaline gases like ammonia and reducing gases like hydrogen sulphide. It is also used in desiccators as a drying agent.

Experiment 22.3 To study the dehydrating action of concentrated tetraoxosulphate(VI) acid on
(a) sugar, (b) ethanedioic acid (oxalic acid),
(c)blue copper (II) tetraoxosulphate(VI) crystals.

Method (a)Place some sugar in a beaker and slowly add concentrated tetraoxosulphate(VI) acid to it. Cover the beaker with a watch-glass.
(b)Place some ethanedioic (oxalic) acid in a round-bottomed flask and set up the apparatus as shown. Add a little concentrated tetraoxosulphate(VI) acid to the ethanedioic acid and warm gently. Apply a lighted splint at the tip of the outlet tube.
(c)Place some blue copper(II) tetraoxosulphate(VI)-pentahydrate crystals on a watch-glass. Add a few drops of concentrated tetraoxosulphate(VI) acid to the crystals.

Fig. 22.12 Dehydrating action of concentrated tetraoxo-sulphate(VI) acid on ethanedioic acid.



Result (a)The sugar is charred and a spongy black mass rises to fill the beaker. A lot of heat is given off together with steam which condenses as droplets of water on the underside of the watch-glass. The spongy black mass that remains in the beaker is known as sugar charcoal.
(b)Effervescence occurs on warming and the lime water turns milky indicating the evolution of carbon(IV) oxide. The gas issuing from the outlet tube burns with a faint blue flame indicating that carbon(II) oxide is also being liberated. (The water that is removed from the ethanedioic acid remains in the flask.)
(c)The blue copper(II) tetraoxosulphate(VI)-pentahydrate crystals turn into a white powdery solid (anhydrous form) showing that the water of crystallization has been removed.

Conclusion Concentrated tetraoxosulphate(VI) acid is a dehydrating agent which is able to remove the elements of water from compounds like sugar, ethanedioic acid and copper(II) tetraoxosulphate(VI)-pentahydrate.

TETRAOXOSULPHATES(VI)

The tetraoxosulphates(VI) are the normal salts formed when all the hydrogen ions in tetraoxosulphate(VI) acid are replaced by metallic or ammonium ions. Most tetraoxosulphates(VI) are crystalline and dissolve readily in water. The important exceptions are

- calcium tetraoxosulphate(VI), $CaSO_4$,
- lead(II) tetraoxosulphate(VI), $PbSO_4$,
- barium tetraoxosulphate(VI), $BaSO_4$, and
- mercury(I) tetraoxosulphate(VI), Hg_2SO_4,

which are all anhydrous salts and insoluble in water.

Laboratory Preparation

The tetraoxosulphates(VI) can be prepared by using the standard methods for the preparation of salts (see page 103). The method chosen for the preparation of a given tetraoxosulphate(VI) depends on the position of its metallic radical in the electrochemical series and the nature of the tetraoxosulphate(VI).

Action of tetraoxosulphate(VI) acid on a metal The tetraoxosulphates(VI) of magnesium and zinc are prepared by the action of dilute tetraoxosulphate(VI) acid on the corresponding metals.

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$
$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

The tetraoxosulphates(VI) of copper(II), silver and mercury(II) are prepared by the oxidizing action of hot concentrated tetraoxosulphate(VI) acid on the corresponding metals.

$$2H_2SO_4(aq) + Cu(s) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$
$$2H_2SO_4(aq) + Hg(l) \rightarrow HgSO_4(aq) + 2H_2O(l) + SO_2(g)$$

Action of tetraoxosulphate(VI) acid on the oxides, hydroxides or trioxocarbonates(IV) of the metal This method is used in the preparation of potassium, sodium and calcium tetraoxosulphates(VI). These tetraoxosulphates(VI) are never prepared by the action of dilute tetraoxosulphate(VI) acid on the metals because the reactions are vigorous and dangerous.

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

$$H_2SO_4(aq) + K_2CO_3(aq) \rightarrow K_2SO_4(aq) + H_2O(l) + CO_2(g)$$

By double decomposition Insoluble tetraoxosulphates(VI) such as the tetraoxosulphates(VI) of lead(II), barium and calcium are prepared by this method.

$$Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$$

$$BaCl2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)$$
$$CaCl_2(aq) + Na_2SO_4(aq) \rightarrow CaSO_4(s) + 2NaCl(aq)$$

Table 22.5 Methods of preparing tetraoxosulphate(VI).

Metal	Method of preparation
K Na Ca	By the action of dilute tetraoxosulphate(VI) acid on the oxides, hydroxides or the trioxocarbonates(IV) of the metals.
Mg Al Zn Fe	By the action of dilute tetraoxosulphate(VI) acid on the metals, their oxides or their trioxocarbonates(IV). Aluminium, however, requires the action of concentrated tetraoxosulphate(VI) acid.
Pb	By double decomposition.
Cu Hg Ag	By the action of hot concentrated tetraoxosulphate(VI) acid on the metals.

Recovery of soluble tetraoxosulphates(VI) from solution

A number of tetraoxosulphates(VI) are decomposed by dry heating. Thus, they are usually recovered from solution by crystallization.

Properties

Most tetraoxosulphates(VI) are colourless unless the metallic ions are coloured. Soluble tetraoxosulphates(VI) form hydrated crystals. There are also many double tetraoxosulphates(VI), such as iron(II) ammonium tetraoxosulphate(VI) and the alums.

The tetraoxosulphate(VI) of sodium, potassium and calcium are very stable to heat. The tetraoxosulphate(VI) of metals lower down in the electrochemical series tend to decompose on heating. When the hydrated tetraoxosulphates(VI) of zinc, copper(II) and iron(II) are heated, they lose their water of crystallization in stages. These changes are reversible. Further heating of the anhydrous salts brings about their decomposition into the metallic oxides, sulphur(IV) oxide and sulphur(VI) oxide.

Heating iron(II) tetraoxosulphate(VI)-heptahydrate

$$FeSO_4.7H_2O(s) \xrightarrow[-6H_2O]{heat} FeSO_4.H_2O(s)$$

$$\xrightarrow[-H_2O]{heat} FeSO_4(s)$$

$$2FeSO_4(s) \xrightarrow{heat} Fe_2O_3(s) + SO_2(g) + SO_3(g)$$

Heating copper(II) tetraoxosulphate(VI)-pentahydrate

$$CuSO_4.5H_2O(s) \xrightarrow[-2H_2O]{heat} CuSO_4\ 3H_2O(s)$$

$$\xrightarrow[-2H_2O]{heat} CuSO_4{\cdot}H_2O(s) \xrightarrow[-2H_2O]{heat} CuSO_4(s)$$

$$CuSO_4(s) \xrightarrow{heat} CuO(s) + SO_3(g)$$

Heating zinc tetraoxosulphate(VI)-heptahydrate

$$ZnSO_4.7H_2O(s) \xrightarrow[-H_2O]{heat} ZnSO_4.6H_2O(s)$$

$$\xrightarrow[-5H_2O]{heat} ZnSO_4.H_2O(s) \xrightarrow[-H_2O]{heat} ZnSO_4(s)$$

$$ZnSO_4(s) \xrightarrow{heat} ZnO(s) + SO_3(g)$$

Test for tetraoxosulphates(VI)

Take some of the unknown solution in a test-tube and acidify it with dilute hydrochloric acid. Then add a few drops of barium chloride solution. A white precipitate of barium tetraoxosulphate(VI) is formed if the unknown solution contains the tetraoxosulphate(VI) ions. This precipitate should be insoluble in an excess of the dilute acid.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

The acidification process is necessary to prevent the precipitation of other insoluble barium compounds like barium trioxocarbonate(IV) or barium trioxosulphate(IV), which are soluble in an acidic solution, unlike the tetraoxosulphate(VI) salt.

NOTE Dilute trioxonitrate(V) acid and barium trioxonitrate(V) can also be used instead of dilute hydrochloric acid and barium chloride.

HYDROGENTETRAOXOSULPHATES(VI)

The hydrogentetraoxosulphates(VI) are acid salts. They are formed when an excess of tetraoxosulphate(VI) acid is reacted with alkalis or soluble trioxocarbonates(IV).

$$KOH(aq) + H_2SO_4(aq) \rightarrow KHSO_4(aq) + H_2O(l)$$

$$Na_2CO_3(aq) + 2H_2SO_4(aq) \rightarrow 2NaHSO_4(aq) + H_2O(l) + CO_2(g)$$

Properties

Hydrogentetraoxosulphates(VI) are acidic because they still contain an ionizable hydrogen. They change the colour of blue litmus solution red. They react with excess alkalis to form normal salts.

$$KOH(aq) + KHSO_4(aq) \rightarrow K_2SO_4(aq) + H_2O(l)$$

SUMMARY

Sulphur

- Sulphur is found in Group 6 of the Periodic Table and has six valence electrons. It readily reacts wit Groups 1 and 2 metals to form the sulphide ion, S^{2-}, or shares electrons to form covalent compounds. I compounds, its oxidation states range from -2 to +6.
- Sulphur occurs freely in the earth's crust and in the combined states as sulphides and tetraoxosulphates(VI
- It exists in several allotropic forms—rhombic, monoclinic and amorphous. Of these, only rhombic sulphu is stable at room temperature.
- Crystalline sulphur is soluble in carbon(IV) sulphide. It is a poor conductor of heat and electricity; i combines directly with most non-metals and metals to form sulphides; it burns readily in excess oxyge to form sulphur(IV) oxide. On heating in a limited amount of air, sulphur melts and passes through severa stages before vaporizing at 444 °C.

Hydrogen sulphide

- Hydrogen sulphide is a colourless, acidic gas which smells like rotten eggs.
- It is prepared by the action of a dilute acid on a metallic sulphide. It is a strong reducing agent, whic is usually oxidized to sulphur in redox reactions.
- It is used in the analysis of metals as it forms insoluble, coloured sulphides with solutions of the salts o many metals. The colour of the sulphides formed, together with their varying solubilities in acids an alkalis, help in the identification of the metal ions.
- *Test for hydrogen sulphide* Besides its characteristic smell, it turns filter paper moistened with lead(II ethanoate or lead(II) trioxonitrate(V) black.

Sulphur(IV) oxide

- Sulphur(IV) oxide is prepared by (i) the burning of sulphur or metallic sulphides, (ii) heating potassium or sodium trioxosulphate(IV) with dilute tetraoxosulphate(VI) acid or hydrochloric acid, or (iii) heating concentrated tetraoxosulphate(VI) with copper turnings.
- It is an acidic gas with a smell of burning firecrackers; it dissolves in water to form trioxosulphate(IV) acid, H_2SO_3; it neutralizes bases; it combines directly with certain metallic oxides; it acts as a strong reducing agent in redox reactions with oxidizing agents; it bleaches dyes by its reducing action; it can also behave as an oxidizing agent in the presence of a stronger reducing agent like hydrogen sulphide.
- *Test for sulphur(IV) oxide* Besides its characteristic smell, it (i) bleaches straws, flowers and fabrics, and (ii) turns acidified potassium tetraoxomanganate(VII) from purple to colourless and acidified potassium heptaoxochromate(VI) from orange to green.

Sulphur(VI) oxide

- Sulphur(VI) oxide is prepared from sulphur(IV) oxide and oxygen in the presence of a heated catalyst like platinized asbestos or vanadium(V) oxide. It is an acidic gas and dissolves exothermically in water to form tetraoxosulphate(VI) acid, H_2SO_4.

Trioxosulphate(IV) acid

- Trioxosulphate(IV) acid is a weak dibasic acid, formed when sulphur(IV) oxide dissolves in water. On exposure to air, it slowly becomes tetraoxosulphate(VI) acid, H_2SO_4. The trioxosulphate(IV) ion, SO_3^{2-} in trioxosulphate(IV) acid is responsible for the reducing and bleaching action of sulphur(IV) oxide in aqueous solution.

ioxosulphates(IV)

- Trioxosulphates(IV) are prepared by (i) neutralizing alkalis with sulphur(IV) oxide, or (ii) precipitating them from a corresponding metallic salt solution by passing in sulphur(IV) oxide.
- Only the trioxosulphates(IV) of ammonia, potassium, sodium and calcium are soluble in water. Trioxosulphates(IV) liberate sulphur(IV) oxide when warmed with acids; and on exposure to air, they are converted to tetraoxosulphate(VI) ions, SO_4^{2-}, slowly.

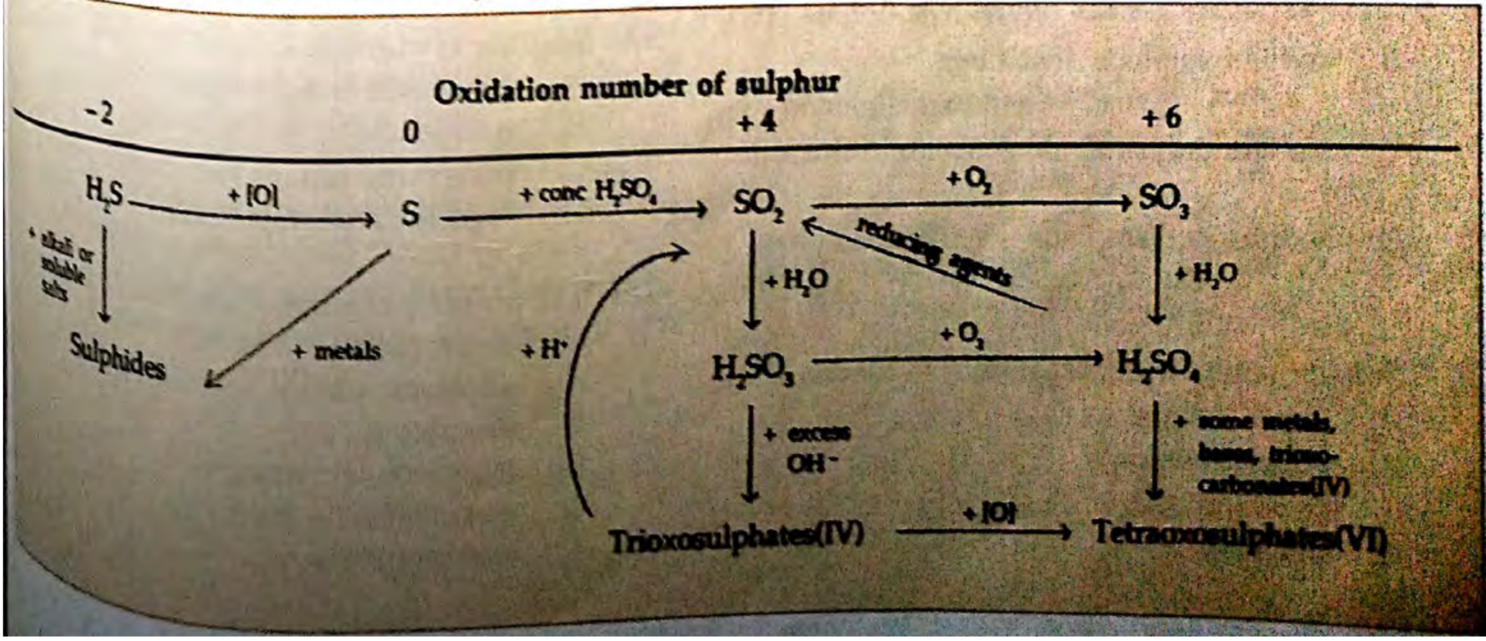
Tetraoxosulphate(VI) acid

- Industrially, tetraoxosulphate(VI) acid is manufactured by the Contact process. This process involves the catalytic combination of sulphur(IV) oxide and oxygen to form sulphur(VI) oxide which is then dissolved in concentrated tetraoxosulphate(VI) acid to form oleum. This is then diluted with water to produce 98% tetraoxosulphate(VI) acid.
- Dilute tetraoxosulphate(VI) acid is a strong, dibasic acid. It neutralizes alkalis; liberates hydrogen with metals and releases carbon(IV) oxide from trioxocarbonates(IV) and hydrogentrioxocarbonates(IV).
- Concentrated tetraoxosulphate(VI) acid is hygroscopic and behaves as a dehydrating agent.
- Hot concentrated tetraoxosulphate(VI) acid is a strong oxidizing agent. It oxidizes metals to the tetraoxosulphate(VI) and is itself reduced to sulphur(IV) oxide; with non-metals, it produces the corresponding oxides and sulphur(IV) oxide; and it also oxidizes reducing agents like hydrogen sulphide.
- Tetraoxosulphate(VI) acid is used to manufacture fertilizers, pigments, textiles, plastics, detergents and other chemicals. It is also used in many manufacturing processes.

Tetraoxosulphates(VI)

- Tetraoxosulphates(VI) are normal salts prepared by the action of dilute tetraoxosulphate(VI) acid on the metals or the oxides, hydroxides or trioxocarbonates(IV) of metals. Insoluble tetraoxosulphates(VI) are prepared by double decomposition of the appropriate salts or acids.
- Tetraoxosulphates(VI) form double salts or alums. The tetraoxosulphates(VI) of sodium, potassium and calcium are stable to heat but the tetraoxosulphates(VI) of metals lower down the electrochemical series tend to decompose to the metallic oxides, sulphur(IV) oxide and sulphur(VI) oxide on heating.
- *Test for tetraoxosulphates(VI)* With barium chloride, they form a white precipitate of barium tetraoxosulphate(VI), which is insoluble in excess hydrochloric acid.

actions of sulphur and its compounds



EXERCISES

1. Extraction of sulphur from the earth's crust is by one of these processes.
   A Solvay process.
   B Contact process.
   C Frasch process.
   D Kiln process.

2. Which of the allotropes of sulphur has amber colour with needle shapes?
   A Rhombic sulphur
   B Pastric sulphur
   C Monoclinic sulphur
   D Flower of sulphur

3. When sulphur is heated gradually and in limited supply of air, it develops a feature at 200°C. This feature is
   A turns into brown vapour.
   B develops a floral pattern.
   C becomes highly viscous.
   D turns into amber-coloured liquid.

4. Sulphur reacts with many metals when heated in the absence of air but sulphur reacts with one of these without heating.
   A Fe B Fe
   C Na D Au

5. Excess sulphur reacts with hot concentrated NaOH solution to form
   A sodium sulphide + sodium trioxosulphate (IV).
   B sodium sulphide + sodium tetraoxosulphate (VI).
   C sodium polysulphide + trioxothiosulphate (VI).
   D sodium polysulphide + tetraoxosulphate (VI).

6. Sulphur reacts with soft rubber to harden it by
   A direct linkage.
   B polymerization.
   C cross linkage.
   D smoking.

7. One of these ionize slightly in water to form dibasic acid.
   A Ag_2S B $K_2Cr_2O_7$
   C $FeCl_3$ D H_2S

8. All sulphides are black except
   A Pbs B ZnS
   C HgS D FeS

9. Yellow paints are prepared (with the presence o Fe^{3+}) by using
   A SbS_3 B MnS
   C ZnS D SnS_2

10. Name Y in the following reactions.
    $Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + 2H_2O(l) + Y$
    A Copper II hydroxide
    B Hydrogen sulphide
    C Sulphur (VI) oxide
    D Sulphur (IV) oxide

11. In balancing this ionic equation,
    $$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(l) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 4H^+(aq)$$
    A You add 2 electrons to the product.
    B You add 2 electrons to the reactant.
    C You remove 2 electrons from the product.
    D You remove 2 electrons from the reactant.

12. Sulphur (IV) oxide bleaches by
    A oxidation. B reduction.
    C decomposition. D carboxylation.

13. Sulphur (IV) oxide is used for these except
    A germicide and fumigant.
    B refrigerant.
    C preserving liquids like orange juice.
    D used for restoring ozone layer.

14. The property of sulphur used in its extraction by the Frasch process is its
    A allotropic nature.
    B unstable nature.
    C transition temperature.
    D non-metallic nature.
    E low melting point.

15. Both hydrogen sulphide and sulphur(IV) oxide decolorize acidified potassium tetraoxomanganate(VII), but in addition, hydrogen sulphide produces

A tetraoxosulphate(VI) acid.
B sulphur(IV) oxide.
C a precipitate of sulphur.
D hydrogen gas.
E a precipitate of manganese(IV) oxide.

(a) Explain how sulphur is extracted from underground deposits.

(b) Describe what happens when sulphur is heated (i) in the absence of air, (ii) in air and the product is dissolved in water. Give the equations of all reactions involved.

(a) What is the difference between the isotopes and the allotropes of a given element?

(b) Name three allotropes of sulphur and show how they are prepared in the laboratory. Two of the sulphur allotropes are related. Name them and show how they are related.

(c) Give four uses of sulphur.

(a) How would you prepare a few jars of dry hydrogen sulphide? Give the equation of the reaction and the diagram of the apparatus.

(b) Give two examples, using equations to show that hydrogen sulphide can act as
(i) a reducing agent, and (ii) an acid.

(c) Compare and contrast how hydrogen sulphide and sulphur(IV) oxide react with acidified potassium tetraoxomanganate(VII), giving the equations of the reactions involved.

(d) With equations, explain what happens when hydrogen sulphide is passed into a solution of sulphur(IV) oxide in water?

(a) With the help of an equation, explain what happens when
(i) a piece of filter paper is dipped into lead(II) trioxonitrate(V) solution and dropped into a jar of hydrogen sulphide,
(ii) hydrogen sulphide is passed into a solution of iron(III) chloride.

(b) Describe Kipp's apparatus. How is it used in the preparation of hydrogen sulphide?

20. (a) How would you prepare a few jars of dry sulphur(IV) oxide from a trioxosulphate(IV)?

(b) Using equations, explain how sulphur(IV) oxide reacts with each of the following:
(i) Potassium hydroxide solution
(ii) Iron(III) chloride solution
(iii) Concentrated trioxonitrate(V) acid
(iv) Heated lead(IV) oxide

(c) Give two uses of sulphur(IV) oxide, one of which depends on its reducing property.

21. (a) Describe the stages in the manufacture of tetraoxosulphate(VI) acid by the Contact process, giving the equations of the reactions involved. What is the catalyst used?

(b) Explain why sulphur(IV) oxide is purified before it is passed into the catalyst chamber in the above process.

(c) Tetraoxosulphate(VI) acid is said to be
(i) a typical acid, and
(ii) an oxidizing agent.
Justify these properties with examples, giving the conditions necessary for each of the reactions to take place.

22. (a) What happens when concentrated tetraoxosulphate(VI) acid is heated with potassium chloride? Give the equation of the reaction.

(b) Using equations, describe the action of concentrated tetraoxosulphate(VI) acid on
(i) sugar,
(ii) ethanedioic acid, and
(iii) blue crystals of copper(II) tetraoxosulphate(VI).

15.

23. How are hydrogentetraoxosulphates(VI) formed? Why are they known as acid salts?

23 NITROGEN AND ITS COMPOUNDS

NITROGEN

Nitrogen occurs chiefly as a free element in the air, making up about 78% by volume of the atmosphere. Free nitrogen in the air is important because it dilutes the oxygen to the point where combustion, respiration and oxidation of metals are reasonably slow. In the combined form, nitrogen occurs abundantly in the earth's crust as trioxonitrates(V) of sodium and calcium, as well as ammonium salts. Combined nitrogen is also found in organic matter such as proteins, urea and the vitamin B compounds.

Laboratory Preparation

Since nitrogen makes up a large percentage of air, it can be obtained from air by removing the other constituents. For example, carbon(IV) oxide and oxygen can be removed by passing air through caustic soda and heated copper turnings respectively. However, the nitrogen obtained this way contains about 1% by volume of rare gases as impurities, and is denser than pure nitrogen.

Nitrogen can also be produced by the following chemical methods.

From ammonium dioxonitrate(III) Pure nitrogen is usually obtained by the thermal decomposition of ammonium dioxonitrate(III), NH_4NO_2. The dioxonitrate(III), however, is not heated directly as the reaction may get out of control and an explosion may occur. This is because ammonium dioxonitrate(III) is unstable and decomposes exothermically.

A mixture of sodium dioxonitrate(III) and ammonium chloride in a ratio of 7:5 is heated to yield ammonium dioxonitrate(III), which in turn decomposes to produce nitrogen and steam. This procedure is safer than heating the dioxonitrate(III) directly because the ammonium dioxonitrate(III) is decomposed as fast as it is formed.

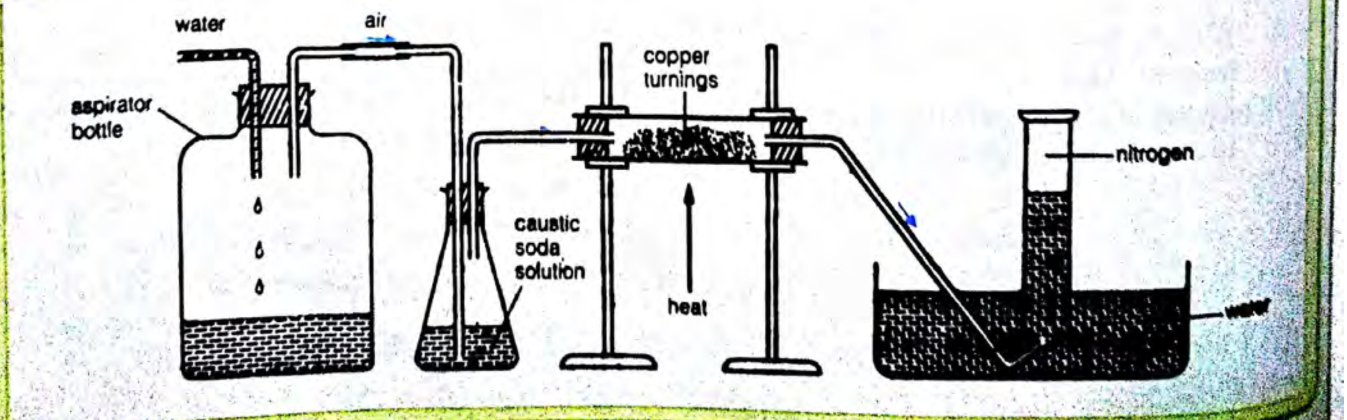
(a) $\underset{69\text{ g}}{NaNO_2(aq)} + \underset{53.5\text{ g}}{NH_4Cl(aq)} \rightarrow NH_4NO_2(aq) + NaCl(aq)$

(b) $NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l)$

From ammonium heptaoxodichromate(VI) When the heptaoxodichromate(VI), $(NH_4)_2Cr_2O_7$, is heated, it decomposes to yield nitrogen.

$$(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(l)$$

Fig. 23.1 Preparation of nitrogen from air.



From ammonia Nitrogen is liberated when ammonia is oxidized by hot copper(II) oxide.

$$2NH_3(g) + 3CuO(s) \rightarrow 3Cu(s) + 3H_2O(g) + N_2(g)$$

From dinitrogen(I) oxide When dinitrogen(I) oxide is passed over red-hot copper, the gas is reduced to nitrogen.

$$N_2O(g) + Cu(s) \rightarrow CuO(s) + N_2(g)$$

Industrial Preparation

Industrially, nitrogen is prepared by the fractional distillation of liquid air. Air, from which carbon(IV) oxide has been removed, is liquefied by subjecting it to successive compression and cooling processes. Upon distillation, nitrogen gas is evolved first at −196 °C (at s.p.) and is separated from oxygen which boils at −183 °C (at s.p.). Nitrogen is stored in steel cylinders and sold as liquid nitrogen or as the compressed gas.

Physical Properties

1 Nitrogen is a colourless, odourless and tasteless gas.
2 Pure nitrogen is slightly lighter than air.
3 It is only slightly soluble in water. Two volumes of the gas dissolve in 100 volumes of water at room temperature.
4 The melting point of nitrogen is −210 °C and its boiling point is −196 °C. These low temperatures are due to the weak van der Waals forces that exist between the nitrogen molecules in the solid and liquid states.

Table 23.1 Oxidation states of nitrogen in its compounds.

Name of compound	Formula	Oxidation sate
Ammonia	NH_3	−3
Hydrazine	N_2H_4	−2
Hydroxylamine	NH_2OH	−1
Nitrogen	N_2	0
Dinitrogen(I) oxide	N_2O	+1
Nitrogen(II) oxide	NO	+2
Dinitrogen(III) oxide	N_2O_3	+3
Dioxonitrate(III)	NO_2^-	+3
Nitrogen(IV) oxide	NO_2	+4
Dinitrogen(V) oxide	N_2O_5	+5
Trioxonitrate(V)	NO_3^-	+5

Chemical Properties

Nitrogen which is in Group 5 of the Periodic Table has five valence electrons. As a result, it achieves its stable octet structure by forming covalent bonds in its compounds. It also forms the nitride ion, N^{3-}, in combinations with the very reactive metals of Groups 1 and 2. Nitrogen shows oxidation states varying from −3 to +5 in its various compounds. Nitrogen gas exists in air as a diatomic molecule with triple covalent bonds between its atoms ($N \equiv N$). The high bond energy of the triple bond (946 kJ mol^{-1}) makes the bond very stable and accounts for the unreactive nature of nitrogen under ordinary conditions. However, at very high temperatures and pressures, nitrogen combines directly with hydrogen, oxygen and certain metals.

With metals Nitrogen combines directly with very electropositive metals, e.g. magnesium, calcium, aluminium and iron, to form nitrides. For example, red-hot magnesium combines directly with nitrogen to produce magnesium nitride. The nitride is readily hydrolyzed when warmed with water to give ammonia gas.

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

$$Mg_3N_2(s) + 6H_2O(l) \xrightarrow{\text{warm}} 3Mg(OH)_2(s) + 2NH_3(g)$$

With non-metals Nitrogen combines reversibly with hydrogen to produce ammonia. It combines directly with oxygen at very high temperatures (about 2 000 °C) or in the presence of a high voltage electric spark to form small amounts of nitrogen(II) oxide. In nature, this reaction occurs in the atmosphere when lightning flashes.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Uses

1 Nitrogen is used in the industrial manufacture of ammonia, cyanide, cyanamide and carbamide (an important fertilizer).
2 Liquid nitrogen is used as a cooling agent.
3 Due to its inert nature, nitrogen is used
  - as a carrier gas in gas chromatography;
  - in providing an inert atmosphere for certain industrial processes involving easily

oxidizable chemicals, e.g. in making electronic components such as transistors, and in the annealing of metals;

- as a preservative to prevent rancidity (due to the oxidation of fats) in packaged foods.

AMMONIA

Ammonia is a hydride of nitrogen. It is a very important chemical in industry. In nature ammonia is produced when nitrogenous matter decays in the absence of air. The decomposition may be brought about by heat or putrefying bacteria. As a result, small traces of ammonia may be present in the air. However, because of its great solubility in water, it rapidly dissolves in rain water and finds its way into the soil where it may be converted into other compounds.

Laboratory Preparation

In the laboratory, ammonia is prepared by heating any ammonium salt with a non-volatile base. Usually, ammonium chloride and calcium hydroxide (slaked lime) are used. Calcium hydroxide is chosen because it is cheap and not deliquescent like the caustic alkalis. Since both the reactants are solids, they should be thoroughly ground to provide the maximum surface area for reaction.

$$\begin{aligned} &Ca(OH)_2(s) + 2NH_4Cl(s) \\ &\qquad \rightarrow CaCl_2(s) + 2H_2O(l) + 2NH_3(g) \\ &74\ g \qquad (2 \times 53.3)\ g \end{aligned}$$

The usual drying agents like concentrated tetraoxosulphate(VI) acid and fused calcium chloride

Experiment 23.1 To prepare ammonia from ammonium chloride.

Method Grind a mixture of ammonium chloride and excess slaked lime. Place it in a round-bottomed flask and set up the apparatus as shown. Heat the mixture and collect the gas formed by upward delivery.

PRECAUTION Mount the flask with its neck sloping downwards so that the water formed during the reaction is prevented from trickling back into the hot part of the flask and cracking it.

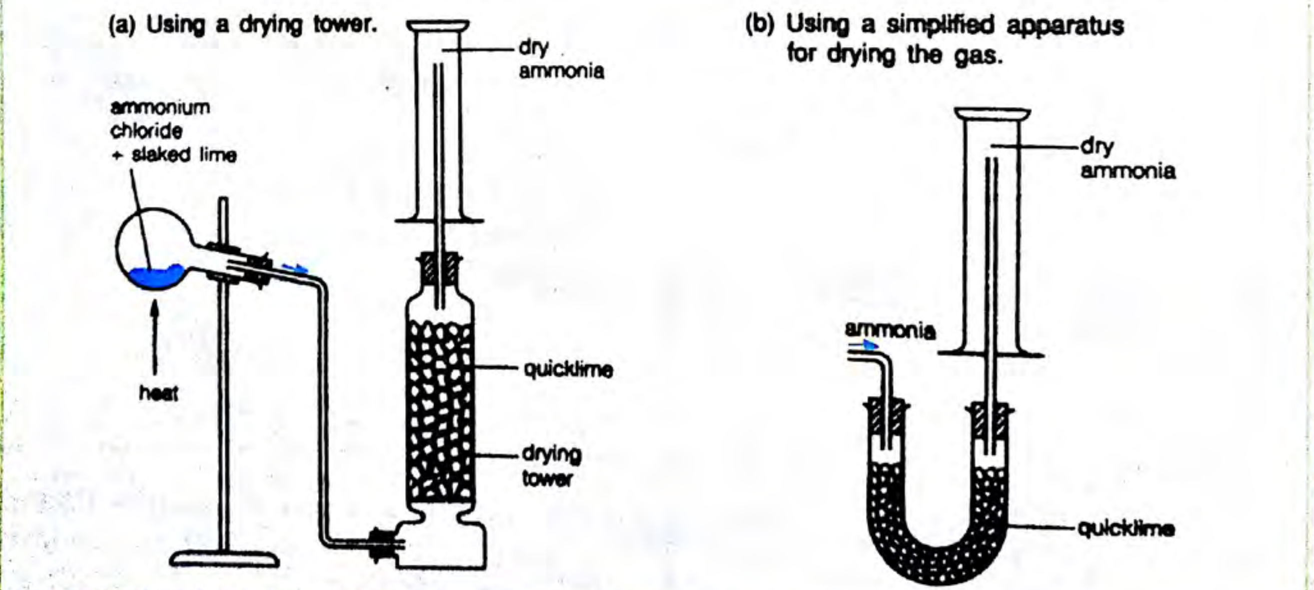


Fig. 23.2 Preparation of ammonia.

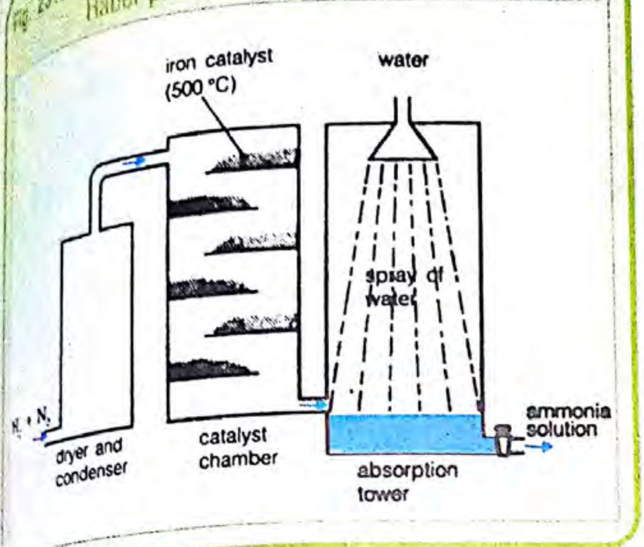
(a) Using a drying tower.

(b) Using a simplified apparatus for drying the gas.

Result Ammonia is evolved on heating and is dried by passing it through quicklime either in a drying tower or a U-tube.

Conclusion Ammonia is produced by heating slaked lime with ammonium chloride.

Fig. 23.3 Industrial preparation of ammonia by the Haber process.



are not suitable for drying ammonia because they react with the gas as follows:

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(s)$$
$$4NH_3(g) + CaCl_2(s) \rightarrow CaCl_2.4NH_3(s)$$

Industrial Preparation

Ammonia is manufactured from nitrogen and hydrogen by the *Haber process*. Since the direct combination between nitrogen and hydrogen is reversible, special conditions of reaction are necessary for the optimum yield of ammonia. Basically, the process involves mixing nitrogen and hydrogen in the volume ratio of 1:3 and passing the mixture

- over finely divided iron (catalyst),
- at a temperature of about 450 °C, and
- a pressure of about 200 atmospheres.

The yield of ammonia is about 15% under these conditions.

The ammonia is then liquefied by cooling, and the unused gases are recirculated over the catalyst for further production of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$$

Structure of the Ammonium Molecule

In the ammonium molecule, there are three single covalent bonds between the nitrogen and hydrogen atoms (N–H) and a pair of lone electrons (see page 58). The shape of the ammonia molecule is that of a pyramid. The lone pair of electrons and the different electronegativities of nitrogen and hydrogen make the ammonia molecule polar. As a result, hydrogen bonds occur readily between ammonia molecules and between ammonia and water molecules.

Physical Properties

1 Ammonia is a colourless gas with a characteristic choking smell.

2 In large quantities, ammonia is poisonous because of its effect on the respiratory muscles.

3 It is an alkaline gas, changing moist red litmus paper blue.

4 It is about 1.7 times less dense than air.

5 Ammonia changes into a liquid at –34.4 °C. It is easily liquefied into a colourless liquid at ordinary temperatures by compression, and is transported in this form.

6 Ammonia has a boiling point of –77.7 °C which is relatively high when compared with other similar compounds because of the presence of hydrogen bonding between its molecules.

7 Ammonia is a very soluble gas, with 1 200 volumes of it dissolving in 1 volume of water at s.t.p. The solubility of ammonia is due to the readiness with which it forms hydrogen bonds with water to give aqueous ammonia, $NH_3.H_2O$. Aqueous ammonia ionizes slightly to produce ammonium, NH_4^+, and hydroxide, OH^-, ions. The hydroxide ions give aqueous ammonia its weakly alkaline properties. On warming, aqueous ammonia decomposes readily to liberate ammonia gas.

(a) $NH_3(g) + H_2O(l) \rightleftharpoons NH_3.H_2O(aq)$

(b) $NH_3.H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

8 A concentrated solution of ammonia known as 880 ammonia has a density of 0.880 g cm^{-3}. It contains 35% by mass of the gas.

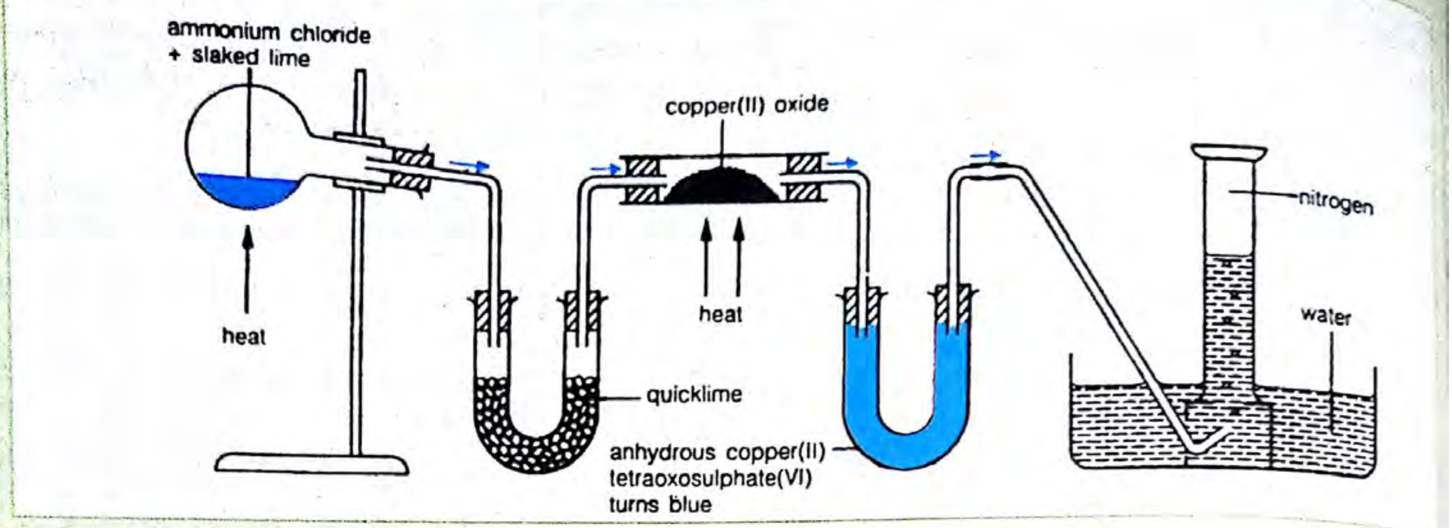
Chemical Properties

Reaction with oxygen

Ammonia does not burn in air, but it burns readily in oxygen with a greenish-yellow flame to form water vapour and nitrogen.

$$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g)$$

Fig. 23.4 Reduction of copper(II) oxide by ammonia.



In the presence of a heated platinum catalyst, ammonia reacts with excess air to produce nitrogen(II) oxide, NO, (instead of nitrogen) and water.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

Ammonia as a reducing agent

With copper(II) oxide Ammonia is not a strong reducing agent. However, it reduces heated copper(II) oxide to copper while it is itself oxidized to water and nitrogen.

$$3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + 3H_2O(l) + N_2(g)$$

To carry out the reduction, the ammonia produced by heating ammonium chloride and slaked lime, is dried and passed over heated copper(II) oxide as shown in fig. 23.4. The anhydrous copper(II) tetraoxosulphate(VI) in the second U-tube turns blue, showing that water is formed during the reaction. Nitrogen collects in the gas jar over water. A reddish-brown residue is left in the combustion tube showing that the black copper(II) oxide has been reduced to copper.

With chlorine In excess, ammonia first reduces chlorine to produce hydrogen chloride and nitrogen. Then the hydrogen chloride reacts with the excess ammonia to produce dense white filmes of ammonium chloride.

(a) $2NH_3(g) + 3Cl_2(g) \rightarrow 6HCl(g) + N_2(g)$

(b) $6NH_3(g) + 6HCl(g) \rightarrow 6NH_4Cl(s)$

The overall reaction is as follows:

(c) $3Cl_2(g) + 8NH_3(g) \rightarrow 6NH_4Cl(s) + N_2(g)$

If chlorine is in excess, nitrogen III chloride, NCl_3, an explosive and oily liquid, is formed.

$$NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(l) + 3HCl(g)$$

Reaction with carbon(IV) oxide

Ammonia reacts with carbon(IV) oxide at 150 °C anc a high pressure of 150 atm to produce urea, ar important organic compound.

$$2NH_3(g) + CO_2(g) \rightarrow \underset{\text{urea}}{(NH_2)_2CO(s)} + H_2O(l)$$

Thermal decomposition

Ammonia is decomposed at temperatures above 500°C or by prolonged sparking to yield nitrogen anc hydrogen.

As a base

Ammonia is a weak base because it can accept protons to form ammonium ions. It reacts with acids to form ammonium salts.

$$NH_3(g) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$
$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(s)$$

If hydrogen chloride gas is used, dense white fumes composed of suspended particles of ammonium chloride are formed.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

As a precipitating agent

Aqueous ammonia precipitates the insoluble hydroxides of metals from solutions of their salts. It is useful in precipitating amphoteric hydroxides which dissolve in an excess of a strong alkali.

$$Pb(NO_3)_2(aq) + 2NH_3(aq) + 2H_2O(l) \\ \rightarrow Pb(OH)_2(s) + 2NH_4NO_3(aq)$$

Ionically,

$$\underset{\text{white}}{Pb^{2+}(aq) + 2CH^-(aq) \rightarrow Pb(OH)_2(s)}$$

Other hydroxides that are commonly precipitated by aqueous ammonia are as follows.

$$Zn^{2+}(aq) + 2OH^-(aq) \rightarrow \underset{\text{white gelatinous}}{Zn(OH)_2(s)}$$

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow \underset{\text{reddish-brown}}{Fe(OH)_3(s)}$$

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow \underset{\text{blue}}{Cu(OH)_2(s)}$$

Some metal hydroxides like copper(II) and zinc hydroxides will dissolve in excess ammonia solution to form complex ions. The presence of the lone pair of electrons in the ammonia molecule allows it to form complex ions.

$$Cu(OH)_2(s) + 4NH_3(aq) \\ \rightarrow \underset{\text{dark blue}}{Cu(NH_3)_4{}^{2+}(aq)} + 2OH^-(aq)$$

$$Zn(OH)_2(s) + 4NH_3(aq) \rightarrow \underset{\text{colourless}}{Zn(NH_3)_4{}^{2+}(aq)} + 2OH^-(aq)$$

In qualitative analysis, the complex ion formation is used as confirmatory tests for copper and zinc ions because the precipitates of the other metallic hydroxides do not dissolve in excess ammonia.

Tests for ammonia

Ammonia has a characteristic choking smell which is easily recognizable. Its presence can be confirmed by doing the following tests.

Action on litmus paper Hold a damp red litmus paper into the jar containing the unknown gas. If the litmus paper turns blue, then the gas is probably ammonia as it is the only common alkaline gas.

Action with hydrochloric acid Dip a glass rod in concentrated hydrochloric acid, and then insert it in the gas jar containing the unknown gas. White fumes are formed if the gas is ammonia.

Uses

1 Aqueous ammonia is used in softening temporarily hard water.
2 Aqueous ammonia is also used in laundries as a solvent for removing grease and oil stains.
3 Liquid ammonia is used as a refrigerant, although it is now being replaced by less toxic and unreactive fluorocarbons.
4 Ammonia is used in the manufacture of
   - trioxonitrate(V) acid,
   - sodium trioxocarbonate(IV) by the Solvay process.
5 The most important use of ammonia is in the manufacture of nitrogenous fertilizers like
   - ammonium tetraoxosulphate(VI),
   - ammonium trioxonitrate(V),
   - carbamide, and
   - ammonium tetraoxophosphate(V).

AMMONIUM SALTS

Ammonium salts are electrovalent compounds which contain the ammonium ion, NH_4^+, as the cation. They resemble the corresponding alkali metal salts in solubility and structure.

Ammonium salts are prepared by dissolving ammonia in the appropriate acid or neutralizing aqueous ammonia with the appropriate acid. The ammonium salts are then separated out of solution by crystallization, and not by evaporation because they are easily decomposed by dry heating.

$$NH_3(g) + HCl(aq) \rightarrow NH_4Cl(aq)$$

$$NH_4^+(aq) + OH^-(aq) + HCl(aq) \\ \rightarrow NH_4Cl(aq) + H_2O(l)$$

$$NH_3(g) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$$

$$NH_4^+(aq) + OH^-(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$

Properties

Appearance and solubility

All common ammonium salts are white crystalline solids which readily dissolve in water. They are completely ionized in solution, and are strong electrolytes.

Action of heat

All ammonium salts decompose when heated. Certain ammonium salts, however, sublime when heated.

- Ammonium chloride sublimes on heating and dissociates to form ammonia and hydrogen chloride which recombine on cooling.

$$NH_4Cl(s) \underset{\text{cold}}{\overset{\text{heat}}{\rightleftharpoons}} NH_3(g) + HCl(g)$$

- Ammonium tetraoxosulphate(VI) decomposes on heating to liberate ammonia and tetraoxosulphate(VI) acid. Being more volatile, the ammonia escapes, leaving the acid behind.

$$(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2SO_4(l)$$

- Ammonium dioxonitrate(III) decomposes on heating to produce nitrogen and water.

$$NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g)$$

- Ammonium trioxonitrate(V) decomposes on heating to nitrogen(I) oxide and water. This reaction is exothermic (see page 374).

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$$

- Ammonium trioxocarbonate(IV) is an unstable compound. It decomposes very readily to yield ammonia, carbon(IV) oxide and water.

$$(NH_4)_2CO_3(s) \rightarrow 2NH_3(g) + CO_2(g) + H_2O(g)$$

Reaction with bases

All ammonium salts liberate ammonia when heated with bases or alkalis. This reaction is used in the laboratory preparation of ammonia. It also helps to distinguish ammonium salts from normal metal salts.

$$NH_4^+(s) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$$

Test for ammonium salts

Heat some of the unknown substance with sodium hydroxide solution. Note the smell of any gas that is given off and test it with a moist red litmus paper. If the unknown substance is an ammonium salt, ammonia gas will be evolved. This gas can be recognized by its smell and its action on red litmus paper, which it turns blue.

$$NH_4^+(s) + NaOH(aq) \rightarrow Na^+(aq) + H_2O(l) + NH_3(g)$$

Some Important Ammonium Salts

Ammonium chloride

Ammonium chloride, NH_4Cl, is a white crystalline salt that does not contain any water of crystallization. It sublimes on heating. If heating is continued, it will dissociate into ammonia and hydrogen chloride gases. These two gaseous products readily recombine to form solid ammonium chloride again when cooled.

$$NH_4Cl(s) \underset{\text{cold}}{\overset{\text{heat}}{\rightleftharpoons}} NH_3(g) + HCl(g)$$

Ammonium chloride is used in Leclanche and dry cells. It is also used as a flux to increase the fusibility of solders and as an analytical reagent in the laboratory.

Ammonium tetraoxosulphate(VI)

Ammonium tetraoxosulphate(VI), $(NH_4)_2SO_4$, is prepared in the laboratory by the neutralization of dilute tetraoxosulphate(VI) acid with aqueous ammonia. In industry, it is usually manufactured by passing ammonia and carbon(IV) oxide into a fine suspension of calcium tetraoxosulphate(VI) or gypsum in water. Calcium trioxocarbonate(IV) is precipitated and filtered off, leaving the soluble ammonium tetraoxosulphate(VI) in solution. The tetraoxosulphate(VI) is then separated from the solution by crystallization.

$$CaSO_4(s) + 2NH_3(g) + CO_2(g) + H_2O(l) \rightarrow (NH_4)_2SO_4(aq) + CaCO_3(s)$$

Ammonium tetraoxosulphate(VI) is used as a fertilizer and, in a more concentrated form, as a weed killer.

Ammonium trioxonitrate(V)

Ammonium trioxonitrate(V), NH_4NO_3 is prepared in the laboratory by the neutralization of aqueous ammonia with trioxonitrate(V) acid. On crystallization, colourless crystals of the salt separate out.

$$NH_4^+(aq) + OH^-(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$

It dissolves readily in water, absorbing large amounts of heat as it does so. A liquid of very low temperature can be obtained by dissolving a large quantity of the trioxonitrate(V) in water, and this can be used as a freezing mixture.

It is used as a fertilizer, e.g. nitrochalk, and in making explosives, e.g. amatol or ammonal.

Ammonium trioxocarbonate(IV)

Ammonium trioxocarbonate(IV), $(NH_4)_2CO_3$, is collected as a sublimate when a mixture of ammonium tetraoxosulphate(VI) and calcium trioxocarbonate(IV) is heated. The sublimate contains ammonium hydrogentrioxacarbonate(IV) in addition to ammonium trioxocarbonate(IV). The trioxocarbonate(IV) is obtained by adding ammonia to a solution of pure sublimate.

$$(NH_4)_2SO_4(s) + CaCO_3(s) \rightarrow (NH_4)_2CO_3(s) + CaSO_4(s)$$

It is used as an analytical reagent in the laboratory. It decomposes slightly even at room temperature to liberate ammonia, and so is commonly used in smelling salts to prevent dizziness and fainting.

OXIDES OF NITROGEN

Nitrogen forms several oxides with oxygen. The formation of these oxides by the direct combination of nitrogen and oxygen requires very high temperatures. In the laboratory, the oxides are prepared by the decomposition of nitrogen compounds. Because of the large amount of energy required for their formation, these oxides of nitrogen are readily interconvertible, and are easily decomposed to their elements.

NITROGEN(I) OXIDE

Nitrogen(I) oxide, N_2O, the first oxide of nitrogen identified, was discovered by Priestley. It is known as laughing gas because it causes uncontrollable fits of laughter when inhaled.

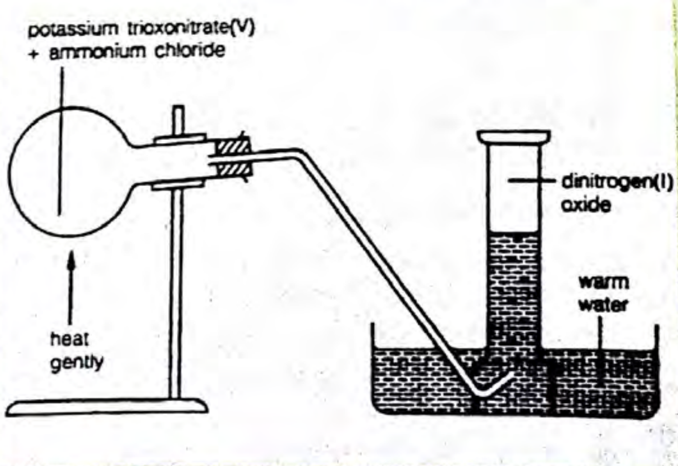
Laboratory Preparation

Nitrogen(I) oxide is liberated by the thermal decomposition of ammonium trioxonitrate(V). The direct heating of ammonium trioxonitrate(V) is dangerous as the reaction, which is exothermic, may become uncontrollable and explosive. Therefore, the gas is prepared by heating any mixture of salts which will yield ammonium trioxonitrate(V). Usually, a finely ground mixture of potassium trioxonitrate(V) and ammonium chloride is used. It is heated gently. The nitrogen(I) oxide evolved is collected over warm water as the gas is fairly soluble in cold water.

(a) $KNO_3(s) + NH_4Cl(s) \rightarrow KCl(s) + NH_4NO_3(s)$

(b) $NH_4NO_3(s) \rightarrow 2H_2O(g) + N_2O(g)$

Fig. 23.5 Preparation of dinitrogen(I) oxide.



Physical Properties

1 Nitrogen(I) oxide is a colourless gas with a faint, pleasant but sickly smell, and a sweetish taste.

2 It is fairly soluble in cold water.

3 It is 1.5 times denser than air.

4 It is neutral to moist litmus paper.

Chemical Properties

Action of heat

Nitrogen(I) oxide does not burn in air. However, it decomposes rapidly at red-heat (about 600 °C) into its component elements, nitrogen and oxygen. Nitrogen(I) oxide rekindles a brightly glowing splinter but extinguishes a feebly glowing one which is not hot enough to decompose the gas to liberate oxygen.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

Similarly, nitrogen(I) oxide supports the combustion of any burning substance which is hot enough to decompose it to yield nitrogen.

$$S(s) + 2N_2O(g) \rightarrow SO_2(g) + 2N_2(g)$$

$$Mg(s) + N_2O(g) \rightarrow MgO(s) + N_2(g)$$

Reduction by heated metals

Nitrogen(I) oxide is reduced to nitrogen when it passes over heated copper or iron.

$$Cu(s) + N_2O(g) \rightarrow N_2(g) + CuO(s)$$

Test for nitrogen(I) oxide

Insert a brightly glowing splinter into a test-tube containing the unknown gas. If the splinter is rekindled, the gas is either nitrogen(I) oxide or oxygen. The nitrogen(I) oxide can be distinguished from oxygen by several differences in their behaviour (see page 364).

Uses

Nitrogen(I) oxide is used as a mild anaesthetic for minor surgical operations, e.g. in dental surgery. It is usually administered with about 20% oxygen, which is required to keep the patient alive, and some traces of carbon(IV) oxide, which is required to maintain breathing.

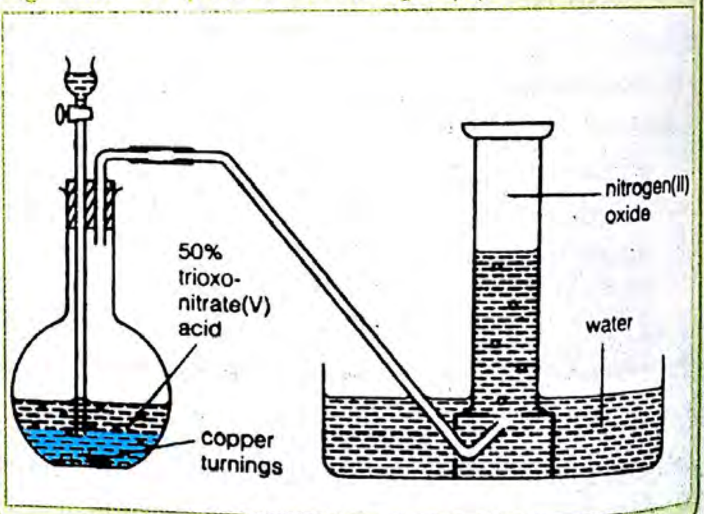
NITROGEN(II) OXIDE

Nitrogen(II) oxide, NO, was discovered by Cavendish in 1770 as one of the products formed on passing an electric spark through air. It is difficult to obtain the gas in the pure state because of its great affinity for oxygen. It reacts readily with oxygen even at ordinary conditions to form nitrogen(IV) oxide, NO_2.

Laboratory preparation

Nitrogen(II) oxide can be prepared by the action of trioxonitrate(V) acid on most metals. Usually, a 50% acid solution and copper turnings are used.

Fig. 23.6 Preparation of nitrogen(II) oxide.



$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

Brown fumes of nitrogen(IV) oxide are always produced during the process, when some of the nitrogen(II) oxide formed reacts with the oxygen in the flask. However, nitrogen(IV) oxide is very soluble in water and so is removed when the gases are bubbled through water.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Physical Properties

1. Nitrogen(II) oxide is a colourless, poisonous gas. Its smell is unknown because it changes immediately to nitrogen(IV) oxide on exposure to air.
2. It is almost insoluble in water.
3. It is slightly denser than air.
4. It is neutral to litmus.

Chemical Properties

Reaction with oxygen

Nitrogen(II) oxide combines readily with oxygen at room temperature to yield brown fumes of nitrogen(IV) oxide.

Action of heat

Nitrogen(II) oxide decomposes into equal volumes of nitrogen and oxygen only at high temperatures of about 1 000 °C. It will only support the combustion of strongly burning substances. For example, burning phosphorus, lead or magnesium will continue to burn in the gas, forming nitrogen and their oxides, but a burning splinter and burning sulphur will be extinguished by the gas.

$$2NO(g) \rightarrow N_2(g) + O_2(g)$$

$$2Mg(s) + 2NO(g) \rightarrow 2MgO(s) + N_2(g)$$

Reduction by hot metals

Nitrogen(II) oxide reacts with heated metals, which reduce it to nitrogen.

$$2Cu(s) + 2NO(g) \rightarrow 2CuO(s) + N_2(g)$$

As a reducing agent

It is a weak reducing agent. Thus, it decolorizes acidified potassium tetraoxomanganate(VII) very slowly.

$$3MnO_4^-(aq) + 4H^+(aq) + 5NO(g)$$
$$\rightarrow 3Mn^{2+}(aq) + 5NO_3^-(aq) + 2H_2O(l)$$

Reaction with iron(II) tetraoxosulphate(VI)

Nitrogen(II) oxide dissolves readily in iron(II) tetraoxosulphate(VI) solution, forming a dark brown solution of an addition compound which decomposes again when heated. This reaction is used for detecting the presence of nitrogen(II) oxide and for purifying it or removing it from a mixture of gases. It is also the basis of the brown ring test for trioxonitrates(V).

$$FeSO_4(aq) + NO(g) \rightleftharpoons FeSO_4.NO(aq)$$

Tests for nitrogen(II) oxide

On exposure to air Remove the stopper of the test-tube containing the unknown gas and note what happens. If the gas turns reddish-brown on exposure to air, then it is probably nitrogen(II) oxide.

With iron(II) tetraoxosulphate(VI) Pour a solution of iron(II) tetraoxosulphate(VI), which has been acidified with a little dilute tetraoxosulphate(VI) acid, into a test-tube containing the unknown gas. If the solution turns dark brown, then the gas is nitrogen(II) oxide.

NITROGEN(IV) OXIDE

Nitrogen(IV) oxide, NO_2, is the reddish-brown gas given off when the trioxonitrates(V) of heavy metals are heated. The yellowish colour of bench concentrated trioxonitrate(V) acid which appears after some time is due to the production and subsequent dissolution of nitrogen(IV) oxide in the acid.

Laboratory Preparation

The trioxonitrates(V) of heavy metals decompose on heating to yield nitrogen(IV) oxide as one of the products. The most suitable trioxonitrate(V) for the preparation of nitrogen(IV) oxide is lead(II) trioxonitrate(V). This is because its crystals do not contain any water of crystallization which would interfere with the preparation.

On heating strongly, lead(II) trioxonitrate(V) crystals crackle, melt and decompose to yield lead(II) oxide, oxygen and nitrogen(IV) oxide. The gases formed are passed through a U-tube immersed in a freezing mixture. The nitrogen(IV) oxide becomes

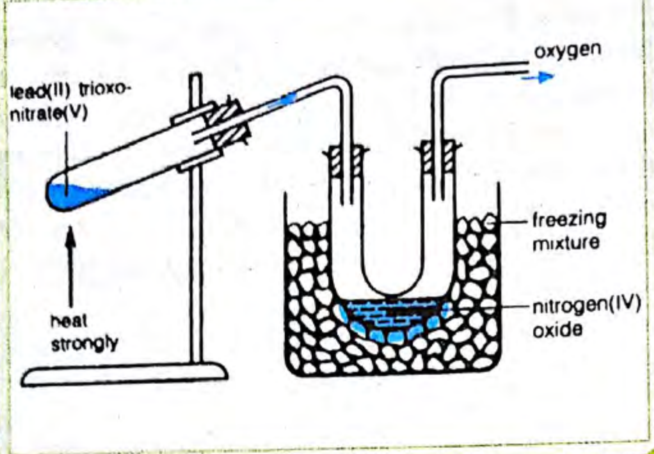


Fig. 23.7 Preparation of nitrogen(IV) oxide.

liquefied in the U-tube as a green liquid (yellow if pure), while the oxygen escapes from the U-tube as a gas. The residue of lead(II) oxide left behind in the boiling tube is reddish-brown when hot, but turns yellow on cooling.

$$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + O_2(g) + 4NO_2(g)$$

Physical Properties

1 Nitrogen(IV) oxide is a reddish-brown gas.
2 It has an irritating smell and is poisonous.
3 It turns damp blue litmus paper red and dissolves in water to form an acidic solution.
4 It is easily liquefied into a yellow liquid at 21 °C.
5 It is much heavier than air and can be 'poured' downwards.

Chemical Properties

Action of heat

Nitrogen(IV) oxide can exist in two molecular forms. At low temperature, it exists mainly as dinitrogen(IV) oxide, N_2O_4. On warming, this molecule dissociates to form two molecules of the reddish-brown nitrogen(IV) oxide, NO_2. As the temperature rises, the colour intensifies due to the increased rate of dissociation of the dinitrogen(IV) oxide. This

Table 23.2 Comparison of the oxides of nitrogen.

Oxide / Property	Dinitrogen(I) oxide	Nitrogen(II) oxide	Nitrogen(IV) oxide/ dinitrogen(IV) oxide
Formula	N_2O	NO	$2NO_2 \rightleftharpoons N_2O_4$
Physical state	Gaseous	Gaseous	Gaseous
Colour	Colourless	Colourless	Reddish-brown to yellow
Smell	Pleasant but sickly	Unknown	Pungent, irritating
Solubility in water	Fairly soluble	Sparingly soluble	Very soluble
Density	1.5 times denser than air	Slightly denser than air	2-5 times denser than air
Damp litmus paper	Neutral to litmus	Neutral to litmus	Turns blue litmus red
Lighted splinter	Rekindles a brightly glowing splinter	Extinguishes even a burning splinter	Extinguishes a glowing splinter but allows a vigorously burning splinter to continue burning
As a supporter of combustion	Readily supports the combustion of burning carbon, sulphur, phosphorus, magnesium, etc.	Supports the combustion of only brightly burning substances like phosphorus and magnesium	Ability to support combustion is intermediate between the other two oxides
Combustion with heated copper	Reduced to nitrogen	Reduced to nitrogen	Reduced to nitrogen or nitrogen(II) oxide

dissociation is complete at 140 °C. Below 140 °C, both nitrogen(IV) oxide and dinitrogen(IV) oxide exist as an equilibrium mixture.

Above 140 °C, nitrogen(IV) oxide dissociates into nitrogen(II) oxide, NO, and oxygen, O_2, which are colourless gases. This dissociation is complete at about 620 °C. The reverse changes take place on cooling

$$\underset{\text{pale yellow}}{N_2O_4(g)} \rightleftharpoons \underset{\text{reddish-brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{colourless}}{2NO(g) + O_2(g)}$$

Supporter of combustion

Like the other two oxides of nitrogen, nitrogen(IV) oxide does not burn in air, but it will support the combustion of any burning substance which is hot enough to decompose it into oxygen and nitrogen.

$$2NO_2(g) \rightarrow N_2(g) + 2O_2(g)$$

As a supporter of combustion, it is intermediate between nitrogen(IV) oxide and nitrogen(II) oxide. It does not rekindle a glowing splinter but will allow a vigorously burning splinter or burning sulphur, carbon, phosphorus or magnesium to continue burning in it.

$$2C(s) + 2NO_2(g) \rightarrow 2CO_2(g) + N_2(g)$$

$$4Mg(s) + 2NO_2(g) \rightarrow 4MgO(s) + N_2(g)$$

Reduction by reducing agents

Like the other two oxides, nitrogen(IV) oxide is reduced to nitrogen by heated copper or iron.

$$4Cu(s) + 2NO_2(g) \rightarrow 4CuO(s) + N_2(g)$$

It is also reduced to nitrogen(II) oxide by hydrogen sulphide and carbon(II) oxide.

$$H_2S(g) + NO_2(g) \rightarrow H_2O(l) + NO(g) + S(s)$$

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$$

Reaction with water

Nitrogen(IV) oxide dissolves in water to form a mixture of dioxonitrate(III) and trioxonitrate(V) acids, i.e. the gas is a mixed acid anhydride. The dioxonitrate(III) acid decomposes at room temperature to form nitrogen(II) oxide and more trioxonitrate(V) acid.

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

$$3HNO_2(aq) \rightarrow HNO_3(aq) + 2NO(g) + H_2O(l)$$

In excess oxygen, only trioxonitrate(V) acid is obtained, as the dioxonitrate(III) acid is oxidized to trioxonitrate(V) acid.

$$2HNO_2(aq) + O_2(g) \rightarrow 2HNO_3(aq)$$

Reaction with alkalis

Since the gas is a mixed acid anhydride, it reacts with alkalis to yield a corresponding mixture of dioxonitrate(III) and trioxonitrate(V) salts.

$$2KOH(aq) + 2NO_2(g) \rightarrow KNO_3(aq) + KNO_2(aq) + H_2O(l)$$

$$2NaOH(aq) + 2NO_2(g) \rightarrow NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$$

Ionically,

$$2OH^-(aq) + 2NO_2(g) \rightarrow NO_3^-(aq) + NO_2^-(aq) + H_2O(l)$$

TRIOXONITRATE(V) ACID

Trioxonitrate(V) acid, HNO_3, is an important acid which is used extensively in the laboratory and in industry. It was first prepared by Glauber, in 1658, from tetraoxosulphate(VI) acid and potassium trioxonitrate(V). The early alchemists used the acid for separating gold from silver. Due to its corrosive action on many metals, it was previously known as *aqua fortis*, meaning *strong water*.

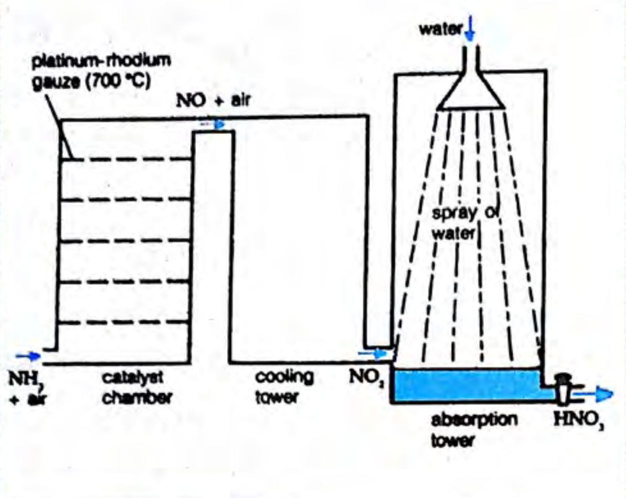
Laboratory Preparation

Trioxonitrate(V) acid can be displaced from any trioxonitrate(V) by concentrated tetraoxosulphate(VI) acid, which is a less volatile acid. The trioxonitrates(V) of potassium and sodium are usually used because they are cheap.

$$KNO_3(s) + H_2SO_4(aq) \rightarrow KHSO_4(aq) + HNO_3(g)$$

$$NaNO_3(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HNO_3(g)$$

Fig. 23.8 Industrial preparation of trioxonitrate(V) acid.



Industrial Preparation

Trioxonitrate(V) acid is obtained by the catalytic oxidation of ammonia. The ammonia reacts with excess air, in the presence of a platinum-rhodium catalyst at 700 °C, to produce nitrogen(II) oxide and steam. About 96% of the ammonia is converted into nitrogen(II) oxide.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

The reaction is exothermic. Once started, the heat released maintains the catalyst at the required temperature. The nitrogen(II) oxide formed is cooled and mixed with excess air to produce nitrogen(IV) oxide.

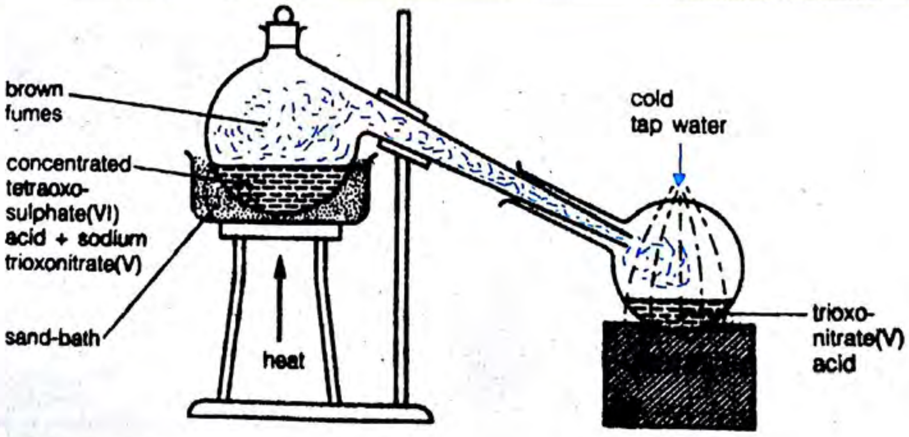
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Experiment 23.2 To prepare trioxonitrate(V) acid from sodium trioxonitrate(V) and tetraoxosulphate(VI) acid.

Method Place some sodium trioxonitrate(V) crsytals in a retort flask and set up the apparatus as shown. Add some concentrated tetraoxosulphate(VI) acid to the trioxonitrate(V) and heat strongly over a sand-bath. The fumes which distill over are collected in a receiving flask which is cooled under a running tap.

NOTE An all-glass apparatus must be used in this preparation because the hydrogentrioxonitrate(V) acid vapour will attack cork or rubber.

Fig. 23.9 Preparation of trioxonitrate(V) acid.



Result On heating, the trioxonitrate(V) dissolves and effervescence occurs. The trioxonitrate(V) acid distils over into the receiving flask, where it condenses as a yellow liquid (it is colourless if pure). Some brown fumes of nitrogen (IV) oxide are also produced due to the slight decomposition of the trioxonitrate(V) acid by heat. The yellow coloration of the acid obtained due to the dissolution of the nitrogen(IV) oxide impurity in the acid. Pure colourless trioxonitrate(V) acid can be obtained by bubbling air through the acid solution to remove this nitrogen(IV) oxide impurity.

Conclusion Trioxonitrate(V) acid is displaced from sodium trioxonitrate(V) by concentrated tetraoxosulphate(VI) acid.

In the presence of more air, the nitrogen(IV) oxide is then dissolved in a spray of hot water to yield a trioxonitrate(V) acid solution of up to 50% concentration.

$$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$$

In more modern plants, the nitrogen(IV) oxide is absorbed under pressure to obtain more concentrated solutions of the acid.

Physical Properties

1. Trioxonitrate(V) acid is a fuming liquid with a sharp choking smell. Although it is colourless when pure, it tends to turn yellowish after some time due to the decomposition of some of the acid to yield nitrogen(IV) oxide, which then dissolves in it.
2. Pure trioxonitrate(V) acid boils at 86 °C and melts at –47 °C.
3. The density of the pure acid is 1.52 g cm^{-3}.
4. Pure trioxonitrate(V) acid is miscible with water in all proportions and forms a constant boiling mixture with it at 121 °C. This mixture, consisting of about 68% trioxonitrate(V) acid, is the ordinary concentrated trioxonitrate(V) acid found in the laboratory. Trioxonitrate(V) acid containing 98% acid is known commonly as fuming trioxonitrate(V) acid.
5. The pure acid is very corrosive and readily destroys organic matter such as skin, rubber, cork and clothing. Even ordinary concentrated trioxonitrate(V) acid must be handled with care.
6. The dilute acid turns blue litmus red.

Chemical Properties

The chemistry of trioxonitrate(V) acid is complicated by the fact that it is a strong oxidizing agent in addition to being a strong acid. In general, its chemical behaviour is dependent on its concentration. In the dilute form, it is almost completely ionized into hydrogen and trioxonitrate(V) ions, and is thus strongly acidic. On the other hand, pure or concentrated trioxonitrate(V) acid is poorly ionized. As its concentration increases, its oxidizing power tends to predominate.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

As an acid

Dilute trioxonitrate(V) acid behaves as a typical acid in its reactions with bases and trioxocarbonates(IV).

With bases It neutralizes bases and alkalis to form metallic trioxonitrates(V) and water only.

$$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$$
$$CaO(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l)$$

Ionically,

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$
$$O^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l)$$

With trioxocarbonates(IV) It reacts with metallic trioxocarbonates(IV) to liberate carbon(IV) oxide.

$$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

Ionically,

$$CO_3^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l) + CO_2(g)$$

With metals Unlike other acids, trioxonitrate(V) acid rarely gives hydrogen with metals, except in the action of very dilute trioxonitrate(V) acid (about 1%) on calcium, magnesium or manganese. This is because any hydrogen which is initially formed is immediately oxidized by more of the acid to form water. At the same time, reduction products of the acid are liberated.

$$Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$$

As an oxidizing agent

Trioxonitrate(V) acid acts readily as an acceptor of electrons, and so is a strong oxidizing agent. It can undergo reduction in many ways. A wide variety of reduction products is possible (e.g. NO_2, HNO_2, NO, N_2O, N_2, NH_2OH, N_2H_4 and NH_4^+), depending on the acid concentration, the strength of the reducing agent and the temperature. More than one product is obtained as a result of secondary reactions. In this section, only the equations representing the main reactions are given.

When dilute trioxonitrate(V) acid acts as an oxidizing agent, the trioxonitrate(V) ion, NO_3^-, is reduced to nitrogen(II) oxide. The oxidation number of nitrogen decreases from +5 to +2.

$$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(g)$$

When concentrated trioxonitrate(V) acid is the oxidizing agent, the trioxonitrate(V) ion is reduced to nitrogen(IV) oxide. Here, the oxidation number of nitrogen decreases from +5 to +4.

$$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$$

With non-metals Hot concentrated trioxonitrate(V) acid oxidizes non-metals to their highest oxides, which may then react with water to form the corresponding acids. At the same time, the acid itself is reduced to nitrogen(IV) oxide.

- Carbon is oxidized to carbon(IV) oxide on heating.

$$C(s) + 4HNO_3(aq) \rightarrow CO_2(g) + 2H_2O(l) + 4NO_2(g)$$

- Sulphur is oxidized to tetraoxosulphate(VI) acid on heating.

$$S(s) + 6HNO_3(aq) \rightarrow H_2SO_4(aq) + 2H_2O(l) + 6NO_2(g)$$

- Red phosphorus is oxidized to tetraoxophosphate(V) acid on heating.

$$P(s) + 5HNO_3(aq) \rightarrow H_3PO_4(aq) + H_2O(l) + 5NO_2(g)$$

- Iodine is oxidized to trioxoiodate(V) acid when boiled with the acid.

$$I_2(s) + 10HNO_3(aq) \rightarrow 2HIO_3(aq) + 4H_2O(l) + 10NO_2(g)$$

With metals Trioxonitrate(V) acid oxidizes metals as follows:

- Pure trioxonitrate(V) acid oxidizes copper to copper(II) trioxonitrate(V) while it is itself reduced to nitrogen(IV) oxide.

$$Cu(s) + 4H^+NO_3^-(aq) \rightarrow Cu^{2+}(NO_3^-)_2(aq) + 2H_2O(l) + 2NO_{2(g)}$$

With moderately concentrated trioxonitrate(V) acid (about 50%), copper is again oxidized to copper(II) trioxonitrate(V), but the acid itself is converted to nitrogen(II) oxide instead of nitrogen(IV) oxide

$$3Cu(s) + 8H^+NO_3^-(aq) \rightarrow 3Cu^{2+}(NO_3^-)_2(aq) + 4H_2O(l) + 2NO_{(g)}$$

- Other metals which are mild reducing agents, like lead, mercury and silver, react with the acid in the same way as copper.
- Aluminium and iron do not react with the concentrated acid, probably due to the formation of a surface coating of oxide which is passive and stops any further action by the acid. Therefore, concentrated trioxonitrate(V) acid is usually transported in containers lined with aluminium or iron.
- Magnesium, zinc and iron react with dilute trioxonitrate(V) acid to form the respective metallic trioxonitrates(V) and ammonium trioxonitrate(V) or nitrogen(I) oxide.

$$4Zn(s) + 10HNO_3(aq) \rightarrow 4Zn(NO_3)_2(aq) + 3H_2O(l) + NH_4NO_3(aq)$$

- Tin reacts with the concentrated acid to form a hydrated oxide, instead of a trioxonitrate(V).

$$Sn(s) + 4HNO_3(aq) \rightarrow SnO_2.H_2O(s) + H_2O(l) + 4NO_2(g)$$

- Gold and platinum are not attacked by trioxonitrate(V) acid at all.

With reducing agents As a strong oxidizing agent, trioxonitrate(V) acid also undergoes redox reactions with the common reducing agents, like hydrogen sulphide and iron(II) salts.

- Trioxonitrate(V) acid oxidizes hydrogen sulphide to sulphur, some of which may be further oxidized to tetraoxosulphate(VI) acid. At the same time, trioxonitrate(V) acid is reduced to nitrogen(IV) oxide.

$$H_2S(g) + 2HNO_3(aq) \rightarrow S(s) + 2H_2O(l) + 2NO_2(g)$$

Iron(II) salts are oxidized to iron(III) salts by trioxonitrate(V) acid. The reduction product of the acid is nitrogen(II) oxide, which is converted to nitrogen(IV) oxide on exposure to air.

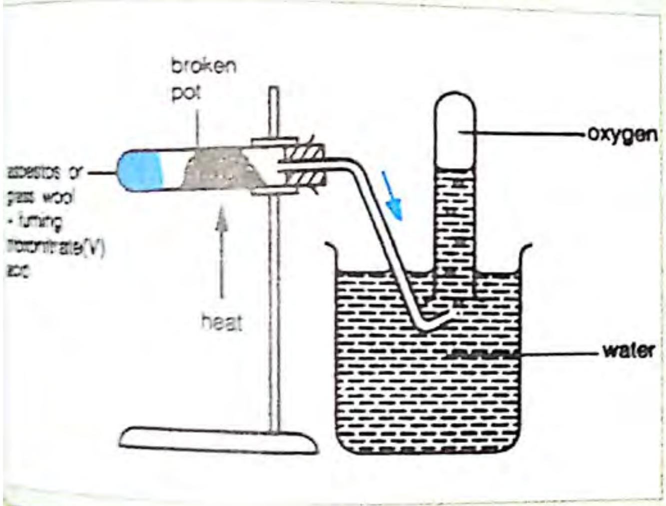
$$6Fe^{2+}(aq) + 8H^+(aq) + 2NO_3^-(aq)$$
$$\rightarrow 6Fe^{3+}(aq) + 4H_2O(l) + 2NO(g)$$

Decomposition

Trioxonitrate(V) acid decomposes slowly at room temperature (especially in the presence of sunlight), and rapidly when heated to yield nitrogen(IV) oxide and oxygen.

$$4HNO_3(aq) \rightarrow 2H_2O(l) + 4NO_2(g) + O_2(g)$$

Fig. 23.10 Decomposition of trioxonitrate(V) acid.



This can be demonstrated by using the apparatus in fig. 23.10. Asbestos or glass wool which is soaked with fuming trioxonitrate(V) acid is placed in the hard-glass tube. The acid decomposes when warmed indirectly by heating the pieces of broken pot in the tube. The nitrogen(IV) oxide formed dissolves in water, while oxygen is collected in a test-tube over water.

Nitration reactions

In the presence of concentrated tetraoxosulphate(VI) acid, trioxonitrate(V) acid dissociates to form the nitryl cation (nitronium ion), NO_2^+, which can replace the hydrogen ions from many organic compounds, e.g. benzene, methyl benzene and phenol. This process is known as nitration and is of great industrial importance.

$$\underset{\text{benzene}}{C_6H_6(l)} + HNO_3(aq) \rightarrow \underset{\text{nitrobenzene}}{C_6H_5NO_2(l)} + H_2O(l)$$

Uses

1 Trioxonitrate(V) acid is used as an acid, an oxidizing agent and a nitrating agent in the laboratory.
2 It is used as an oxidizing agent in the production of important polymers like nylon and Terylene.
3 It is also used as a rocket fuel.
4 A mixture of three parts of hydrochloric acid and one part of trioxonitrate(V) acid (known as *aqua regia*) is used as a solvent for gold and platinum.
5 It is an important starting material in the manufacture of many trioxonitrates(V) and organic nitro-compounds which are used for the production of

- fertilizers (e.g. nitrochalk),
- dyes,
- drugs, and
- explosives (e.g. methyl-2,4,6-trinitrobenzene, commonly known as TNT).

TRIOXONITRATES(V)

Trioxonitrate(V) acid forms a series of normal salts known as the trioxonitrates(V).

Preparation

The trioxonitrates(V) can be prepared by any of the general methods of salt preparation, namely

- the neutralization of trioxonitrate(V) acid with the appropriate alkali; or
- the action of trioxonitrate(V) acid on a metal, a metallic oxide or a trioxocarbonate(IV).

Trioxonitrates(V) cannot be prepared by precipitation because all trioxonitrates(V) are soluble. The trioxonitrate(V) salts can be separated out of solution only by crystallization since they are all easily decomposed by dry heating.

Properties

Action of heat

All trioxonitrates(V) are decomposed by heat. However, the products of decomposition of a metallic trioxonitrate(V) depend on the position of the metal in the electrochemical series.

All metallic trioxonitrates(V), except that of sodium, lead(II) and potassium, contain water of crystallization. On heating, these salts crackle and dissolve in their own water of crystallization. The salts will only decompose after all the water has been driven off. Therefore, these trioxonitrates(V) must be heated carefully.

The decomposition of some trioxonitrates(V) are as follows:

(a) $2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$

white — pale yellow

(b) $2Zn(NO_3)_2(s) \rightarrow 2ZnO(s) + O_2(g) + 4NO_2(g)$

colourless — yellow (hot) white (cold) — brown

Table 23.3 Thermal ...
trioxonitrates(V)

Metal	Decomposition of the corresponding trioxonitrates(V)
K Na	These trioxonitrates(V) decompose to the corresponding dioxonitrates(III) and oxygen, e.g. $2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$
Ca Mg Zn Pb H Cu	These trioxonitrates(V) decompose to the corresponding oxides of metals, oxygen and brown fumes of nitrogen(IV) oxide, e.g. $2Zn(NO_3)_2(s) \rightarrow 2ZnO(s) + O_2(g) + 4NO_2(g)$
Hg Ag Au	These trioxonitrates(V) decompose to the corresponding metals, oxygen and brown fumes of nitrogen(IV) oxide, e.g. $2AgNO_3(s) \rightarrow 2Ag(s) + O_2(g) + 2NO_2(g)$

Experiment 23.3 To investigate the thermal decomposition of the trioxonitrates(V) of sodium, zinc, lead(II), copper(II) and silver.

Method Fill separate test-tubes each with one of the trioxonitrates(V) under study to a depth of 2 cm. Heat strongly and observe what happens. At the same time, insert a glowing splinter into each test-tube to test for the presence of oxygen.

Result *Sodium trioxonitrate(V)* On heating, it melts to give a colourless liquid which decomposes slowly. The glowing splinter is rekindled, showing the liberation of oxygen. A pale yellow residue of sodium dioxonitrate(III) is left.

Zinc trioxonitrate(V) On heating, brown fumes of nitrogen(IV) oxide are given off. The glowing splinter is rekindled, indicating the presence of oxygen. The residue, which is zinc oxide, is yellow when hot but becomes white on cooling.

Lead(II) trioxonitrate(V) On heating, crackling occurs and brown fumes of nitrogen(IV) oxide are given off as the crystals melt. At the same time, the glowing splinter is rekindled, indicating the evolution of oxygen. The lead(II) oxide residue is reddish-brown when hot but yellow when cold.

Copper(II) trioxonitrate(V) Brown fumes of nitrogen(IV) oxide are given off. The glowing splinter is rekindled, indicating that the oxygen is also evolved. The copper(II) oxide residue is black.

Silver trioxonitrate(V) Brown fumes of nitrogen(IV) oxide are given off. At the same time, oxygen is also evolved, as indicated by the rekindling of the glowing splinter. The residue is metallic silver which may appear brownish due to the coloration of the brown fumes.

Conclusion Metallic trioxonitrates(V) decompose on heating to yield different products.

(c) $\underset{\text{white}}{2Pb(NO_3)_2(s)} \rightarrow \underset{\substack{\text{reddish-brown (hot)}\\ \text{yellow (cold)}}}{2PbO(s)} + O_2(g) + \underset{\text{brown}}{4NO_2(g)}$

(d) $\underset{\text{greenish-blue}}{2Cu(NO_3)_2(s)} \rightarrow \underset{\text{black}}{2CuO(s)} + O_2(g) + \underset{\text{brown}}{4NO_2(g)}$

(e) $\underset{\text{colourless}}{2AgNO_3(s)} \rightarrow \underset{\substack{\text{lustrous}\\ \text{white}}}{2Ag(s)} + O_2(g) + \underset{\text{brown}}{2NO_2(g)}$

Ammonium trioxonitrate(V), unlike all the metallic trioxonitrates(V), decomposes on heating to give nitrogen(I) oxide and water.

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$$

Action of tetraoxoshulphate(VI) acid

All trioxonitrates(V) liberate trioxonitrate(V) acid when heated with concentrated tetraoxosulphate(VI) acid. This is the basis of the preparation of trioxonitrate(V) acid in the laboratory.

$$NO_3^-(s) + H_2SO_4(aq) \rightarrow HSO_4^-(aq) + HNO_3(g)$$

Formation of a brown ring

When concentrated tetraoxosulphate(VI) acid is added slowly down the sides of a test-tube containing an aqueous solution of a trioxonitrate(V) and iron(II) tetraoxosulphate(VI), the acid sinks to the bottom and two liquid layers are formed. At the junction of the two layers, the trioxonitrate(V), the concentrated acid and the iron(II) tetraoxosulphate(VI) react to form a brown compound in the following way:

1 The trioxonitrate(V) ion in solution reacts with the concentrated tetraoxosulphate(VI) acid to yield trioxonitrate(V) acid.

$$H_2SO_4(aq) + NO_3^-(aq) \rightarrow HSO_4^-(aq) + HNO_3(aq)$$

2 Some of the trioxonitrate(V) acid formed is reduced by iron(II) tetraoxosulphate(VI) to yield nitrogen(II) oxide, NO.

$$2HNO_3(aq) + 3H_2SO_4(aq) + 6FeSO_4(aq) \rightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$$

3 The nitrogen(II) oxide then combines with more of the iron(II) tetraoxosulphate(VI) to form a brown addition compound, $FeSO_4.NO$, which appears at the junction of the two liquid layers as a brown ring.

$$FeSO_4(aq) + NO(g) \rightarrow FeSO_4.NO(aq)$$

The brown ring disappears if the solution is shaken because the brown addition compound is decomposed by the heat produced when the water mixes with the cconcentrated tetraoxosulphate(VI) acid.

Tests for trioxonitrates(V)

Brown ring test This is carried out on a solution of the unknown compound in the following way.

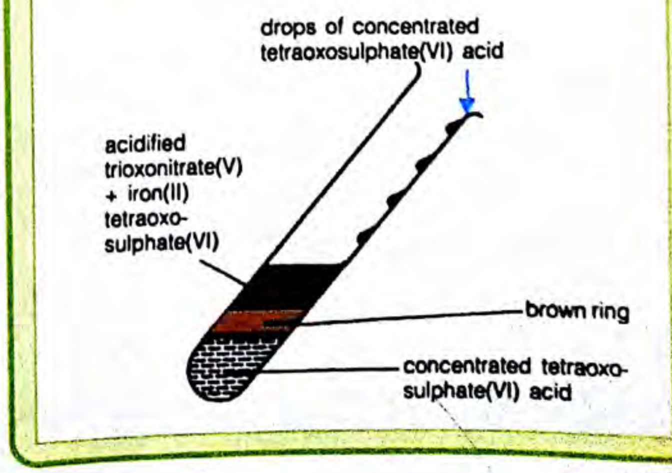
Fill a test-tube with a solution of the unknown compound to a depth of about 2 cm. Acidify the solution with a little dilute tetraoxosulphate(VI) acid. Add some freshly prepared iron(II) tetraoxosulphate(VI) solution and shake well to mix. Hold the test-tube in a slanting position and carefully pour a stream of concentrated tetraoxosulphate(VI) acid down the side of the tube.

If the unknown compound is a trioxonitrate(V), a brown ring appears at the junction of the acid and aqueous layers.

The brown ring test is unreliable in the presence of iodides and bromides since they too give coloured rings. Dioxonitrates(III) form a brown solution before the addition of the concentrated acid and so must be removed before the test can be carried out. Metallic radicals which form insoluble tetraoxosulphates(VI) also interfere with the test.

With tetraoxosulphate(VI) acid Warm the unknown

Fig. 23.11 Brown ring test.



solid with a little concentrated tetraoxosulphate(VI) acid in a test-tube. If a trioxonitrate(V) is present, some trioxonitrate(V) acid will be condensed as oily drops on the upper part of the tube. On further heating, the acid will decompose, yielding brown fumes of nitrogen(IV) oxide.

$$H_2SO_4(aq) + NO_3^-(s) \rightarrow HNO_3(l) + HSO_4^-(aq)$$
$$4HNO_3(l) \rightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)$$

With copper turnings Warm a mixture of the unknown solid and copper turnings with some concentrated tetraoxosulphate(VI) acid. If a trioxonitrate(V) is present, reddish-brown fumes of nitrogen(IV) oxide will be formed.

$$H_2SO_4(aq) + NO_3^-(s) \rightarrow HNO_3(aq) + HSO_4^-(aq)$$

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

NITROGEN CYCLE

The continuous circulation of nitrogen between the free gaseous nitrogen in the atmosphere and the combined nitrogen in the proteins of the living tissues is known as the *Nitrogen Cycle*. The intermediate compounds which can be converted to proteins or gaseous nitrogen are the trioxonitrates(V) in the soil.

Processes using soil trioxonitrates(V)

All living cells contain protoplasm which consists mainly of proteins. Nitrogen is an essential constituent of proteins. Animals consume proteins directly by eating other animals or plants, since they are incapable of making their own proteins from simpler nitrogenous compounds. Plants, on the other hand, can synthesize their own proteins, although they cannot make use of the free nitrogen which makes up about 78% of the air. Instead, they use the ammonium or trioxonitrate(V) salts which they absorb from the soil. In addition to the removal of soil trioxonitrates(V) by the plants, some soil trioxonitrates are also reduced by denitrifying bacteria to gaseous nitrogen which then escapes into the air.

Processes replenishing soil trioxonitrates(V)

Nature has several means of replenishing the trioxonitrates(V) in the soil that are being continuously removed by plants and bacteria to proteins or gaseous nitrogen.

Oxidation of atmospheric nitrogen During electrical discharges in the atmosphere, e.g. lightning, some of the atmospheric nitrogen undergoes oxidation to form the oxides of nitrogen which then dissolve in rain water as dioxonitrate(III) and trioxonitrate(V)

Intensive crop cultivation leads to depletion of soil nitrogen. Since natural processes cannot restore the soil nitrogen level rapidly, fertilizers containing suitable nitrogen compounds have to be added to the soil.

acids. When these acids go into the soil, they react with mineral salts to produce trioxonitrates(V) eventually.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$$

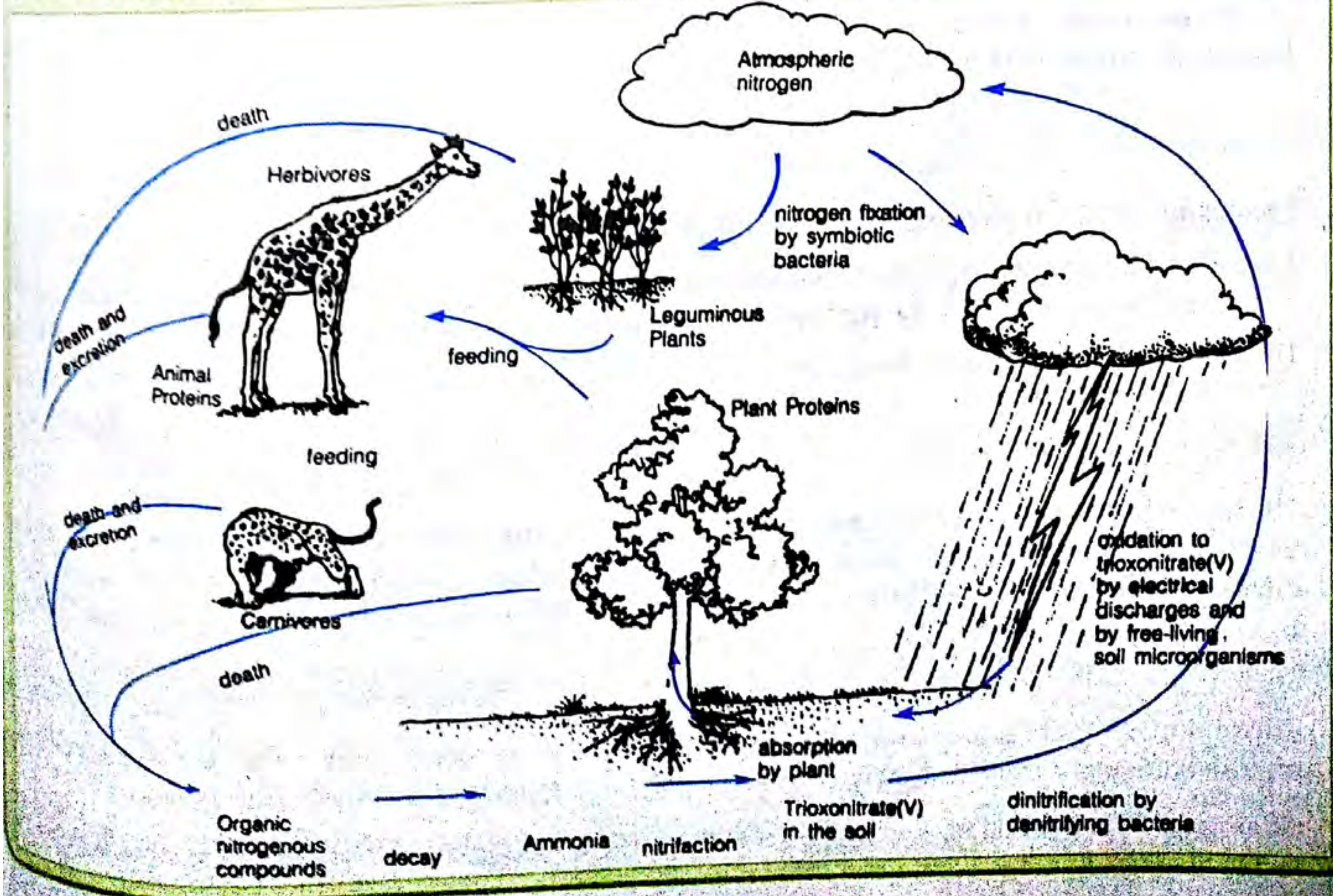
Action of nitrogen-fixing bacteria Soil micro-organisms are also active in replenishing soil trioxonitrates(V). Such organisms include the symbiotic bacteria (e.g. *Rhizobium*) living in the root nodules of leguminous plants. They are able to convert atmospheric nitrogen into organic nitrogenous compounds, namely simple proteins, which are used directly by the host plants. These compounds are released into the soil when these plants die. Other free-living micro-organisms living in the soil, e.g. *Nostoc*, *Clostridium* and *Azotobacter*, are also able to fix atmospheric nitrogen into trioxonitrates(V) which then pass into the soil. These processes are known as *nitrogen fixation*.

Decay of organic matter The nitrogen which has been taken up by plants and animals is returned to the soil in the form of excretory products and dead materials. The organic nitrogenous compounds in these are then converted into ammonia by putrefying bacteria and fungi in the soil. Another group of bacteria known as nitrifying bacteria, oxidizes the ammonia first into dioxonitrates(III) and then into trioxonitrates(V). This is known as *nitrification*.

Maintenance of the nitrogen cycle

Under natural conditions, the processes which replenish the soil nitrogen and those which diminish it are in equilibrium. However, agricultural and several other practices, e.g. soil erosion, and the discharge of human waste into the sea, have upset this delicate balance. In order to maintain the soil nitrogen level, artificial fertilizers have to be used, e.g. in the form of sodium trioxonitrate(V) and ammonium tetraoxosulphate(VI). Fertilizers are also made from atmospheric nitrogen, which is first converted into ammonia (by the Haber process) and eventually into trioxonitrates(V). Other methods of replacing soil nitrogen include the use of compost heaps to promote the decay of waste vegetable material, and the practice of crop rotation using leguminous plants.

Fig. 23.12 Nitrogen cycle.



SUMMARY

Nitrogen

- Nitrogen which occurs in Group 5 of the Periodic Table has five valence electrons. It can exist in oxidation states of -3 to +5 in its compounds.
- Nitrogen occurs in the free form in air; in the combined form as trioxonitrates(V) and ammonium salts; and in organic matter.
- It is prepared in the laboratory by (a) action of heat on a mixture of sodium dioxonitrate(III) and ammonium chloride, (b) oxidation of ammonia, (c) reduction of certain oxides of nitrogen, and industrially by the fractional distillation of liquid air.
- It is chemically unreactive but it combines directly with certain metals to form nitrides; it reacts with hydrogen to give ammonia; and it forms nitrogen(II) oxide with oxygen.
- Nitrogen is used in the manufacture of ammonia and fertilizers. Liquid nitrogen is used as a cooling agent.

Ammonia

- Ammonia is prepared industrially by the Haber process, and in the laboratory by heating lime and ammonium chloride.
- It is an alkaline gas which forms dense white fumes with hydrogen chloride gas; it burns in oxygen forming nitrogen, but in the presence of a catalyst, it forms nitrogen(II) oxide; it reduces copper(II) oxide to metallic copper; it reduces chlorine to chlorides; and it undergoes thermal decomposition to the component elements.
- Aqueous ammonia is a weak alkali which neutralizes acids; it precipitates hydroxides of metals (except copper and zinc); and it sometimes forms complex salts when in excess.
- ***Test for ammonia*** It(a) has a characteristic, pungent smell, (b) turns red litmus paper blue, and (c) forms dense white fumes with hydrogen chloride gas.

Ammonium salts

- Ammonium salts are prepared by the neutralization of acids with aqueous ammonia.
- They are white crystalline solids which are water soluble; they release ammonia with strong alkalis (test for ammonium salts); and they are decomposed by heat to ammonia, nitrogen or oxides of nitrogen.
- They are used extensively as fertilizers and to manufacture explosives.

Oxides of nitragen

- The important oxides of nitrogen are dinitrogen(I) oxide, nitrogen(II) oxide and nitrogen(IV) oxide. They are all reduced to nitrogen by heated metals. Dinitrogen(I) oxide and nitrogen(II) oxide are neutral to litmus. Nitrogen(IV) oxide dissolves in water to form dioxonitrate(III) acid and trioxonitrate(V) acid.

Trioxonitrate(V) acid

- Trioxonitrate(V) acid is prepared in the laboratory by the action of concentrated tetraoxosulphate(VI) acid on trioxonitrates(V), and industrially by the catalytic oxidation of ammonia with excess air.
- ***As an acid*** The very dilute acid neutralizes bases; it liberates carbon(IV) oxide from trioxocarbonates(IV); and it liberates hydrogen from magnesium.

- *As an oxidizing agent* It oxidizes non-metals to their highest oxides; it oxidizes metals (except iron and aluminium) including copper to the oxides or trioxonitrates(V), and is itself reduced to nitrogen(II) oxide with moderately concentrated trioxonitrate(V) acid, or nitrogen(IV) oxide with the pure acid; it undergoes redox reactions with reducing agents like hydrogen sulphide and iron(II) salts; and it decomposes at room temperature liberating oxygen and nitrogen(IV) oxide.
- The acid is used industrially as an oxidizing agent and a nitrating agent. It is used in the manufacture of trioxonitrates(V) and organo-nitrate compounds which are used as fertilizers, dyes and explosives.

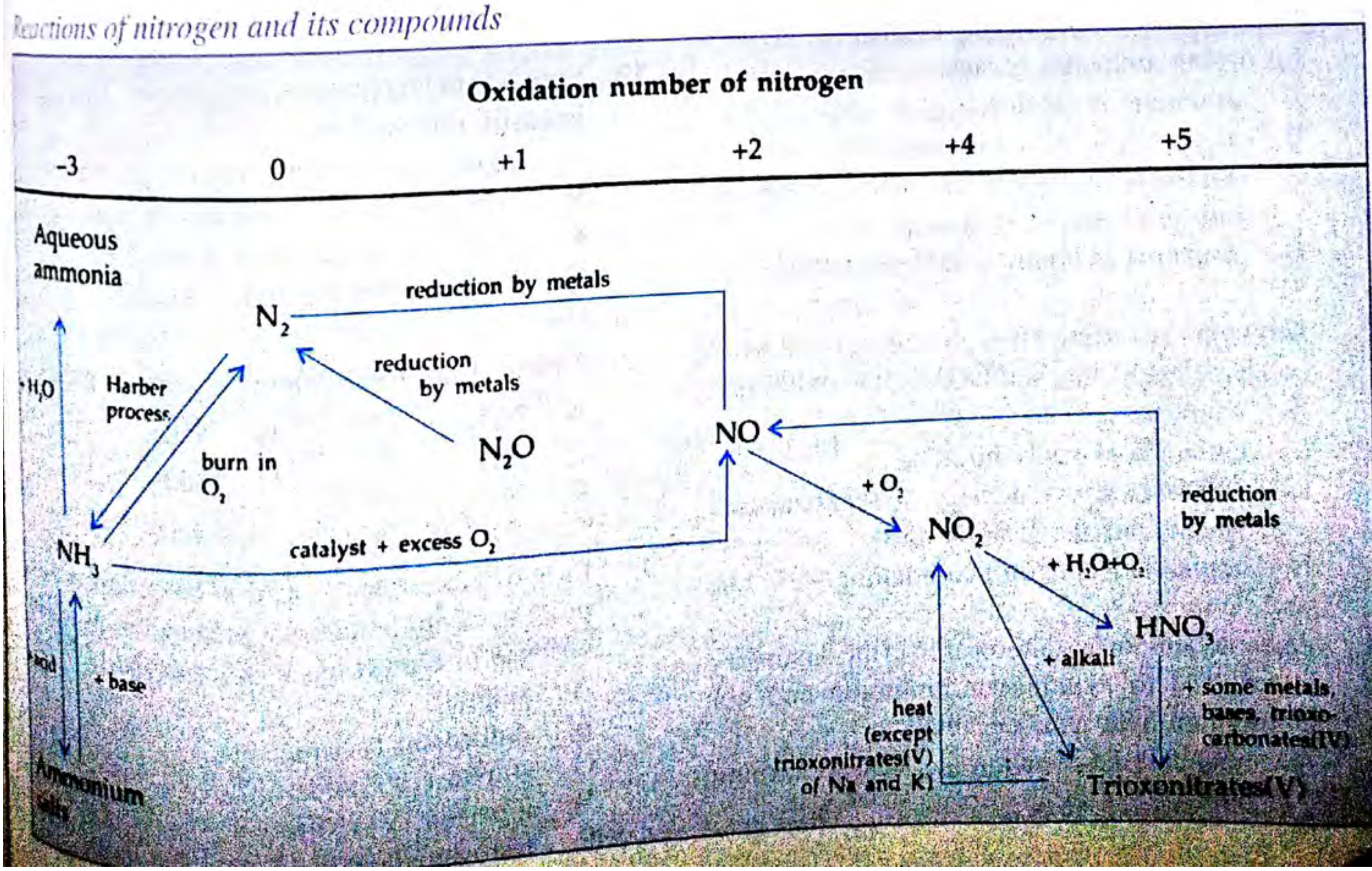
Trioxonitrates(V)

- Nitrates are decomposed by heat, giving off oxygen and nitrogen(IV) oxide, except sodium, potassium and ammonium trioxonitrates(V); all are crystalline, water-soluble solids; and they produce trioxonitrate(V) acid when they react with concentrated tetraoxosulphate(VI) acid.
- *Tests for trioxonitrate(V)* It (a) gives a brown ring with iron(II) tetraoxosulphate(VI) and concentrated tetraoxosulphate(VI) acid, (b) gives off nitrogen(IV) oxide with copper turnings in concentrated tetraoxosulphate(VI) acid, and (c) produces oily trioxonitrate(V) acid droplets with concentrated tetraoxosulphate(VI) acid.

Nitrogen cycle

- Nitrogen is being continuously recycled between the free gaseous nitrogen in the atmosphere and the combined nitrogen in the proteins of the living organisms.
- The soil trioxonitrates(V) are the intermediate compounds in this cyclic process. Soil micro-organisms, plants and thunderstorms are the agents that convert the soil trioxonitrates(V) to gaseous nitrogen or to proteins, and thereby maintain the nitrogen cycle.
- Agricultural activities have depleted the nitrogen level in the soil, so fertilizers are added to restore its level.

Reactions of nitrogen and its compounds



EXERCISES

1. One of these methods produces impure nitrogen.
A $NaNO_2(aq) + NH_4Cl \rightarrow$
B $(NH_4)_2\ Cr_2O_7(s) \rightarrow$
C $NH_3(g) + CuO \rightarrow$
D Removing CO_2 and O_2 from dust free air.

2. Nitrogen combines directly with metals except
A Cu B Mg
C Ca D Al

3. Oxidation of nitrogen in Mg_3N_2 is
A −3 B +3
C −2 D +2

4. Nitrogen combines reversibly with hydrogen under
A catalyst.
B high voltage electric spark.
C the presence of traces of NO.
D in vacuum.

5. Hydride of nitrogen which is capable of turning red litmus blue makes nitrogen to have an oxidation state of
A +2 B −2
C +3 D −3

6. Common laboratory drying agents are not used for drying ammonia because
A ammonia is alkaline.
B ammonia forms complexes with them.
C ammonia reacts with them and disappears into products.
D ammonia is highly soluble in water.

7. Ammonia has relatively high boiling point when compared with other similar compounds because
A ammonia is stable.
B ammonia is easily liquified.
C ammonia has a density of 0.880 g cm^{-3} which contains 35% by mass.
D ammonia has hydrogen bonding.

8. Aqueous ammonia solution used in the laboratory is referred to as aqueous ammonia and not ammonium hydroxide because
A ammonia dissolves in water without forming bonds.
B ammonia solution easily decomposes and liberates free ammonia when the temperature of the room rises leaving water in the bottle.
C the bond between ammonia and OH^- of water is weakly acidic.
D ammonia is less dense than air.

9. Ammonia reacts with excess chlorine to produce
A a chloride and free nitrogen.
B ammonia chloride.
C double chloride.
D a chloride and nitrogen II oxide.

10. The following ammonium salts decompose when heated mildly except
A $(NH_4)_2SO_4$ B NH_4NO_2
C $(NH_4)_2CO_3$ D NH_4lCl

11. Nitrogen I oxide rekindles a brightly glowing splint just like oxygen, but it is different from oxygen because
A it is less dense than oxygen.
B it is fairly soluble in water.
C it thermally decomposes before it rekindles glowing splint.
D it is only laughing gas.

12. Pure NO in an open gas jar is brown. This colour is easily removed by
A blowing excess air into the gas jar.
B bubbling the gas into caustic alkali.
C bubbling the gas into water.
D bubbling the gas into oxygen.

13. Which of the following is an alkaline gas?
A NO_2 B NH_3
C NO D N_2O
E N_2O_4

14. Pure trioxonitrate(V) acid is colourless but the product of its laboratory preparation is yellow because of the presence of dissolved
A sulphur.
B dinitrogen(I) oxide.
C sulphur(IV) oxide.
D nitrogen(IV) oxide.
E nitrogen(II) oxide.

(a) With the aid of diagrams and equations, show how you would obtain nitrogen

(i) from air.

(ii) starting with ammonium chloride.

Compare the two nitrogen samples.

(b) What happens when magnesium is burned in a jar of nitrogen and the product is warmed after moistening with water? Give the equations of the reactions involved.

(c) Give two uses of nitrogen.

(d) The method of collection of any gas depends on its solubility in water and also its density as compared with that of air. Justify this statement with specific examples.

(a) With the aid of a diagram and equation describe and explain how dry ammonia may be prepared in the laboratory. Give the reason for your method of drying and collection.

(b) Give an example of a reaction in which ammonia behaves as a

(i) reducing agent,

(ii) base,

(iii) precipitating agent.

(c) Describe what happens when aqueous ammonia is slowly poured into a beaker containing a solution of zinc trioxonitrate(V) until there is excess ammonia solution.

How is trioxonitrate(V) acid manufactured from ammonia? Give the conditions of the process and the equations of the reactions.

(a) What happens if ammonium chloride is heated in a test-tube with a long neck?

(b) What will happen if ammonium chloride is heated very strongly in a closed container, and the products formed are cooled?

(c) Give two common uses of a named ammonium salt.

(d) Give the equation for the thermal decomposition of ammonium trioxonitrate(V).

19. (a) Describe with the aid of a diagram and equation how trioxonitrate(V) acid is prepared in the laboratory.

(b) Explain why dilute trioxonitrate(V) acid rarely liberates hydrogen with metals.

(c) Explain why aluminium and iron containers are used to keep concentrated trioxonitrate(V) acid.

(d) With the aid of equations, explain how trioxonitrate(V) acid reacts with

(i) sulphur,

(ii) copper,

(iii) carbon.

20. (a) With the aid of an equation and a diagram, show how dinitrogen(I) oxide, N_2O, may be prepared in the laboratory.

(b) How is dinitrogen(I) oxide distinguished from oxygen which also supports combustion?

(c) Nitrogen(II) oxide does not rekindle a glowing splinter but supports the combustion of carbon, phosphorus, lead and magnesium. Explain why, giving the equations of the reactions.

21. (a) Describe how is nitrogen(IV) oxide, NO_2, prepared in the laboratory.

(b) What are the effects of heating and cooling on nitrogen(IV) oxide?

(c) How does nitrogen(IV) oxide react with

(i) copper,

(ii) phosphorus,

(iii) sodium hydroxide?

What property of nitrogen(IV) oxide is exhibited by these reactions?

22. Describe how atmospheric nitrogen may be fixed for use by plants. Outline other factors which disturb the natural Nitrogen Cycle.

24 PHOSPHORUS AND ITS COMPOUNDS

PHOSPHORUS

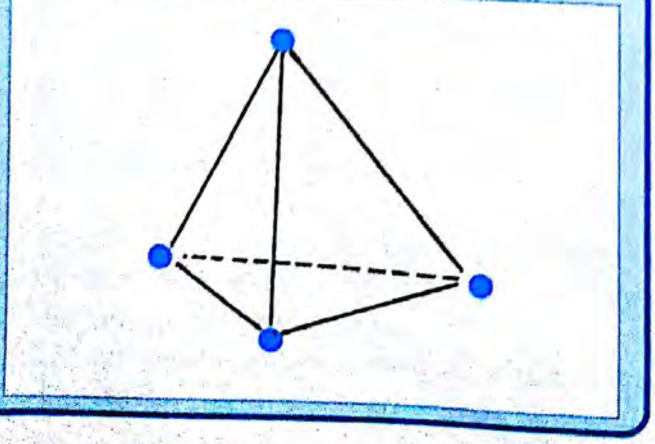
Phosphorus, like nitrogen, is a non-metallic element belonging to Group 5 of the Periodic Table. It is never found in the free, uncombined state in nature because of its extremely reactive nature. It is widely distributed in the combined state as tetraoxophosphate(V) minerals. The most abundant of these is *rock phosphate* or *phosphorite* which contains largely calcium tetraoxophosphate(V), $Ca_3(PO_4)_2$. Another rock phosphate is *apatite,* $CaF_2 . 3Ca_3(PO_4)_2$. Phosphorus, usually in the form of tetraoxophosphate(V), is also an essential constituent of living matter. Bones and teeth have a high percentage of calcium tetraoxo-phosphate(V). Many proteins, especially in seeds, eggs, nerve tissues and brain cells, contain phosphorus. In fact, the element makes up about 1% by mass of the human body.

Allotropes of Phosphorus

Phosphorus is a solid which exists essentially in three allotropic forms, namely white, red and black phosphorus. Of these, white and red phosphorus are the more important and common forms.

White phosphorus

Fig. 24.1 Tetrahedral white phosphorus molecule.



White phosphorus exists as tetratomic molecules. Each phosphorus atom is attached to three others by simple covalent bonds to produce tetrahedral molecules of P_4 as shown. Phosphorus also exists as tetratomic molecules in the vapour state (below 700 °C), and in solution in carbon(IV) sulphide.

White phosphorus is a white, waxy, soft and translucent solid. It is not very stable at room temperature and changes slowly but spontaneously to red phosphorus. This process is accelerated by raising the temperature.

White phosphorus is twice as dense as water. It is insoluble in water but is readily soluble in carbon(IV) sulphide, benzene and other organic solvents. White phosphorus has a melting point of 44 °C. Since it has a low ignition temperature of 35 °C, it would catch fire spontaneously in air and so should always be stored under water. Slow oxidation also occurs when it is exposed to air. resulting in a greenish glow. This phenomenon is known as *phosphorescence.*

White phosphorus is poisonous. Any contact with the skin would result in serious burns.

Red phosphorus

When white phosphorus is heated to 250 °C, in the absence of air and in the presence of a little iodine or sulphur as a catalyst, the tetratomic molecules combine to form macromolecules. The product is a red brittle powder known as red phosphorus, which is the stable allotrope of phosphorus.

Red phosphorus has a higher density than the white allotrope. It is insoluble in water, carbon(IV) sulphide and most common solvents. It has an ignition temperature of 250 °C and can thus be handled safely. Besides, it is non-toxic when pure. If sublimed at 290 °C in the absence of air, the vapour condenses to form white phosphorus.

$$\text{white phosphorus} \underset{\text{cool the vapour}}{\overset{250°\text{C; } I_2/\text{S catalyst}}{\rightleftharpoons}} \text{red phosphorus}$$

ble 24.1 *Comparing the physical properties of white and red phosphorus.*

	White phosphorus	Red phosphorus
Appearance	White translucent solid (turns yellow gradually on exposure to light)	Opaque red solid
Melting point	44 °C	600 °C (under pressure)
Boiling point	280 °C	Sublimes at 400 °C
Density	1.8 g cm^{-3}	2.2 g cm^{-3}
Solubility in water	Insoluble	Insoluble
Solubility in carbon(IV) sulphide	Very soluble	Insoluble
Ignition temperature	35 °C	250 °C
Toxicity	Toxic	Non-toxic
Phosphorescence	Glows in the dark	Does not glow

Chemical Properties

oth white and red phosphorus are chemically entical although red phosphorus tends to be less active than the white allotrope. Phosphorus has five ectrons in its valence shell and so generally forms valent compounds. It exhibits valencies 3 and 5, d so forms two series of compounds. The following e some of the common chemical reactions of osphorus.

eaction with air

osphorus burns vigorously with a dazzling flame a plentiful supply of air to produce dense white mes of phosphorus(V) oxide, P_4O_{10}. In moist air, ese fumes dissolve to form misty droplets of tetraoxophosphate(V) acid. In a limited supply of air, phosphorus burns to produce phosphorus(III) oxide, P_4O_6.

(a) $P_4(s) + \underset{\text{excess}}{5O_2(g)} \rightarrow P_4O_{10}(g)$

(b) $P_4O_{10}(g) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

$P_4(s) + \underset{\text{limited}}{3O_2(g)} \rightarrow P_4O_6(g)$

Reaction with metals and non-metals

Phosphorus ignites spontaneously in chlorine to form phosphorus(III) chloride or phosphorus(V) chloride depending on whether the phosphorus or the chlorine

ble 24.2 *Comparing the chemical properties of white and red phosphorus.*

<table>
<tr><th>Reactions with</th><th>White phosphorus</th><th>Red phosphorus</th></tr>
<tr><td>air</td><td>Rapidly oxidized at ordinary temperatures; P_4O_6 or P_4O_{10} formed</td><td>Oxidized only on heating; P_4O_6 or P_4O_{10} formed</td></tr>
<tr><td>chlorine</td><td>Ignites spontaneously; PCl_3 or PCl_5 formed</td><td>Ignites only when heated; PCl_3 or PCl_5 formed</td></tr>
<tr><td>sulphur</td><td colspan="2">Sulphides formed on heating</td></tr>
<tr><td>metals</td><td colspan="2">Phosphides formed on heating</td></tr>
<tr><td>concentrated HNO_3</td><td colspan="2">Tetraoxophosphate(V) acid formed</td></tr>
<tr><td>hot NaOH solution</td><td>Phosphine formed</td><td>No reaction</td></tr>
</table>

is in excess. It also reacts vigorously with bromine and iodine. When heated with sulphur and many metals, it forms sulphides and phosphides respectively.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$
$$P_4(s) + \underset{\text{excess}}{10Cl_2(g)} \rightarrow 4PCl_5(s)$$

As a reducing agent

Phosphorus is a reducing agent. It readily reacts with oxidizing agents to form oxides of phosphorus which can dissolve in water to form acids. For example, when heated with concentrated trioxonitrate(V) acid, phosphorus is oxidized to tetraoxophosphate(V) acid. Phosphorus also readily reduces copper(II) tetraoxosulphate(VI) to metallic copper.

$$P(s) + 5HNO_3(aq) \rightarrow H_3PO_4(aq) + H_2O(l) + 5NO_2(g)$$

Reaction with alkalis

White phosphorus reacts with hot solutions of caustic alkalis to form phosphorus(III) hydride, PH_3.

$$4P(s) + 3NaOH(aq) + 3H_2O(l) \rightarrow 3NaH_2PO_2(aq) + PH_3(g)$$

Uses

1 Phosphorus is used to prepare
   - tetraoxophosphate(V) acid, H_3PO_4,
   - trioxophosphate(III) acid, H_3PO_3,

   and their salts. The salts are mainly used as fertilizers.
2 Phosphorus is used in the making of certain tin and bronze alloys like phosphor-bronze. These alloys are used for the manufacture of machine parts such as gears, bearings, boiler fittings and parts exposed to sea water to enable them to resist wear and corrosion.
3 White phosphorus is used in smoke and incendiary bombs and fireworks.
4 The sides of the match-box are coated with red phosphorus and a combustible substance, usually antimony sulphide, while the match heads are coated with an oxidizing agent and an abrasive. When the match-head is rubbed against the side of the match-box, the friction generates enough heat to ignite the phosphorus compound which in turn initiates the reaction between the antimony sulphide and the oxidizing agent.
5 Organo-phosphorus compounds are used in weed killers, rat-poisons, insecticides and oil additives.

PHOSPHINE

Phosphorus forms two hydrides, namely phosphorus(III) hydride, PH_3, and the less important diphosphane, P_2H_4. Phosphorus(III) hydride is an analogue of ammonia, NH_3.

Preparation

Phosphorus(III) hydride is prepared by heating white phosphorus with concentrated sodium hydroxide in a flask in which the air has been displaced by town gas or natural gas to provide an inert atmosphere.

$$P_4(s) + 3NaOH(aq) + 3H_2O(l) \rightarrow 3NaH_2PO_2(aq) + PH_3(g)$$

Phosphorus(III) hydride can also be made by the action of water or acid on calcium phosphide, Ca_3P_2.

$$Ca_3P_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(s) + 2PH_3(g)$$

Properties

Phosphorus(III) hydride is a colourless and poisonous gas. It has a characteristic smell like that of rotting fish. Unlike ammonia, it dissolves only slightly in water to form a neutral solution. This is because phosphorus(III) hydride does not form hydrogen bonds with water as readily as ammonia.

Thermal decomposition

Phosphorus(III) hydride decomposes in the same way as ammonia but at a lower temperature of 440 °C. This reaction is exothermic, whereas the decomposition of ammonia is endothermic.

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g),\ \Delta H = -ve$$

Reaction with oxygen

Pure phosphorus(III) hydride is not spontaneously inflammable in air, but it will readily burn in air, even explosively, at about 150 °C. Phosphorus(V) oxide and steam are formed which react further to give tetraoxo-phosphate(V) acid.

$$4PH_3(g) + 8O_2(g) \rightarrow P_4O_{10}(s) + 6H_2O(g) \rightarrow 4H_3PO_4(aq)$$

Reducing action

Phosphorus(III) hydride is a strong reducing agent which reduces solutions of silver or copper(II) salts to the metals or phosphides.

$$6AgNO_3(aq) + PH_3(g) + 3H_2O(l) \rightarrow 6Ag(s) + H_3PO_3(aq) + 6HNO_3(aq)$$

It also ignites spontaneously in chlorine, producing phosphorus(III) chloride.

$$PH_3(s) + 3Cl_2(g) \rightarrow PCl_3(l) + 3HCl(g)$$

Basic nature and ability to from complexes

Phosphorus(III) hydride is weakly basic in nature. It forms similar salts to those of ammonia, e.g. phosphonium chloride, PH_4Cl (compare this with NH_4Cl). Phosphonium salts are less common and not as stable as ammonium salts. Phosphorus(III) hydride also does not form many stable complexes, unlike ammonia.

PHOSPHORUS(III) CHLORIDE

Phosphorus forms stable halides with all the halogens. The most commonly known of these is phosphorus(III) chloride, PCl_3. It is prepared by warming white phosphorus with dry chlorine in an inert atmosphere of dry carbon(IV) oxide.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$

Phosphorus(III) chloride is a colourless liquid with a boiling point of 76 °C. It fumes in moist air and reacts with cold water and other compounds containing the hydroxyl group, –OH, replacing it with a chlorine atom. Thus, phosphorus(III) chloride is often used in organic chemistry for preparing alkyl chlorides and acid chlorides. Phosphorus(III) chloride also combines readily with oxygen, sulphur and chlorine to form phosphorus(V) compounds.

$$PCl_3(l) + 3H_2O(l) \rightarrow \underset{\text{trioxophosphate(III) acid}}{H_3PO_3(aq)} + 3HCl(aq)$$

$$3C_2H_5OH(aq) + PCl_3(g) \rightarrow \underset{\text{chlorethane}}{3C_2H_5Cl(g)} + H_3PO_3(aq)$$

PHOSPHORUS(V) CHLORIDE

Phosphorus(V) chloride is prepared by the action of dry chlorine on phosphorus(III) chloride. It is a pale yellow solid which is made up of PCl_4^+ and PCl_6^- ions although the vapour is composed of covalent PCl_5 molecules. Phosphorus(V) chloride fumes in moist air. It sublimes at 160 °C, and when heated further, dissociates into chlorine and phosphorus(III) chloride. Phosphorus(V) chloride is reformed on cooling.

$$PCl_5(s) \underset{\text{cold}}{\overset{\text{heat}}{\rightleftharpoons}} PCl_3(l) + Cl_2(g)$$

Like phosphorus(III) chloride, it reacts violently with cold water and is hydrolyzed to form tetraoxophosphate(V) acid.

$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$$

It also reacts with other compounds containing the hydroxyl group, replacing it with a chlorine atom and liberating hydrogen chloride. As a result, phosphorus(V) chloride can be used as a chlorinating agent. This reaction can be used as a test for hydroxyl groups in straight-chain organic compounds.

$$C_2H_5OH(l) + PCl_5(s) \rightarrow C_2H_5Cl(g) + POCl_3(l) + HCl(g)$$

PHOSPHORUS(III) OXIDE

Phosphorus(III) oxide is an important oxide of phosphorus. It was once thought to be P_2O_3 but is now known to be a dimer with a molecular formula of P_4O_6. It is prepared by burning phosphorus in a limited supply of air. The less volatile phosphorus(V) oxide, P_4O_{10}, which may also be formed as a by-product, can be removed by filtering the vapour through a plug of glass wool. The phosphorus(III) oxide vapour can then be condensed by cooling in a freezing-mixture to form a white volatile solid with the characteristic smell of garlic.

$$P_4(s) + 3O_2(g) \rightarrow P_4O_6(g)$$

Phosphorus(III) oxide is an acid anhydride. It dissolves slowly in cold water to form trioxo phosphate(III) acid, H_3PO_3. With hot water, it reacts vigorously to produce phosphorus(III) hydride and tetraoxo-phosphate(V) acid.

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

cold

$$P_4O_6(s) + 6H_2O(l) \rightarrow 3H_3PO_4(aq) + PH_3(g)$$

hot

Phosphorus(III) oxide is easily oxidized. It burns in air at 60 °C, forming phosphorus(V) oxide.

$$P_4O_6(s) + 2O_2(g) \rightarrow P_4O_{10}(s)$$

PHOSPHORUS(V) OXIDE

Phosphorus(V) oxide, P_4O_{10} is the other important oxide of phosphorus. It is a white solid and is formed when phosphorus burns with a brilliant flame in a plentiful supply of dry air or oxygen. The solid sublimes on heating.

$$P_4(S) + 5O_2(g) \rightarrow P_4O_{10}(g)$$

Phosphorus(V) oxide combines readily with water. It reacts vigorously with cold water, producing a hissing noise and a large amount of heat. It also reacts vigorously with hot water to form tetraoxo-phosphate(V) acid.

$$P_4O_{10}(s) + 2H_2O(l) \rightarrow 4HPO_3(aq)$$

cold

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

hot

Phosphorus(V) oxide is a very effective drying agent and is usually used to remove the last traces of moisture from gases. It is also a dehydrating agent, and it can be used to dehydrate trioxonitrate(V) acid to dinitrogen(V) oxide, N_2O_5 and acid amides to acid nitriles.

$$2HNO_3(aq) \xrightarrow{-H_2O} N_2O_5(g)$$

$$\underset{\text{ethanamide}}{CH_3CONH_2(s)} \xrightarrow{-H_2O} \underset{\text{ethanonitrile}}{CH_3CN(l)}$$

TRIOXOPHOSPHATE(III) ACID

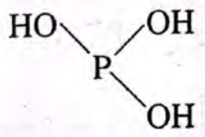
Trioxophosphate(III) acid, H_3PO_3, is the most important acid based on phosphorus(III) oxide. It can be prepared from the oxide by the action of cold water or by hydrolysis of phosphorus(III) chloride.

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

cold

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$$

Pure trioxophosphate(III) acid is a deliquescent solid. It dissolves readily in water to form a moderately strong acid solution. The acid has a basicity of two i.e. it possesses two ionizable hydrogen atoms. Therefore, it is thought to have only two hydroxyl groups. Thus its structural formula may be represented as shown below.

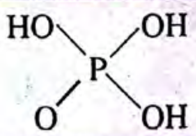


Trioxophosphate(III) acid is a strong reducing agent. When heated to 200 °C, it decomposes to phosphine, which is also a powerful reducing agent, and tetraoxophosphate(V) acid.

$$4H_3PO_3(s) \rightarrow PH_3(g) + 3H_3PO_4(s)$$

TETRAOXOPHOSPHATE(V) ACID

There are three acids based on phosphorus(V) oxide, each differing from the others only in the degree of hydration of the oxide. The most hydrated and most important of these is tetraoxophosphate(V) acid, H_3PO_4, which has the following structure.



$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

Preparation

Tetraoxophosphate(V) acid is prepared in the laboratory by the action of concentrated trioxonitrate(V) acid on red phosphorus. Commercially, the pure acid is obtained by igniting white phosphorus in a plentiful supply of air and then dissolving the phosphorus(V) oxide produced in water. Sometimes, it is also prepared by treating rock phosphate, i.e. calcium tetraoxophosphate(V) with 60% tetraoxosulphate(VI) acid.

$$\underset{\text{rock phosphate}}{Ca_3(PO_4)_2(S)} + 3H_2SO_4(aq) \rightarrow 3CaSO_4(s) + 2H_3PO_4(aq)$$

Properties

Tetraoxophosphate(V) acid is a colourless crystalline solid. It is frequently found as a concentrated viscous solution because of its deliquescence. Tetraoxophosphate(V) acid is a weak acid with a basicity of three. It ionizes successively in three stages as follows:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$
$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

It can thus form three series of salts, i.e. tetraoxophosphates(V), by neutralization.

When heated, tetraoxophosphate(V) acid is progressively dehydrated. These changes are reversible.

$$2H_3PO_4(s) \overset{200\ ^\circ C}{\rightleftharpoons} H_4P_2O_7(s) + H_2O(l)$$
$$\rightleftharpoons 2HPO_3(s) + 2H_2O(l)$$

TETRAOXOPHOSPHATES(V)

The tetraoxophosphates(V) come in three forms, for example, sodium dihydrogen tetraoxophosphate(V), NaH_2PO_4, sodium hydrogen tetraoxophosphate(V), Na_2HPO_4, and sodium tetraoxophosphate(V), Na_3PO_4. Two important tetraoxophosphates(V) are ammonium and calcium tetraoxophosphates(V).

Uses

1 The most important use of tetraoxophosphates(V) is in the manufacture of inorganic fertilizers.

Fertilizers Fertilizers which contain essential plant nutrients, are added to the soil to promote the healthy growth of plants. The three most important plant nutrients are nitrogen, phosphorus and potassium. The plants absorb the soluble salts of these elements.

The supply of plant nutrients in the soil is continuously being depleted through absorption by plants, soil erosion and other processes. This supply must be replenished by the use of fertilizers. In Nigeria, the commonly used inorganic fertilizers contain nitrogen, phosphorus and potassium (or NPK) in definite proportions.

Several phosphorus compounds are used as fertilizers to replenish the level of phosphorus in the soil. Calcium tetraoxophosphate(V), in the form of bone ash or rock phosphate, is not very useful because it is insoluble. Instead, the compound is treated with 65% tetraoxo-sulphate(VI) acid to form a mixture of calcium dihydrogen tetraoxophosphate(V) and calcium tetraoxosulphate(VI). This mixture, known as *superphosphate,* is one of the most commonly used phosphorus fertilizer. A more effective fertilizer, known as *triple phosphate,* can be made by treating calcium tetraoxophosphate(V) with tetraoxophosphate(V) acid. Another commonly used fertilizer is ammonium tetraoxophosphate(V), which also contains nitrogen. Nitrogenous fertilizers include ammonium compounds and trioxonitrates(V) while potassium is usually supplied as potassium tetraoxo-sulphate(VI).

$$Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \rightarrow \underbrace{Ca(H_2PO_4)_2(s) + 2CaSO_4(s)}_{\text{superphosphate}}$$

$$Ca_3(PO_4)_2(s) + 4H_3PO_4(aq) \rightarrow \underset{\text{triple phosphate}}{3Ca(H_2PO_4)_2(s)}$$

2 Tetraoxophosphate(V) acid and its salts are used in processed foods and drinks and in the making of baking powder and self-raising flour.

3 The acid and its salts are also used
- in making enamels, matches and glazes for pottery;
- refining petroleum;
- for fireproofing textiles and timber;
- for rustproofing steel articles before painting;
- as catalysts, water-softeners and detergents.

Intensive crop cultivation decreases soil fertility. Fertilizers are added to the soil to replenish the essential plant nutrients

SUMMARY

- Phosphorus is a non-metallic element belonging to Group 5 of the Periodic Table. It has five valence electrons and forms 3- and 5-covalent compounds.
- There are three allotropic forms of phosphorus, namely white, red and black phosphorus.
- Phosphorus reacts with oxygen to form oxides; sulphur to form sulphides; metals to form phosphides; chlorine to form chlorides; and hydrogen to form phosphine. It also reacts with alkalis. Phosphorus is a good reducing agent.
- Important compounds of phosphorus are tetraoxophosphate(V) acid and the tetraoxophosphates(V). They are especially important in the manufacture of fertilizers.

EXERCISES

1. One of the commonest allotropes of phosphorus is white phosphorus. Solvent for sulphur and phosphorus is
   A benzene.
   B carbon tetrachloride.
   C carbon IV sulphide.
   D methyl benzene.

2. White phosphorus is stored in the lab
   A under paraffin oil.
   B in desicator.
   C under water.
   D in the fume chamber.

3. Which allotrope of carbon is the most stable at room temperature?
   A White phosphorus
   B Red phosphorus
   C Black phosphorus
   D Yellow phosphorus

4. Phosphorus used in making safety matches is red phosphorus because
   A it is stable when mixed with oxidizing agents.
   B it has low ignition temperature.
   C it has low specific heat capacity.
   D it has high ignition temperature.

The following are drying agents except

A P_2O_5
B $CaCl_2$
C silica gel.
D NaOH pellets.

Which of these compounds is not used as a fertilizer?

A Potassium tetraoxosulphate(VI)
B Carbamide
C Ammonium tetraoxophosphate(V)
D Ammonium trioxonitrate(V)
E Sodium hydroxide

White phosphorus is stored under water because it

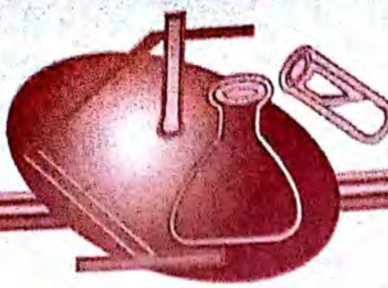
A is corrosive.
B has a low ignition temperature.
C reacts with carbon(IV) oxide.
D is poisonous.
E is hydrolyzed by atmospheric moisture.

8. Discuss the inclusion of nitrogen and phosphorus in the same group of the Periodic Table by comparing the physical and chemical properties of

(a) the two elements;
(b) their hydrides; and
(c) their chlorides.

9. Briefly compare and contrast the properties of the oxides and oxyacids of nitrogen and phosphorus.

10. (a) Describe the two main allotropes of phosphorus and compare their properties.
(b) What are the uses of phosphorus and its compounds?



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SILICON AND ITS COMPOUNDS

SILICON

Silicon is a metalloid which belongs to the same group in the Periodic Table as carbon. It does not occur free in nature but is found in the combined form as silicon(IV) oxide and trioxosilicates(IV). In fact, silicon is the second most abundant element in the earth's crust, after oxygen.

Naturally occurring silicon compounds exist mainly as silicon(IV) oxide, SiO_2, and as metallic trioxosilicates(IV). Silicon(IV) oxide, which is commonly called *silica*, may be found in pure crystalline form as *quartz,* and in less pure forms as *flint, opal, horn-stone* and *jasper.* It is also the main constituent of sand and *kieselguhr* (which is a porous material formed from the remains of the small plant organisms known as diatoms). Metallic trioxosilicates(IV) are found in *slate* and igneous rocks like *granite and basalt,* while *clay* and *kaolin* consist mainly of hydrated aluminium trioxosilicate(IV).

Preparation

Amorphous silicon may be prepared by heating a mixture of pure dry sand and magnesium powder in a fire-clay crucible. The reaction is very violent and should be performed carefully. Dilute hydrochloric acid is then added to dissolve any unreacted magnesium and compounds of magnesium that are formed. The residue that is left behind contains mainly silicon.

$$SiO_2(s) + 2Mg(s) \rightarrow 2MgO(s) + Si(s)$$

Crystalline silicon is manufactured by heating crushed coke (carbon) and an excess of sand in an electric furnace. The product has a purity of 98% and is suitable for making alloys.

$$SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$$

Very pure silicon is manufactured by heating silicon(IV) chloride, $SiCl_4$, with zinc; or reducing trichlorosilane, $SiHCl_3$, with hydrogen at a high temperature.

$$SiCl_4(l) + 2Zn(s) \rightarrow Si(s) + 2ZnCl_2(s)$$
$$SiHCl_3(l) + H_2(g) \rightarrow Si(s) + 3HCl(g)$$

Properties

Silicon, like carbon, is a non-volatile solid with a very high melting point. It is also insoluble in most of the common solvents. However, unlike carbon, silicon does not exhibit the phenomenon of allotropy, although it can exist either as a brown amorphous powder or as grey, lustrous crystals. Both forms are not regarded as allotropes since they possess the same diamond-like structure.

Silicon has the same valency as carbon and forms analogous compounds. Amorphous silicon, however, is more reactive than graphite and crystalline silicon.

Action of heat

When heated strongly in air, silicon forms silicon(IV) oxide, which is a white solid. Graphite too reacts in a similar way to form an oxide, but at a higher temperature.

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$

Reaction with steam and chloride

Silicon decomposes steam at red heat to liberate hydrogen. It also combines with chlorine under similar conditions to form silicon tetrachloride. Graphite also reacts with steam in a similar way to form hydrogen, but it does not react with chlorine.

$$Si(s) + 2H_2O(g) \rightarrow SiO_2(s) + 2H_2(g)$$
$$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$$

Reaction with concentrated alkalis

Silicon dissolves in hot concentrated sodium or potassium hydroxide solution to yield the corresponding trioxosilicates(IV) with the evolution of hydrogen. Graphite does not give this reaction.

$$Si(s) + 2NaOH(aq) + H_2O(l) \rightarrow Na_2SiO_3(aq) + 2H_2(g)$$
$$Si(s) + 2KOH(aq) + H_2O(l) \rightarrow K_2SiO_3(aq) + 2H_2(g)$$

Uses

1. Silicon is used in bronze and steel alloys to increase their tensile strength.
2. Very pure silicon is used in making semiconductors which are of great importance in the computer and electronics industries. Advances in technology have made it possible to create very complex integrated circuits (with more than a million components) on a wafer-thin silicon crystal or chip. A whole range of integrated circuits can be combined to give the microprocessor which forms the core of microcomputers. Microcomputers are used widely in homes, schools, offices and factories to perform a variety of functions from games to controlling industrial "robots".
3. Silicon is used for making silicones, which are rubber-like liquids or solids that are insoluble in water and chemically unreactive. They are used as lubricants, water repellents and electric insulators, and in paints, varnishes and polishes.

SILICON(IV) OXIDE

Silicon(IV) oxide or silica occurs naturally in three main crystalline forms, namely *quartz, tridymite* and *crystobalite*. The commonest of these is quartz. Silicon(IV) oxide can be prepared by heating silicon in air. It can also be obtained in a hydrated form, as a gelatinous precipitate, by warming sodium trioxosilicate(IV) with concentrated hydrochloric acid.

$$Na_2SiO_3(aq) + 2HCl(aq) \rightarrow SiO_2.H_2O(s) + 2NaCl(aq)$$

Physical Properties

1. Silicon(IV) oxide exists as a colourless crystalline solid when pure.
2. It is a macromolecular compound, with the silicon and oxygen atoms linked together covalently in tetrahedral basic units. In crystobalite, these units are joined as in diamond, while in quartz and tridymite they are arranged spirally around an axis. Because of its structure, silicon(IV) oxide is non-volatile and hard (unlike carbon(IV) oxide, the analogous oxide of silicon, which is a gas at ordinary temperatures).
3. Silicon(IV) oxide melts at about 1 500 °C. When cooled, it forms a glass-like solid known as *fused silica* (also called *quartz glass*) which has a very low coefficient of expansion and so is very heat-resistant. In addition, fused silica is also acid-resistant and is frequently used in making laboratory apparatus.

Chemical Properties

Reaction with hydrofluoric acid

Silicon(IV) oxide is insoluble in water and in all acids except hydrogen hexafluorosilicates(IV).

$$SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(aq) + 2H_2O(l)$$

Reaction with concentrated alkalis

Silicon(IV) oxide is an acidic oxide. It dissolves in hot concentrated potassium or sodium hydroxide solution to form the corresponding trioxosilicates(IV) and water.

$$2KOH(aq) + SiO_2(s) \rightarrow K_2SiO_3(aq) + H_2O(l)$$

Heating with metallic salts

Silicon(IV) oxide is not volatile. When it is heated strongly with metallic salts, it displaces the more volatile acidic oxides to form the corresponding trioxosilicates(IV). The displaced oxides come off as gases or vapours.

$$SiO_2(s) + Na_2CO_3(s) \rightarrow Na_2SiO_3(s) + CO_2(g)$$
$$SiO_2(s) + Na_2SO_4(s) \rightarrow Na_2SiO_3(s) + SO_3(g)$$

Combination reactions

Silicon(IV) oxide also combines with metallic oxides at high temperatures to form trioxosilicates(IV).

$$SiO_2(s) + CaO(s) \rightarrow CaSiO_3(s)$$

Reaction with carbon

Silicon(IV) oxide reacts with carbon at high temperatures to give silicon carbide, SiC. The carbide is used in the manufacture of abrasives because of its hardness.

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g)$$

Uses

1 Silicon(IV) oxide, as sand, is widely used in making mortar, cement, concrete, glass and refractory silica bricks.
2 Fused silica is used in making optical lenses and prisms, heat-resistant articles, and other scientific apparatus. Very fine threads of fused quartz are very strong. They are used to suspend component parts in electrical instruments.
3 Large quartz crystals are used for lenses of optical instruments, since they are transparent to ultraviolet light. Quartz crystals are also used for accurate control of the frequency of radio transmitters.
4 Powdered quartz is used in the making of silicon carbide, silicon tetrafluoride, sodium trioxosilicate(IV), and silica bricks for lining furnaces.
5 Kieselguhr absorbs liquids readily, and is used as an absorbent for nitroglycerine (explosive) in the making of dynamite. It is also used in medicine for making dry antiseptic dressings.

TRIOXOSILICATES(IV)

Trioxosilicates(IV) are salts of trioxosilicate(IV) acid, H_2SiO_3. They occur abundantly in nature, for example, as trioxosilicates(IV) of iron, aluminium and magnesium, which form the bulk of all structural materials in the earth's crust, and as gem-stones like jade and emerald. Some trioxosilicates(IV) are also manufactured industrially. All trioxosilicates(IV) are insoluble in water, except those of the alkali metals. All trioxosilicates(IV) are thermally stable.

Sodium trioxosilicate(V)

Sodium trioxosilicate(IV), Na_2SiO_3, is made by strongly heating two parts by mass of silicon(IV) oxide with one part by mass of sodium trioxocarbonate(IV) until the mixture melts.

$$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(s) + CO_2(g)$$

It is obtained as a colourless glass-like solid with a melting point of 1 090 °C.

Water-glass Sodium trioxosilicate(IV) dissolves in hot water under pressure to form a viscous liquid which is known as *water-glass*. Water-glass is used for sizing paper, for the fire-proofing of wood and textiles and for making glue. Eggs are preserved by immersing them in a solution of water-glass to form insoluble calcium trioxosilicate(IV). This blocks up the tiny pores in the egg shell and prevents germs from entering the egg, thus preserving it. A dilute solution of water-glass can be used to make a silica garden or chemical garden.

Silica gel On acidification, a solution of waterglass sets into a gel, $SiO_2.xH_2O$. When this gel is heated until it is almost completely dehydrated, a hard porous material, known as silica gel, is obtained. Due to its large surface area, silica gel is a good absorbent. It is used to dry gases, recover valuable vapours from industrial effluents and refine petroleum.

Glass

Glass is made up of a mixture of metallic trioxosilicates(IV). It is prepared by heating a mixture of silicon(IV) oxide and the appropriate metallic oxides and trioxocarbonates(IV) at 1 300–1 400 °C. Small quantities of powdered glass and coke are usually added to improve the quality. The quality of the glass produced is dependent on its composition. The following are some of the common types of glass.

Lime-soda glass Ordinary glass is also called lime-soda glass because it is made from a mixture of silica, washing soda and limestone. On heating this mixture, carbon(IV) oxide is evolved, leaving behind a mixture of sodium and calcium trioxosilicates(IV).

$$Na_2CO_3(s) + SiO_2(s) \rightarrow Na_2SiO_3(s) + CO_2(g)$$
$$CaCO_3(s) + SiO_2(s) \rightarrow CaSiO_3(s) + CO_2(g)$$

Ordinary glass is soft, i.e. it is easily scratched, and it melts at low temperatures. It is also easily cracked by sudden changes in temperature. This is because glass, being a poor conductor of heat, does not expand or contract uniformly. This sets up a strain in the glass which causes it to break easily. A harder glass can be obtained by using potassium trioxo-carbonate(IV) instead of sodium trioxocarbonate(IV), or by increasing the proportion of silicon(IV) oxide.

Flint glass Flint glass contains trioxosilicates(IV) of lead. It has a high refractive index and looks brilliant when cut. It is used in prisms and achromatic lenses because it has a higher refractive index than other types of glass.

Heat-resistant glass This type of glass is prepared by using about 80% of silicon(IV) oxide, 12% of boron(III) oxide and small amounts of sodium and aluminium oxides. It has a higher softening point and a lower coefficient of expansion than ordinary glass. It is used for making laboratory apparatus and cooking utensils. *Pyrex* is an example of heat-resistant glass.

Coloured glass The different colours of glass are produced by the addition of small quantities of suitable metallic compounds to molten glass.

Glass does not possess a sharp melting point. Instead, it slowly softens before turning into a liquid when it is heated. Glass is frequently described as a super-cooled liquid because its molecules are randomly arranged as in a liquid and not in a definite crystalline form as in a solid.

The softening of glass before it melts is an important property because it allows glass to be shaped as desired (by blowing or pressing). All glass articles made by these processes should be *annealed*, i.e. it has to be heated until it is near its softening point and then allowed to cool slowly and uniformly so that no stress is set up within the glass. Otherwise, the glass will shatter easily.

Clay

Clay is formed by the weathering of certain silicate rocks, which slowly break down to fine particles of hydrated aluminium trioxosilicates(IV) and silicon(IV) oxide. It is usually coloured by impurities, e.g. iron(III) oxide. The purest form of clay is china clay or kaolin, which is white and soft. Like graphite, clay is made up of layers of molecules, loosely bound to each other, making it slippery and plastic.

Clay is used in various types of pottery and ceramics. During the manufacturing process, the clay mixture is heated strongly or fired to the appropriate temperature to drive off all water of hydration. The product is a hard infusible solid which does not hydrate on cooling again. Clay is also used in the making of tiles, bricks and cement, and as fillers for paper, rubber, soap and paint. Cement is made by heating clay with limestone.

Zeolites and resins

Aluminotrioxosilicates(IV) or zeolites are used as water softeners while sodium aluminium trioxosilicates(IV) are used as resins in ion-exchange columns for removal of calcium ions.

SUMMARY

- Silicon is a metalloid used as a semi-conductor in the electronics and computer industries.
- Silicon(IV) oxide or silica is found in large amounts in sand. It also occurs naturally in the pure crystalline form as quartz. Silica is used in making mortar, cement, concrete and glass.
- Trioxosilicates(IV) are used together with silica to make glass.
- Clay consists mainly of hydrated aluminium trioxosilicates(IV) and silica. It is used in pottery and ceramics.

EXERCISES

1. The purest form of silica is
A flint. B opal.
C quartz. D $ZnSiO_3$

2. Silicon (Si) may be prepared in the laboratory from the following equations except
A pure dry sand + magnesium.
B silicon IV oxide + coke.
C silicon IV chloride + zinc.
D silicon III chloride + hydrogen.

3. Though carbon and silicon appear in the same group of the periodic table, they differ extensively from each other because
A silicon is a metalloid but carbon is not.
B carbon exhibits allotropy but silicon does not.
C silicon is volatile but carbon is not.
D carbon is more abundant in nature than carbon.

4. Solvent for silicon II oxide is
A HF B CCl_4
C CS_2 D Benzene.

5. Water glass is a
A solid.
B amorphous solid.
C viscous liquid.
D brittle cast.

6. Silica gel is commonly used in packaging electronics because
A it extends the life of the integrated circuits in them.
B it keeps away rats and cockroaches.
C it is stable in porous packs.
D it is hygrocopic.

7. Discuss the chemistry of carbon and silicon in relation to their position in the Periodic Table.

8. What are the various uses of silicon and its compounds?

SECTION
THREE

METALS

Note Hydrogen, which is usually considered as a on-metal, is the only exception to this definition as it is usually an electron donor.

Some characteristic chemical properties of metals re as follows.

nization behaviour Metallic atoms have few alence electrons, and so have a great tendency to nize and form positive ions by losing electrons, i.e. ey are electropositive, e.g.

$$Na \rightarrow Na^+ \text{ (univalent)} + e^-$$
$$Zn \rightarrow Zn^{2+} \text{ (divalent)} + 2e^-$$
$$Al \rightarrow Al^{3+} \text{ (trivalent)} + 3e^-$$

hese positive ions usually enter into chemical mbinations with negative ions or radicals (mainly mposed of non-metals) to form electrovalent mpounds.

The atoms of non-metals usually have four to ven valence electrons. Those with six or seven lence electrons have a great tendency to ionize by cepting electrons to form negative ions, i.e. they e electronegative, e.g.

$$Cl_2 + 2e^- \rightarrow 2Cl^- \quad \text{(univalent)}$$
$$S + 2e^- \rightarrow S^{2-} \quad \text{(divalent)}$$

hese negative ions enter into chemical combination ith positive ions or groups to form electrovalent mpounds. Those atoms with four or five valence lectrons share electrons during chemical reactions form covalent compounds.

educing and oxidizing agents Metals are reducing gents by definition because they tend to donate their lectrons readily during chemical reactions. On the ther hand, non-metals are oxidizing agents because hey accept electrons readily during chemical eactions. Thus, in the formation of sodium oxide, odium (metal) acts as a reducing agent while oxygen (non-metal) acts as an oxidizing agent.

$$2Na(s) + \frac{1}{2} O_2(g) \rightarrow {Na^+}_2O^{2-}(s)$$

Reaction with acids A metal which is more electropositive than hydrogen readily displaces the hydrogen ion, H^+, from an acid. This is a redox reaction with

- the metallic atoms donating electrons to form metallic ions, and
- the hydrogen ions accepting electrons to form gaseous hydrogen.

For hydrochloric acid and zinc, the reaction is:

Oxidation $Zn \rightarrow Zn^{2+} + 2e^-$

Reduction $2H^+ + 2e^- \rightarrow H_2$

Overall reaction

$$Zn(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Zn^{2+}(Cl^-)_2(aq) + H_2(g)$$

A non-metal cannot displace the hydrogen from an acid.

Nature of the oxides Most metals react with oxygen to form basic oxides which are mainly ionic compounds. Soluble basic oxides form alkalis, e.g.

$$Ca(s) + \frac{1}{2}O_2(g) \rightarrow Ca^{2+}O^{2-}(s)$$
$$Ca^{2+}O^{2-}(s) + H_2O(l) \rightarrow Ca^{2+}(OH^-)_2(aq)$$

Some metals like aluminium and zinc, however, form amphoteric oxides.

Non-metallic oxides are covalent compounds formed by electron sharing. The non-metallic oxides in which the non-metal exercises its maximum valency dissolve in water to give an acidic solution, due to the formation of hydrogen ions, H^+. Examples include carbon(IV) oxide, CO_2, and sulphur(VI) oxide, SO_3.

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq) \rightarrow 2H^+(aq) + CO_3^{2-}(aq)$$

Other non-metallic oxides are either acidic, e.g sulphur(IV) oxide, SO_2, or neutral, e.g. carbon(II) oxide, CO.

Comparing the Properties of Metals

Metals differ in their ability to lose the valence electrons in their atoms to form positive ions. As a result, they can be arranged in a series according to

Table 26.1 Activity series of metals showing their properties

Activity series of metals		Electro-positivity	Chemical activity	Combustion	Action with water	Action with dilute acids	Action with concentrated acids			Action with other metallic salts
							HCl	H_2SO_4	HNO_3	
Potassium	**K**	Decreasing electropositivity ↓	Decreasing chemical activity ↓	Burn readily in air to form the oxide	Displace oxygen from cold water	React to form hydrogen and a salt (Al reacts only with dilute HCl)	React to form hydrogen and a salt	React to form SO_2		Each metal will displace a metal lower in the series from a solution of a salt of the lower metal
Sodium	**Na**									
Calcium	**Ca**									
Magnesium	**Mg**				Displace hydrogen from steam at red heat				No reaction	
Aluminium	**Al**								Forms N_2O	
Zinc	**Zn**								No reaction	
Iron	**Fe**			Form the oxide when heated in air	Do not react with cold water or steam	No reaction (Pb reacts with dilute HNO_3 to form the oxides of nitrogen)			React to form NO or NO_2 depending on the acid concentration	
Tin	**Sn**						No reaction			
Lead	**Pb**									
Copper	**Cu**									
Mercury	**Hg**									
Silver	**Ag**			No reaction with oxygen						
Gold	***Au***							No reaction	No reaction	

Table 26.2 Activity series of metals showing the nature of some of their compounds

Activity series of metals		Reaction of the oxide			Characteristics of			Solubility of chloride	Solubility of sulphide
		with water	with heat	with carbon	hydroxide	trioxocarbonate(IV)	trioxonitrate(V)		
Potassium	K	Dissolve to form hydroxides	Stable to heat	Not reduced when heated	Soluble in water; stable to heat	Soluble in water; stable to heat	Decomposed to dioxo-nitrate(III) and O_2 by heat	Soluble in water	Soluble in water, except $PbCl_2$ which i insoluble in cold water but slightly soluble in warm water
Sodium	Na								
Calcium	Ca				Insoluble in water except $Ca(OH)_2$ which is sparingly soluble; decomposed to the oxide by heat	Insoluble in water; decomposed to the oxide, and CO_2 by heat; $Al_2(CO_3)_3$ does not exist		Insoluble in water; soluble in dilute HCl	
Magnmium	Mg	Insoluble							
Aluminium	Al			Reduced to the metal when heated					
Zinc	Zn						Decomposed to the oxide, NO_2 and O_2 by heat		
Iron	Fe								
Tin	Sn							*Insoluble in water and dilute HCl*	
Lead	Pb								
Copper	Cu								Insoluble in water
Mercury	Hg		Decomposed to the metal		Hydroxides do not exist	Insoluble; decomposed to the metal, CO_2	Decomposed to the metal, NO_2 and O_2 by heat		
Silver	Ag								
Gold	Au								

Metal		Reactivity	Process	$E^{\ominus}$ in volts
Potassium	K	Very reactive	$K^+ + e^- \rightarrow K$	−2.92
Sodium	Na		$Na^+ + e^- \rightarrow Na$	−2.71
Calcium	Ca		$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87
Magnesiun	Mg		$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
Aluminium	Al	Moderately reactive	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
Zinc	Zn		$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
Iron	Fe		$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
Tin	Sn		$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
Lead	Pb		$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
Hydrogen	**H**		$\mathbf{2H^+ + 2e^- \rightarrow H_2}$	**0.00**
Copper	Cu	Least reactive	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Mercury	Hg		$Hg^+ + e^- \rightarrow Hg$	+0.62
Silver	Ag		$Ag^+ + e^- \rightarrow Ag$	+0.80
Gold	Au		$Au^{3+} + 3e^- \rightarrow Au$	+1.50

NOTE $E^{\ominus}$ is the standard electrode potential.

their comparative tendencies to give up their valence electrons (i.e. according to their electropositivity). This series is known as the *electrochemical series*. The relative position of a metal in the series indicates the chemical activity of the metal as well as the chemical properties of its compounds. A similar series is the *activity series of metals*.

Tables 26.1 and 26.2 show the positions of the common metals in the activity series, and the gradation in some of the properties of these metals and their compounds. Table 26.3 compares the activity series of metals with the electrochemical series which is based on the standard electrode potential values of elements. From this table, we note that the more reactive metals are the ones that have highly negative electrode potential values.

EXTRACTION OF METALS

More than 80 of the known elements are metals. They are widely distributed in the earth's crust either as free metals or in combination with other elements. The form in which a metal exists in nature is related to its reactivity. The most reactive metals, e.g. sodium and potassium, are found as chlorides or trioxocarbonates(IV), which are very stable compounds; the moderately reactive metals, e.g. zinc and lead, are found as oxides or sulphides; while the least reactive metals like gold and silver are found in the uncombined state.

Preliminary preparation

Most metals are found in combined forms of more or less definite chemical composition known as *minerals*. Often, these minerals are found mixed with earthy material as *ores*. Ores are usually

- concentrated, and
- changed to oxides before extraction.

Concentration of the ore

Ores may be concentrated by one of these ways:

- washing away the earthy material in a stream of water to leave behind the heavier ores, as in the case of tin ore.
- By froth-flotation, as in the case of zinc ore. The ore is churned up with oil and water to form a froth. The froth, which contains the ore, is skimmed off by blowing air.
- By passing ores which are magnetic, e.g. copper ore, through a magnetic separator. Ores with a

Electronic configurations and related properties of some Group 1 metals

al		Electronic configuration	First ionization energy (kJ mol⁻¹)	Atomic radius (nm)
Lithium	Li	$1s^2\ 2s^1$	519	0.133
Sodium	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$	498	0.157
Potassium	K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	419	0.203

athode acts as a reducing region by supplying ectrons to the metallic ions in the electrolyte, sulting in the deposition of the free metal. The ectrolyte is usually a salt of the metal, e.g. a chloride r an oxide, with a high melting point.

Electrolytic processes are expensive to install and aintain. They are used only when chemical or ermal reduction of the ores is not possible.

ROUP 1 ELEMENTS

ith the exception of hydrogen, all Group 1 elements e metals. They include lithium, sodium and assium, known as the *alkali metals* since they react th water to form alkalis. They exhibit similar ysical and chemical properties.

The atoms of Group 1 metals have only one ectron in their outermost shells. They are very ectropositive, and ionize to form univalent positive ns. They are very good reducing agents.

The metallic bonding in the crystal lattices of roup 1 metals is weak because each atom in the ystal can only contribute one valence electron for e electron cloud that forms the metallic bond. As a sult, Group 1 metals tend to be soft and light with w melting points.

As we go down Group 1, the atoms of the elements crease in size, so there is also a decrease in the rength of the electrostatic attraction between the lence electrons and the nuclei of the atoms. Thus, e first ionization energy, i.e. the energy required to move one electron from the atom, decreases down e column resulting in a corresponding increase in emical reactivity.

The relative reactivities of the alkali metals are flected by their reactions with water. Thus, potassium reacts explosively with water, while sodium reacts vigorously and lithium readily.

$$2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$$
$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$
$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

All alkali metals and their ions give characteristic flame colours which are used to identify them.

SODIUM

Sodium is a typical member of Group 1. It does not occur as the free metal in nature because it is too reactive. It is found in sea water as sodium chloride, sodium bromide and sodium iodide. It also occurs in deposits as sodium chloride (rock salt), sodium trioxonitrate(V) and sodium trioxocarbonate(IV). Sodium trioxonitrate(V) is often known as *Chile saltpetre* because it is found abundantly in Chile. Sodium also occurs in borax, and in complex trioxosilicates(IV) found in clay soil.

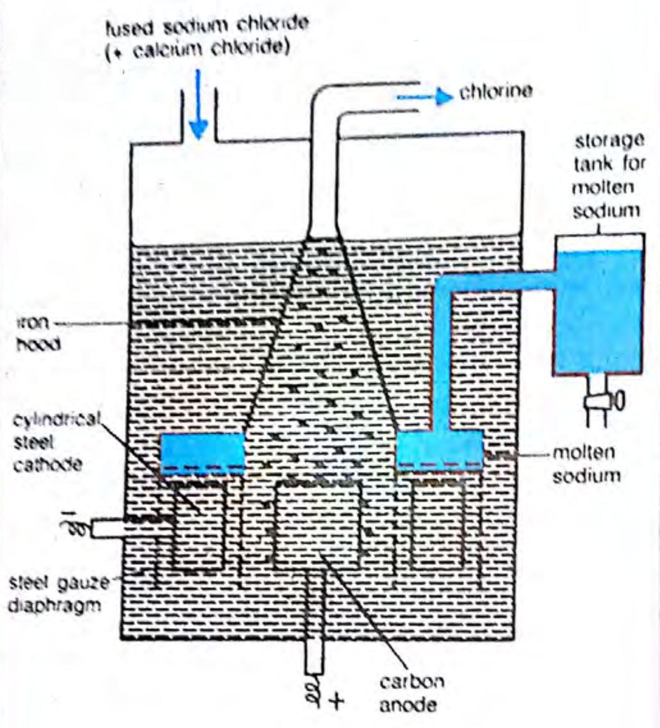
Extraction

Sodium is extracted commercially from fused sodium chloride by electrolysis using the *Downs cell*. The Downs cell consists of a rectangular steel container lined on the inside with firebricks. The anode is a graphite rod which projects centrally up through the base of the cell, while the cathode is a steel cylinder surrounding the anode. Fused sodium chloride (m.p. 801 °C) is placed in the cell and heated electrically to keep it molten. To make the process economically more feasible, calcium chloride is usually added to lower the melting point of sodium chloride to about 600 °C. The anode and cathode are screened from each other by a cylindrical steel gauze diaphragm so that the two products of electrolysis, namely sodium and chlorine, are kept apart and can be collected separately.

During electrolysis, the molten sodium collects in the cathode compartment where it rises to the top and is tapped off via a pipe. Gaseous chlorine, the by-product which forms at the anode, is guided by a hood and collected from another pipe.

Chemistry of the reaction Fused sodium chloride contains sodium and chloride ions.

Fig. 26.1 Extraction of sodium (Downs cell).



At the cathode The Na^+ ions receive an electron each, and become reduced to metallic sodium.

$$Na^+ + e^- \rightarrow Na \quad (\textit{Reduction})$$

At the anode The Cl^- ions give up an electron each, and become oxidized to atomic chlorine, which then pair up to form gaseous chlorine molecules.

$$Cl^- \rightarrow Cl + e^- \quad (\textit{Oxidation})$$
$$Cl + Cl \rightarrow Cl_2$$

Overall electrolytic reaction

$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(s) + Cl_2(g)$$

Physical Properties

Appearance	Silvery solid with metallic lustre
Relative density	0.98 (floats on water)
Malleability	Very malleable (very soft)
Melting point	97 °C (low for a metal)
Conductivity	Good conductor of electricity and heat

Chemical Properties

Reaction with air Sodium tarnishes easily when exposed to air because it is readily oxidized by atmospheric oxygen to form sodium oxide. This oxide reacts with water vapour in the air to form sodium hydroxide, which slowly absorbs atmospheric carbon(IV) oxide to form crystals of hydrated sodium trioxocarbonate(IV).

(a) $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

(b) $Na_2O(s) + H_2O(g) \rightarrow 2NaOH(aq)$

(c) $2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(s) + H_2O(l)$

Thus, sodium is always stored under paraffin oil, toluene or naphtha to prevent its oxidation by the atmospheric gases.

When sodium is heated in air, it burns with a golden yellow flame to form sodium peroxide, Na_2O_2. Sodium oxide, Na_2O, is formed only in the presence of a limited supply of air or oxygen.

$$2Na(s) + \underset{\text{excess}}{O_2(g)} \rightarrow Na_2O_2(s)$$

$$Na(s) + \underset{\text{(limited)}}{O_2(g)} \rightarrow Na_2O(s)$$

Combination reactions On heating, sodium combines directly with hydrogen, the halogens, sulphur, phosphorus and most other non-metals (except boron, carbon and nitrogen).

$$2Na(s) + H_2(g) \rightarrow 2NaH(s)$$
$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$
$$2Na(s) + S(s) \rightarrow Na_2S(s)$$
$$3Na(s) + P(s) \rightarrow Na_3P(s)$$

Sodium, dissolves in mercury to give sodium amalgam, which reacts quietly with water to form hydrogen and sodium hydroxide.

$$Na(s) + Hg(l) \rightarrow Na.Hg(l)$$

Reaction with water Sodium reacts violently with cold water releasing a lot of heat. If a small piece of sodium is placed in a trough of cold water, coloured with red litmus, the metal will dart about on the surface of the water, and melt into a silvery ball because of the heat liberated. Hydrogen and sodium hydroxide are formed (see page 337)

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Ionically,

$$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$

Reaction with acids Sodium reacts explosively with dilute acids to form hydrogen and a salt. The reaction is extremely dangerous and should not be carried out in the laboratory.

$$2Na(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2(g)$$

Ionically,

$$2Na(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2(g)$$

Reaction with ammonia Sodium reacts with ammonia to form sodamide and hydrogen.

$$2Na(s) + 2NH_3(g) \rightarrow 2NaNH_2(s) + H_2(g)$$

Test for sodium ions

Flame test Sodium compounds give a golden-yellow colour to a non-luminous flame.

Moisten the unknown compound with a few drops of concentrated hydrochloric acid. Dip the tip of a clean platinum wire into the mixture and hold it in a non-luminous flame. If a golden-yellow flame is produced, view it through a blue glass. If the golden-yellow colour cannot be seen through the blue glass, the presence of sodium ions in the unknown compound is confirmed.

NOTE Potassium gives a lilac flame which looks crimson when viewed through a blue glass.

Uses

1 Sodium is used in manufacturing compounds such as sodium peroxide, sodamide and sodium cyanide. It is also employed in the production of lead(IV) tetraethyl which serves as an anti-knock agent in petrol.
2 Sodium vapour lamps (which give a bright orange-yellow light) are used for lighting highways and airports.
3 Liquid sodium is used as a coolant in nuclear reactors.
4 Mixtures of sodium and ethanol, or sodium amalgam and water are useful reducing agents, especially in organic chemistry. Sodium is also used in the extraction of titanium to reduce titanium tetrachloride to the metal.

COMPOUNDS OF SODIUM

Like all Group I metals, sodium forms ionic compounds with high melting points. These compounds are water soluble and mostly white in colour unless the negative ions are coloured.

Sodium Oxide

Sodium oxide, Na_2O, is prepared by heating sodium peroxide gently with excess sodium, or by burning sodium in a limited supply of air.

$$Na_2O_2(s) + 2Na(s) \rightarrow 2Na_2O(s)$$

It is a colourless solid with strongly basic properties. It reacts violently with water to give the hydroxide solution, and explosively with acids to form salts and water.

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

Sodium Peroxide

Sodium peroxide, Na_2O_2, is prepared by heating sodium in an excess of dry air or oxygen.

$$2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$

It is a pale yellow solid which, on exposure to air, gradually changes to sodium hydroxide and sodium trioxocarbonate(IV). To prevent this from happening, it is stored in air-tight containers.

Sodium peroxide is a strong oxidizing agent used in the production of dyes. It reacts with water to liberate oxygen.

$$2Na_2O_2(s) + 2H_2O(l) \rightarrow 4NaOH(s) + O_2(g)$$

With ice-cold water, however, sodium peroxide reacts to form hydrogen peroxide, and so can be used for bleaching.

$$Na_2O_2(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2O_2(aq)$$

It also produces hydrogen peroxide with cold dilute acids.

$$Na_2O_2(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O_2(aq)$$

Ionically,

$$2O_2^{2-}(s) + 2H^+(aq) \rightarrow H_2O_2(aq)$$

Sodium peroxide is used in air purifiers in submarines and portable breathing apparatus, where it reacts with carbon(IV) oxide, to form oxygen and sodium trioxocarbonate(IV).

$$2Na_2O_2(s) + 2CO_2(g) \rightarrow 2Na_2CO_3(s) + O_2(g)$$

Ionically,

$$2O_2^{2-}(s) + 2CO_2(g) \rightarrow 2CO_3^{2-}(s) + O_2(g)$$

Sodium peroxide oxidizes many organic compounds, often igniting them. Therefore, it should not be left in contact with organic matter like filter-paper, cotton-wool and wood.

Sodium Hydroxide

Preparation

Sodium hydroxide, NaOH, commonly known as *caustic soda*, is industrially manufactured by the electrolysis of brine. In the laboratory, it is prepared by heating an excess of slaked lime with 10% sodium trioxocarbonate(IV) solution. The insoluble calcium trioxocarbonate(IV) that is formed is filtered off, leaving behind a solution of sodium hydroxide, which is concentrated by evaporation.

$$Na_2CO_3(aq) + Ca(OH)_2(s) \rightarrow CaCO_3(s) + 2NaOH(aq)$$

Properties

Sodium hydroxide is a white, crystalline solid. It is deliquescent and melts at about 320 °C without decomposing. It readily dissolves in water with the evolution of a lot of heat, to give a strongly alkaline solution with caustic properties.

CAUTION It is dangerous to handle the solid or i concentrated solutions.

With acids and acidic oxides Sodium hydroxide solution is a strong electrolyte which ionizes completely in solution.

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

It is a typical base, neutralizing all acids.

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O($$

Ionically,

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

Sodium hydroxide reacts with acidic oxides t form sodium salts. For example, it reacts wit sulphur(IV) oxide to form the trioxosulphate(IV) o the hydrogentrioxosulphate(IV) of sodium.

$$2NaOH(aq) + SO_2(g) \rightarrow Na_2SO_3(aq) + H_2O(l)$$
$$NaOH(aq) + SO_2(g) \rightarrow NaHSO_3(aq)$$

It readily absorbs carbon(IV) oxide, a weak acidi oxide, to form sodium trioxocarbonate(IV).

$$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)$$

With ammonium salts Ammonia gas is liberate when sodium hydroxide is heated with an ammoniu salt.

$$NaOH(aq) + NH_4Cl(s) \rightarrow NaCl(aq) + H_2O(l) + NH_3($$

With metals Aluminium and zinc readily dissolve in sodium hydroxide solution to form sodiu aluminate(III) and sodium zincate(II) respectively with the evolution of hydrogen gas.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l)$$
$$\rightarrow 2NaAl(OH)_4(aq) + 3H_2($$

$$Zn(s) + 2NaOH(aq) + 2H_2O(l)$$
$$\rightarrow Na_2Zn(OH)_4(aq) + H_2($$

Note sodium hydroxide should **not** be kept aluminium or zinc containers.

To precipitate hydroxides Sodium hyd solution is often used to precipitate ins hydroxides.

$$ZnSO_4(aq) + 2NaOH(aq) \rightarrow Zn(OH)_2(s) + Na_2SO_4(aq)$$

$$Pb(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Pb(OH)_2(s) + 2NaNO_3(aq)$$

Ionically,

$$Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s)$$
$$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$$

In the case of zinc, aluminium, tin(II) and lead(II) salts, the resultant hydroxides are amphoteric and will redissolve in an excess of sodium hydroxide to form complex salts.

$$Zn(OH)_2(s) + 2NaOH(aq) \rightarrow \underset{\text{(sodium tetrahydroxozincate II)}}{Na_2Zn(OH)_4(aq)}$$

Ionically,

$$Zn(OH)_2(s) + 2OH^-(aq) \rightarrow Zn(OH)_4{}^{2-}(aq)$$

In qualitative analysis, sodium hydroxide is used to precipitate the insoluble hydroxides of metal cations in solution and identify the cations present by

- the colours of the hydroxides; and
- the solubility of the hydroxides in an excess of the alkali.

NOTE Sodium trioxocarbonate(IV) is also used in qualitative analysis to identify metal cations in solution.

With non-metals Sodium hydroxide reacts with a variety of non-metals like the halogens, sulphur, phosphorus and silicon to form sodium salts.

Reaction with glass Molten and concentrated solutions of sodium hydroxide attack glass, forming sodium trioxosilicate(IV). This is why glass stoppers become sealed into reagent bottles containing the concentrated alkali, and burette taps tend to get stuck after the alkali has been used in the burette. This is called etching.

Uses

In the laboratory, sodium hydroxide is commonly used

- as a strong alkali,
- as an analytical and precipitating reagent, and
- for absorbing carbon(IV) oxide.

Industrially, sodium hydroxide is used in

- the making of soap, rayon (artificial silk), paper and a wide variety of compounds like sodium trioxochlorate(V), sodium methanoate and phosphine;
- the purification of bauxite;
- the refining of petroleum;
- the bleaching of cotton textiles.

Sodium Chloride

Sodium chloride, NaCl, known simply as common salt, is found in sea water to the extent of about 3% by mass. In some areas, it occurs as rock salt which can be mined as a solid or pumped out of the ground as brine. In many coastal regions of West Africa, it is obtained by the solar evaporation of sea water. It is usually prepared by neutralizing sodium hydroxide with dilute hydrochloric acid.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

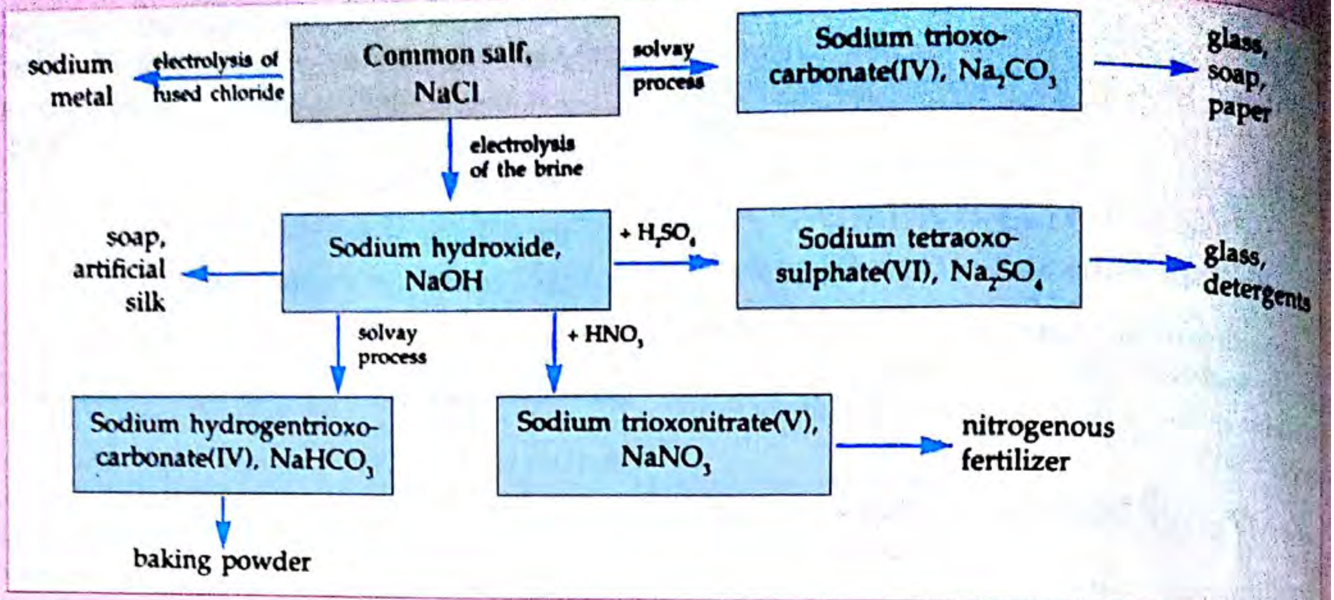
Sodium chloride forms white anhydrous crystals which melt at 801 °C and boil at 1420 °C. The sodium chloride crystal consists of a three-dimensional network of sodium and chloride ions. Pure sodium chloride is not deliquescent but the impure salt may be, due to the presence of magnesium chloride.

Sodium chloride is an essential part of our diet. It is commonly used as a food preservative. It is an important raw material in the chemical industry. It is used to manufacture sodium, sodium hydroxide, chlorine, sodium trioxocarbonate(IV), sodium oxochlorate(I), sodium trioxochlorate(V), and other related compounds. Its other uses are in glazing earthenware, regenerating water softeners and salting out soap.

Sodium Tetraoxosulphate(VI)

Sodium tetraoxosulphate(VI), Na_2SO_4, is prepared in the laboratory by the neutralization of dilute tetraoxosulphate(VI) acid with sodium hydroxide. In industry, it is prepared by heating sodium chloride and concentrated tetraoxosulphate(VI) acid at a high temperature. Sodium hydrogen-tetraoxosulphate(VI) is first formed as the intermediate product.

Fig. 26.2 Some products manufactured from common salt.



$$NaCl(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g)$$
$$NaHSO_4(aq) + NaCl(aq) \rightarrow Na_2SO_4(aq) + HCl(g)$$

Sodium tetraoxosulphate(VI) can exist

- in the anhydrous form known as *salt-cake*, and
- as a decahydrate, $Na_2SO_4.10H_2O$, known as *Glauber's salt*.

The decahydrate is efflorescent, so it loses all its water of crystallization slowly when left exposed to the atmosphere for some time.

Sodium tetraoxosulphate(VI) is used in the production of sodium sulphide. This is done by heating the tetraoxosulphate(VI) with carbon. It is also used as a purgative and in the manufacture of wood pulp, glass and detergents.

Sodium Trioxonitrate(V)

Sodium trioxonitrate(V), $NaNO_3$, occurs naturally as the main component of *caliche* deposits in Chile, and is also known as *Chile saltpetre*. The sodium trioxonitrate(V) is extracted from caliche deposits by dissolving it in hot water and evaporating the solution formed to recover the trioxonitrate(V). In the laboratory, it may be prepared by the action of sodium hydroxide on dilute trioxonitrate(V) acid.

$$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$$

It is a white solid which melts at 310 °C an decomposes on further heating

$$2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$$

It is used as a nitrogenous fertilizer and in makin trioxonitrate(V) acid, potassium trioxonitrate(V) an sodium dioxonitrate(III). The latter is used in th manufacture of aniline dyes. However, bein deliquescent, it cannot be used for making gunpowde

Sodium Trioxocarbonate(IV)

Sodium trioxocarbonate(IV), Na_2CO_3, can exist

- in the anhydrous state known as *soda ash*,
- as a monohydrate, $Na_2CO_3.H_2O$, or
- more often as a decahydrate, $Na_2CO_3.10H_2O$, commonly called *washing soda*.

When soda ash is boiled in water and allowed t cool, it crystallizes as washing soda, which on heatin loses all its water of crystallization to becom anhydrous.

Laboratory preparation

Sodium trioxocarbonate(IV) can be obtained b passing excess carbon(IV) oxide through a solutio of sodium hydroxide. The sodium hydrogentriox carbonate(IV) which is formed as a white precipitat translucent and crystalline. Although the former is slightly less soluble than the latter, both dissolve in water to form an alkaline solution by hydrolysis. Washing soda is efflorescent. When it is left exposed to the atmosphere for some time, it loses nine out of the ten molecules of water of crystallization to form the monohydrate. Unlike most other trioxocarbonates(IV), sodium trioxocarbonate(IV) does not decompose on heating. However, it does react with acids to liberate carbon(IV) oxide.

Uses

Industrially, sodium trioxocarbonate(IV) is used extensively in the manufacture of glass, as a water-softener, in detergents, and in the manufacture of sodium hydroxide, water-glass, borax, soap and paper. In the laboratory, it is used to standardize acids and as an analytical reagent.

Sodium Hydrogentrioxocarbonate(IV)

The most important hydrogentrioxocarbonate(IV) is sodium hydrogentrioxocarbonate(IV), $NaHCO_3$. It is formed as a white precipitate when excess carbon(IV) oxide gas is bubbled through a concentrated solution of sodium hydroxide. It can also be prepared by bubbling carbon(IV) oxide gas through a solution of sodium trioxocarbonate(IV). Industrially, it is made by the Solvay process.

Sodium hydrogentrioxocarbonate(IV) is a white crystalline solid which dissolves slightly in water to give an alkaline aqueous solution because of hydrolysis. It decomposes on heating to liberate carbon(IV) oxide and is used as a constituent of baking powder. (The sodium trioxocarbonate(IV) that is formed is neutralized by an acidic constituent, usually a tarate.) Sodium hydrogentrioxocarbonate(IV) also reacts with acids to form water, carbon(IV) oxide and a salt.

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

COMPOUNDS OF POTASSIUM

Potassium compounds are similar to those of sodium but tend to be less soluble. They are of great importance in agriculture as fertilizers.

Potassium Chloride

Potassium chloride, KCl, is usually found in association with magnesium chloride in a mineral called *carnallite*, $KCl.MgCl_2.6H_2O$. It is prepared by the neutralization of potassium hydroxide with dilute hydrochloric acid. The chloride can then be recovered from the solution as white anhydrous crystals by heating the neutral solution to dryness.

$$KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$$

Potassium chloride is used as a fertilizer and in the manufacture of most other potassium compounds.

Potassium Tetraoxosulphate(VI)

Potassium tetraoxosulphate(VI), K_2SO_4, is another important fertilizer. It is prepared in the laboratory by the neutralization of dilute tetraoxosulphate(VI) acid with potassium hydroxide. In industry, it is prepared by heating potassium chloride with concentrated tetraoxosulphate(VI) acid at a very high temperature. Potassium hydrogentetraoxosulphate(VI) is first formed, but this reacts with more of the potassium chloride to yield potassium tetraoxosulphate(VI) as the final product. The salt is then crystallized out of solution. These crystals contain no water of crystallization, unlike most soluble tetraoxosulphates(VI).

$$KCl(s) + H_2SO_4(aq) \rightarrow KHSO_4(aq) + HCl(g)$$
$$KHSO_4(aq) + KCl(aq) \rightarrow K_2SO_4(aq) + HCl(g)$$

POTASSIUM TRIOXONITRATE(V)

Potassium trioxonitrate(V), KNO_3, is prepared in the laboratory by the neutralization of potassium hydroxide with trioxonitrate(V) acid.

$$KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$$

It is manufactured industrially by boiling saturated solutions of potassium chloride and sodium trioxonitrate(V), both of which are obtained from natural sources. The potassium trioxonitrate(V) formed is then separated out of solution by fractional crystallization.

$$K^+Cl^-(aq) + Na^+NO_3^-(aq) \rightarrow K^+NO_3^-(aq) + Na^+Cl^-(aq)$$

Table 26.6 Electronic configurations and related properties of some Group 2 metals

Metal	Electronic configuration	First ionization energy (kJ mol^{-1})	Atomic radius (nm)
Magnesium Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$	737	0.136
Calcium Ca	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	590	0.174
Strontium Sr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 4p^6\ 5s^2$	549	0.191
Barium Ba	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 4p^6\ 5s^2\ 5p^6\ 6s^2$	502	0.198

At a high temperature, sodium chloride is the least soluble salt present. It crystallizes out and is filtered off. On cooling to room temperature, potassium trioxonitrate(V) becomes the least soluble salt and crystallizes out.

Potassium trioxonitrate(V) is a white solid which melts on heating to form a colourless liquid. This decomposes on further heating to oxygen and potassium dioxonitrate(III) which is a yellow solid when cooled.

Potassium trioxonitrate(V) is also called *nitre*. It is chiefly used in gunpowder, a mixture of nitre, sulphur and charcoal, and in other explosive mixtures. It is also used as a preservative in food industries.

Table 26.7 Relative reactivities of Group 2.

Metal	Ignition in air	Action with water
Magnesium	Ignites above melting point	Reacts with steam
Calcium	Ignites on heating	Reacts steadily with cold water
Barium	Inflames spontaneously	Reacts vigorously with cold water

GROUP 2 ELEMENTS

The Group 2 elements are all metals. They are known as the *alkaline earth metals* and include magnesium, calcium, strontium and barium. The alkaline earth metals are reactive but less so than the alkali metals.

The atoms of the metals in this group have two valence electrons and ionize readily to form divalent positive ions. The metallic bonds in Group 2 metals are stronger than those in Group 1.

Group 2 metals, with their greater ionization energies, are less reactive than the Group 1 metals. As we go down Group 2, the atomic radius increases and the ionization energy decreases resulting in a corresponding increase in the reactivity of the metals from magnesium to barium.

The Group 2 metals tend to form mainly electrovalent compounds. Calcium, strontium and barium and their ions give characteristic flame colours which are used to identify them.

CALCIUM

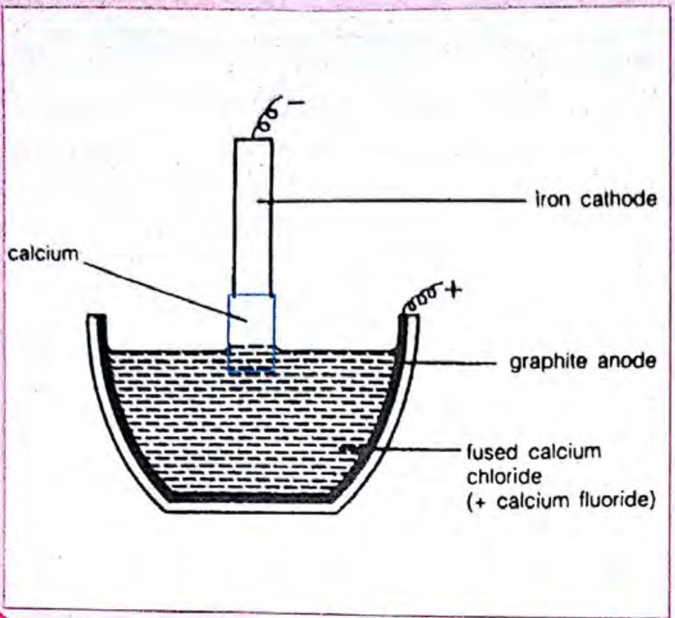
Calcium is too reactive to occur as the free metal in nature. Instead, it occurs abundantly in the combined state as calcium trioxocarbonate(IV), $CaCO_3$, in *limestone*, *marble*, *chalk*, *aragonite*, *calcite* and *coral*; as calcium tetraoxosulphate(VI), $CaSO_4$, in *gypsum* and *anhydrite*; as a double trioxocarbonate(IV), $CaCO_3.MgCO_3$, in *dolomite*; as calcium fluoride, CaF_2, in *fluorspar*; and as various trioxosilicates(IV). Bones and teeth contain calcium tetraoxophosphate(V).

In Nigeria, limestone is found at Nkalagu in Ebonyi State; north of Calabar in Cross River State; at Ewekoro, near Abeokuta, in Ogun State; near Sokoto in Sokoto State; at Ukpilla in Delta State; and in the Benue-Gongola river valleys. In most of these areas, limestone is actively quarried. It is used locally in manufacturing cement.

Extraction

Since calcium compounds are very stable, metallic calcium is commonly extracted electrolytically from fused calcium chloride, a by-product of the Solvay process. Some calcium fluoride is usually added to the fused calcium chloride to lower the melting point from 850 °C to about 650 °C. The mixture is placed in a large crucible, lined on the inside with graphite which serves as the anode of the cell. The cathode consists of an iron rod which just touches the surface of the electrolyte. As electrolysis proceeds, metallic calcium collects on the cathode which is gradually raised so that an irregular stick of calcium is formed on it. Chlorine gas is liberated at the anode.

Fig. 26.4 Extraction of calcium.



Chemistry of the reaction Fused calcium chloride consists of calcium and chloride ions.

At the cathode The calcium ions receive two electrons each to become reduced to the metal.

$$Ca^{2+} + 2e^- \rightarrow Ca \qquad (\textit{Reduction})$$

At the anode Two chloride ions give up an electron each to become atomic chlorine. The two atoms then combine to become liberated as a gaseous molecule.

$$Cl^- \rightarrow Cl + e^- \qquad (\textit{Oxidation})$$
$$Cl + Cl \rightarrow Cl_2$$

Overall electrolytic reaction

$$Ca^{2+}(l) + 2Cl^-(l) \rightarrow Ca(s) + Cl_2(g)$$

Physical Properties

Appearance	Silvery-grey solid
Relative density	1.55
Malleability and ductility	Malleable and ductile
Tensile strength	Relatively low tensile strength
Melting point	851 °C
Conductivity	Good conductor of heat and electricity

Chemical Properties

Reaction with air Calcium is a very electropositive and reactive metal. On exposure to air, it rapidly tarnishes and loses its metallic lustre, due to the formation of a white film of calcium oxide or quicklime on the surface of the metal. In the presence of atmospheric moisture and carbon(IV) oxide, some calcium hydroxide and calcium trioxocarbonate(IV) may also be formed.

When calcium is heated in air, it burns with a brick-red flame to form calcium oxide.

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$
$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$
$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

Reaction with other non-metals On heating, calcium combines directly with nitrogen, chlorine, sulphur and hydrogen.

$$3Ca(s) + N_2(g) \rightarrow Ca_3N_2(s)$$
$$Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$$
$$Ca(s) + H_2(g) \rightarrow CaH_2(s)$$

Reaction with water Calcium reacts slowly with cold water and rapidly with warm water to form calcium hydroxide and hydrogen.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Reaction with acids Calcium reacts vigorously to displace hydrogen from dilute acids.

$$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$$

Reaction with ammonia If ammonia is passed over heated calcium, it reacts as follows:

$$3Ca(s) + 2NH_3(g) \rightarrow \underset{\text{(calcium nitride)}}{Ca_3N_2(s)} + 3H_2(g)$$

Tests for calcium ions

Flame test Calcium compounds give an orange-red colour to a non-luminous flame. Moisten the unknown compound with a few drops of concentrated hydrochloric acid. Dip the tip of a clean platinum wire into the mixture and hold it in a non-luminous Bunsen flame. If a bright brick-red flame is produced, the unknown compound probably contains calcium ions. View the brick-red flame through a blue glass. If the flame appears green, the presence of calcium ions is confirmed.

NOTE Barium gives a pale green flame while strontium gives a bright red flame.

With sodium hydroxide Add a few drops of sodium hydroxide solution to a solution of the unknown salt. The formation of a white precipitate, which is insoluble in excess sodium hydroxide, indicates the presence of calcium ions.

$$2NaOH(aq) + Ca^{2+}(aq) \rightarrow Ca(OH)_2(s) + 2Na^+(aq)$$

With ammonium ethanedioate Add a solution of ammonium ethanedioate to a solution of the unknown salt. The formation of a white precipitate, which is soluble in dilute hydrochloric acid but insoluble in ethanoic acid, indicates the presence of calcium ions.

$$(NH_4)_2C_2O_4(aq) + Ca^{2+}(aq) \rightarrow CaC_2O_4(s) + 2NH_4^+(aq)$$

Instead of using ammonium ethanedioate, ammonium trioxocarbonate(IV) may be used. The formation of a white precipitate indicates the presence of calcium ions.

$$(NH_4)_2CO_3(aq) + Ca^{2+}(aq) \rightarrow CaCO_3(s) + 2NH_4^+(aq)$$

NOTE Barium and strontium salts also undergo similar reactions with ammonium ethanedioate and ammonium trioxocarbonate(IV).

Tests to distinguish calcium salts from barium and strontium salts

Barium and strontium salts also give positive tests with the above reagents just like calcium salts. However, calcium salts do not give a precipitate with

- potassium tetraoxochromate(VI) solution, unlike barium salts; and
- saturated calcium tetraoxosulphate(VI) solution, unlike both barium and strontium salts.

Uses

Calcium is used as a deoxidant in steel castings and copper alloys. It is also used in the manufacture of calcium fluoride and calcium hydride, and in the extraction of uranium. It is needed in the diet of young children and pregnant mothers for the development of strong bones and teeth.

COMPOUNDS OF CALCIUM

Calcium tends to form ionic compounds. Although these compounds have high melting points, they are less stable to heat than those of Group 1 metals. The chloride, however, is not easily decomposed and is used in the electrolytic extraction of the metal. Calcium compounds are of great economic importance, especially in the building industry and the extraction of metals.

Calcium Oxide

Preparation

Calcium oxide, CaO, is obtained by the thermal decomposition of calcium trioxocarbonate(IV). Commercially, lumps of limestone are heated strongly in a furnace called a *lime kiln*. The limestone starts to decompose at around 900 °C to give calcium oxide and carbon(IV) oxide. This reaction is reversible, so the forward reaction is favoured by the continuous removal of the products and addition of reactants. To achieve this, the kiln is opened at the top and air is blown in from the bottom. Calcium oxide is removed from the bottom of the kiln as it is formed, while limestone is added from the top.

$$CaCO_3(s) \xrightleftharpoons{900\ ^\circ C} CaO(s) + CO_2(g)$$

Ionically,

$$Ca^{2+}CO_3^{2-}(s) \rightleftharpoons Ca^{2+}O^{2-}(s) + CO_2(g)$$

Properties

Calcium oxide is popularly known as *quicklime* or just *lime*. It is a white solid that can easily be ground into powder. It is one of the most refractory solids known because it can withstand very high temperatures. It merely becomes incandescent when heated strongly, emitting an intensely bright light (known as *limelight*), and melts at about 2 600 °C.

Calcium oxide is very hygroscopic and is used to dry ammonia gas. When water is added drop by drop to the oxide, it cracks with a hissing noise and breaks up into a powdery form accompanied by the liberation of heat. This process is known as *slaking*, and the end-product is calcium hydroxide, $Ca(OH)_2$, which is more commonly known as *slaked lime*. The reaction is as follows:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

Ionically,

$$O^{2-}(s) + H_2O(l) \rightarrow 2OH^-(s)$$

If more water is added to the slaked lime, a suspension known as *milk of lime* is obtained. On standing, a supernatant known as *lime water* is obtained.

Calcium oxide is a strong base which reacts vigorously with acids to form calcium salts. It also reacts with all ammonium salts to liberate ammonia gas.

$$CaO(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l)$$

$$CaO(s) + 2NH_4Cl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + 2NH_3(g)$$

Uses

1. Calcium oxide is used in the manufacture of slaked lime, mortar, cement and calcium carbide. It is also used to make refractory furnace linings, in smelting processes and in glass-making.
2. In agriculture, lime is used to treat acidic soils. The pH is too low in most acidic soils for agriculturally important bacteria to function properly. Lime, which is a cheap base, is used to reduce the acidity.
3. In industry, lime is used to neutralize acidic waste substances. The treated wastes can then be emptied into natural waterways without harming aquatic life.
4. In the laboratory, it is used for drying ammonia gas and for making soda-lime (obtained by slaking calcium oxide with concentrated sodium hydroxide).

Calcium Hydroxide

Calcium hydroxide, $Ca(OH)_2$, or slaked lime is manufactured by heating limestone to a high temperature (1 000 °C) and then adding water to the calcium oxide.

Calcium hydroxide is slightly soluble in water. The solution is alkaline and is known as lime water. Calcium hydroxide is a strong base. It neutralizes acids and displaces ammonia from ammonium salts. It decomposes on heating to give the oxide.

Some uses of calcium hydroxide are as follo

1. Slaked lime is a cheap alkali and is comm used in treating acidic soils.
2. Mortar is prepared by mixing one part of slaked lime and three parts of sand with water. The mixture hardens or sets to bind the grains of sand by reacting with the carbon(IV) oxide in the atmosphere to form the trioxocarbonate(IV). Mortar is used to bind the bricks in walls and buildings.

   $$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

3. Temporary hard water is softened by the addition of calcium hydroxide.
4. Calcium hydroxide can be used to recover ammonia from ammonium chloride in the Solvay process. It is also commonly used in the laboratory preparation of ammonia.
5. Bleaching powder is manufactured by passing chlorine over moist calcium hydroxide.
6. A suspension of calcium hydroxide in water, known as milk of lime, is used as whitewash. Lime water is used as a test for carbon(IV) oxide in the laboratory.

Calcium Chloride

Calcium chloride, $CaCl_2$, is found in soil water and sea-water. It is prepared by the action of dilute hydrochloric acid on calcium trioxocarbonate(IV).

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Calcium chloride crystals are white and very deliquescent. The anhydrous salt is used in desiccators and as a drying agent for all gases except ammonia.

Calcium Tetraoxosulphate(VI)

Calcium tetraoxosulphate(VI), $CaSO_4$, occurs naturally as *anhydrite*, $CaSO_4$, and *gypsum*, $CaSO_4.2H_2O$. Calcium tetraoxosulphate(VI) may be prepared by the addition of a soluble calcium salt, for example calci chloride, to a sodium tetraoxosulphate(VI) solu The calcium tetraoxosulphate(VI) formed is slightly soluble and comes out of solution as a precipitate.

$$CaCl_2(aq) + Na_2SO_4(aq) \rightarrow CaSO_4(s) + 2N$$

Calcium tetraoxosulphate(VI) is responsible for he permanent hardness of water. Anhydrous calcium raoxosulphate(VI) is used in the manufacture of hemical compounds such as tetraoxosulphate(VI) id and ammonium tetraoxosulphate(VI).

Gypsum is used for the manufacture of *plaster of* ris, $CaSO_4.\frac{1}{2}H_2O$ or $(CaSO_4)_2.H_2O$. On heating dihydrate at about 100 °C, some water of stallization is lost and plaster of Paris, the mihydrate, is formed. When mixed with water and standing, plaster of Paris sets into a very hard ss. Plaster of Paris is widely used for making plaster ts, moulds, cements, wall-plasters, and in surgery keep a broken limb rigid and undisturbed.

$$aSO_4.2H_2O)(s) \rightarrow \underset{\text{plaster of Paris}}{(CaSO_4)_2.H_2O(s)} + 3H_2O(g)$$

alcium Trioxonitrate(V)

cium trioxonitrate(V), $Ca(NO_3)_2$, may be prepared he laboratory by the action of dilute trioxonitrate(V) l on calcium oxide or calcium trioxocarbonate(IV). cooling, the salt is obtained as white deliquescent ahydrate crystals, $Ca(NO_3)_2.4H_2O$.

$$O(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l)$$

$$CO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

Calcium trioxonitrate(V) mixed with lime is used a fertilizer.

alcium Trioxocarbonate(IV)

lcium trioxocarbonate(IV), $CaCO_3$, occurs undantly in the earth's crust as *limestone*, *marble* d *chalk*, as well as in natural ores like *calcite*, lomite and *Iceland spar*. It is found in caves in any parts of the world as stalactites and stalagmites. is also an important constituent of the bones of nimals and the external skeletons of marine rganisms. For all industrial uses requiring calcium ioxocarbonate(IV), one of the natural forms is used. n the laboratory, however, it can be precipitated by nixing solutions of sodium trioxocarbonate(IV) and alcium chloride.

Properties

Calcium trioxocarbonate(IV) is a white solid which is insoluble in pure distilled water. However, it dissolves gradually in water containing dissolved carbon(IV) oxide to form calcium hydrogentrioxocarbonate(IV). This is an important cause of hard water in limestone districts.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

When it is heated strongly, calcium trioxocarbonate(IV) decomposes to give calcium oxide and carbon(IV) oxide. It is also attacked by dilute acids to liberate carbon(IV) oxide. However, if tetraoxosulphate(VI) acid is used and the calcium trioxocarbonate(IV) is in lump form, the reaction may stop after some time due to the formation of an insoluble protective layer of calcium tetraoxosulphate(VI) around the trioxocarbonate(IV).

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$
$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Uses

Limestone is a major raw material in chemical industry. It is used in making sodium trioxocarbonate(IV), glass, cement, quicklime and steel. Chalk is used in making putty, pigments, glass and paper.

Marble and limestone are used as building materials. Limestone is used for making *cement* which

Limestone quarries provide raw materials for many chemical industries.

Concrete is used extensively in the building industry.

is a mixture of calcium trioxosilicate(IV) and calcium aluminate. Cement is formed by heating limestone and clay to 1 500 °C in a rotary kiln. When water is added to the cement complex chemical changes occur and it sets into a hard mass. This property of cement is used in brick laying. Cement is also mixed with sand or gravel to form *concrete*, which sets hard when water is added. Concrete is a very important building material because of its hardness and strength. Concrete with steel rods embedded inside is called *reinforced concrete*. This provides further support and is used for building structures such as tall buildings and bridges.

In the extraction of iron, limestone provides the calcium oxide which is used to remove impurities as slag.

Finely ground limestone is used to neutralize excess acid in acidic soils. Chalk mixed with ammonium trioxonitrate(V), known as *nitrochalk*, is widely used as a fertilizer.

NOTE Blackboard chalk is mainly calcium tetraoxosulphate(VI).

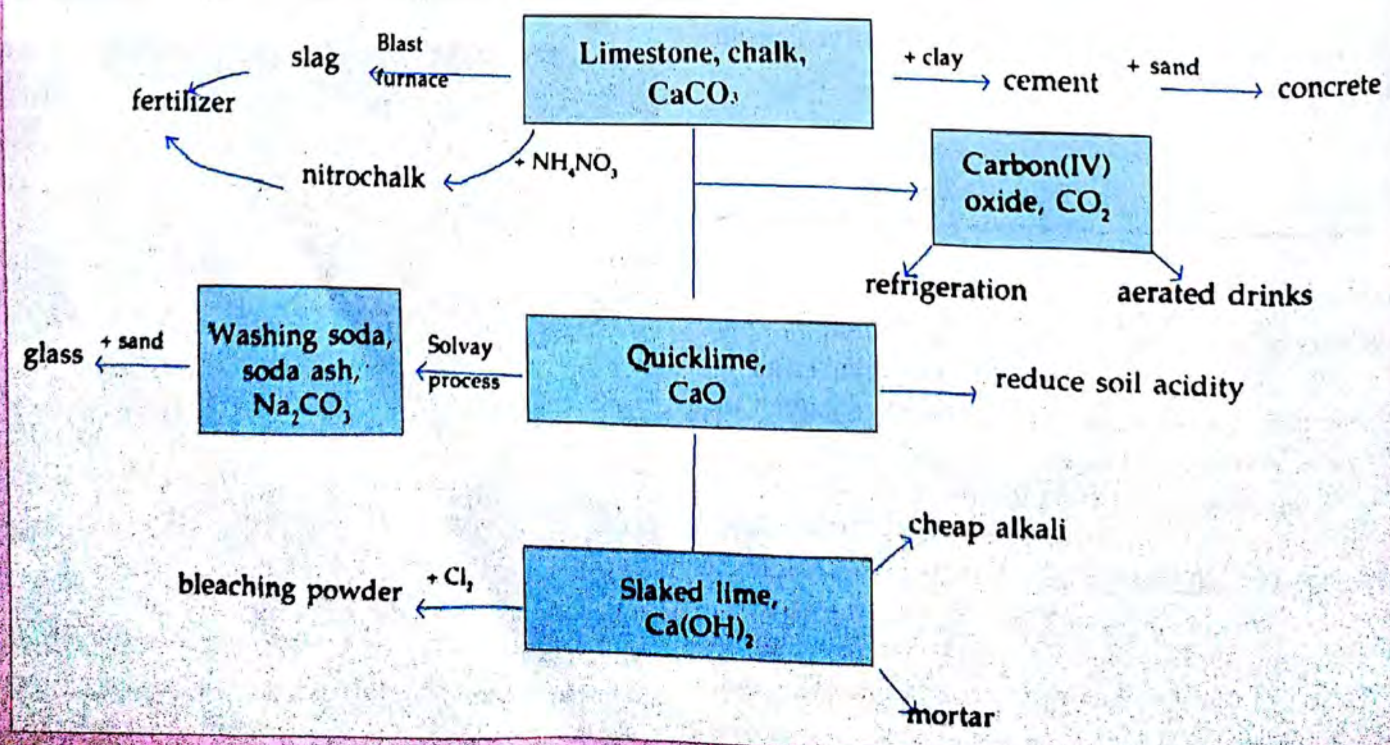
MAGNESIUM

Magnesium is also a member of the alkaline earth metals. It occurs in nature, only in the combined state, as *dolomite*, $CaCO_3.MgCO_3$, *kieserite*, $MgSO_4.H_2O$, *carnallite*, $KCl.MgCl_2.6H_2O$, *Epsom salt*, $MgSO_4.7H_2O$, and in many trioxosilicates(IV) including *talc* and *asbestos*. Magnesium chloride, bromide and tetraoxosulphate(VI) are also present in sea-water. Magnesium is also an essential constituent of chlorophyll in green plants.

Extraction

Magnesium is commonly extracted from fused magnesium chloride by electrolysis. Some potassium

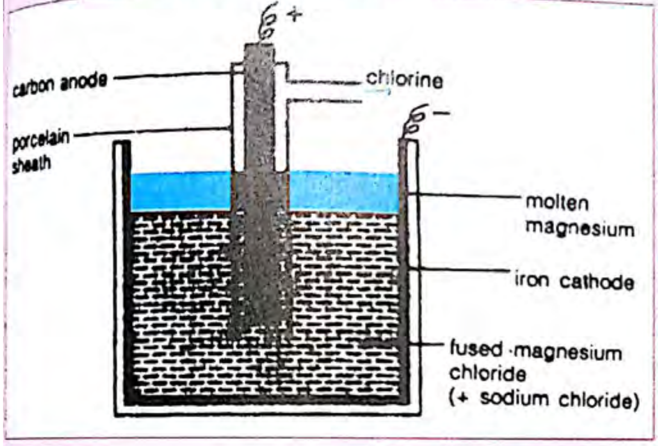
Fig. 26.5 Commercial uses of limestone and chalk.



or sodium chloride is added to lower the melting point of the electrolyte. The anode of the cell is a central carbon rod, while the iron lining of the container for the electrolyte acts as the cathode. The magnesium metal that is formed floats on the electrolyte and is skimmed off and cast into blocks. The chlorine gas formed at the anode is prevented from coming into contact with the magnesium by a porcelain sheath which surrounds the anode.

Chemistry of the reaction Fused magnesium chloride consists of magnesium and chloride ions.

Fig. 26.6 Extraction of magnesium.



At the cathode The magnesium ions receive two electrons each from the cathode, and are deposited as metallic magnesium.

$$Mg^{2+} + 2e^- \rightarrow Mg \qquad (\textit{Reduction})$$

At the anode The chloride ions give up an electron each to the anode to become atoms, which then pair up to form gaseous molecules.

$$Cl^- \rightarrow Cl + e^- \qquad (\textit{Oxidation})$$
$$Cl + Cl \rightarrow Cl_2$$

Overall electrolytic reaction

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

Physical Properties

Appearance	Silvery-white solid
Relative density	1.74
Malleability and ductility	Malleable and ductile
Melting point	650 °C
Conductivity	Good conductor of heat and electricity

Chemical Properties

Reaction with air Magnesium is a very electropositive metal with a strong affinity for oxygen. It gradually undergoes oxidation in moist air to form a protective film of magnesium oxide, which prevents further action.

Magnesium burns in air with a very brilliant white flame to form white ashes of magnesium oxide.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

As a reducing agent Magnesium is a powerful reducing agent, especially in the powdered form. Once it is ignited, magnesium will continue to burn in steam, sulphur(IV) oxide, carbon(II) oxide, carbon(IV) oxide, and the oxides of nitrogen, reducing the gas in each case.

$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$
$$Mg(s) + CO(g) \rightarrow MgO(s) + C(s)$$

Reaction with dilute acids Magnesium displaces hydrogen from dilute acids.

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

Reaction with non-metals When heated, magnesium combines directly with sulphur, phosphorus, chlorine and nitrogen, but not with hydrogen.

$$Mg(s) + S(s) \rightarrow MgS(s)$$
$$3Mg(s) + 2P(s) \rightarrow Mg_3P_2(s)$$
$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$
$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

Test for magnesium ions

Add an excess solution of aqueous ammonia and ammonium chloride to the unknown salt solution, followed by a solution of sodium hydrogentetraoxophosphate(V), Na_2HPO_4. Shake well and let the solution stand for a while. The formation of a white precipitate indicates the presence of magnesium ions.

$$Mg^{2+}(aq) + NH_4^+(aq) + OH^-(aq) + Na_2HPO_4(aq) \rightarrow MgNH_4PO_4(s) + 2Na^+(aq) + H_2O(l)$$

Note All metallic ions other than those of sodium, potassium and magnesium must be removed before this test is carried out.

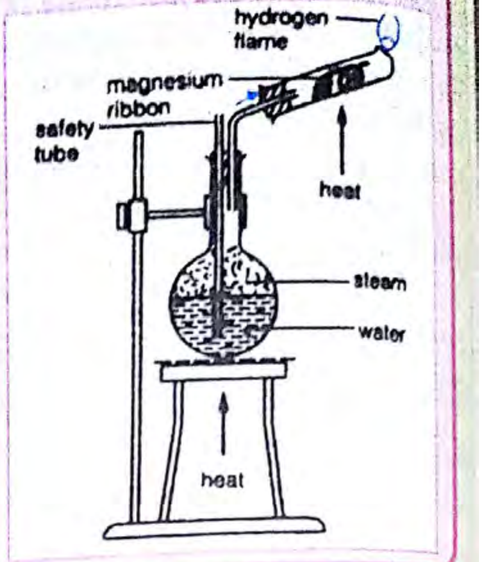
Experiment 26.1 To reduce steam using magnesium.

Method Place a short length of magnesium ribbon in a hard glass tube which has a narrow jet at one end. Set up the apparatus as shown. Generate steam by boiling the water in the round-bottomed flask. Heat the magnesium ribbon as the steam passes over it and ignite the hydrogen formed as it leaves the jet.

Result On heating, the magnesium ribbon burns brilliantly in steam to liberate hydrogen, leaving behind white ashes of magnesium oxide in the tube.

Conclusion Heated magnesium reduces steam to hydrogen while it is oxidized to magnesium oxide.

Fig. 26.7 Reduction of steam by magnesium.



Uses

1 Because of its low density, magnesium is used in preparing light but tough alloys, such as duralumin (a mixture of Al, Cu, Mg, Mn) and magnalium (a mixture of Al, Mg). These alloys are used for the construction of spacecraft, aircraft, cars and the moving parts of machines.

2 It is also used in photographic flashlight powder, flares and fireworks.

3 It is used as a deoxidant in metallurgy and in the extraction of titanium and uranium.

COMPOUNDS OF MAGNESIUM

Like calcium, compounds of magnesium are mainly ionic but they tend to show covalent characteristics as well. Only the chloride of magnesium is stable to heat and is used in the electrolytic extraction of the metal.

Magnesium Tetraoxosulphate(VI)

Magnesium tetraoxosulphate(VI), $MgSO_4$, occurs naturally as the mineral *kieserite*, $MgSO_4.H_2O$. It may be prepared by the action of dilute tetraoxosulphate(VI) acid on magnesium oxide.

$$MgO(s) + H_2SO_4(aq) \rightarrow MgSO_4(s) + H_2O(l)$$

On crystallization, the heptahydrate, $MgSO_4.7H_20$, known as Epsom salt, is obtained. Epsom salt is found naturally in some springs. Magnesium tetraoxosulphate(VI) is used as a mild purgative.

Magnesium Trioxonitrate(V)

Magnesium trioxonitrate(V), $Mg(NO_3)_2$, may be prepared in the laboratory by the action of magnesium or its oxide on dilute trioxonitrate(V) acid. It crystallizes out of solution as a white deliquescent hexahydrate, $Mg(NO_3)_2.6H_2O$.

$$Mg(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$$
$$MgO(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2O(l)$$

The anhydrous form is unknown since it readily decomposes on heating to give magnesium oxide, oxygen and nitrogen(IV) oxide.

GROUP 3 ELEMENTS

Boron and aluminium are the two familiar elements in Group 3 of the Periodic Table. Boron is a metalloid, while aluminium and the other elements in the groups are metals.

Each of the atoms of the Group 3 elements has three valence electrons which it can lose successively. A large amount of energy is involved in the formation of the aluminium ion, Al^{3+}. Thus, most compounds of aluminium are covalently bonded, although aluminium ions are found to exist in aqueous solution.

As the atomic number increases from boron to aluminium, the metallic properties of the elements also become more predominant.

ALUMINIUM

Aluminium is the third most plentiful element in the earth's crust, being found abundantly as trioxosilicates(IV) in rocks and clays. The main source of aluminium is the mineral *bauxite*, $Al_2O_3.2H_2O$. Other important minerals include *kaolin*, $Al_2O_3.2SiO_2.2H_2O$, *cryolite*, Na_3AlF_6, *corundum*, Al_2O_3, and *mica*, $K_2O.Al_2O_3.6SiO_2$.

Extraction

Although aluminium occurs so abundantly in rocks and clays, no economical process has yet been devised for extracting the metal from them, owing to their high silica content. Instead, aluminium is extracted from bauxite by electrolysis. The extraction proceeds in two stages. In the first stage, the crude bauxite is purified to yield pure anhydrous aluminium oxide, which is then electrolyzed in the second stage.

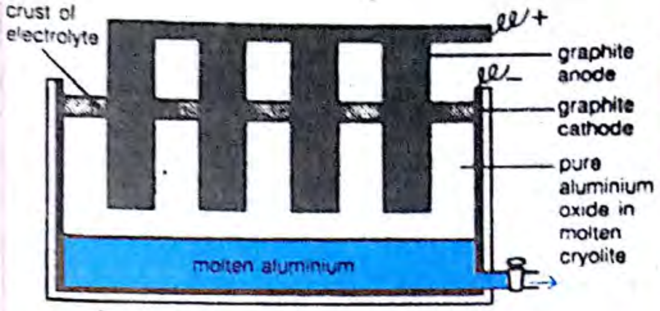
Purification of bauxite The bauxite is first heated with caustic soda solution under pressure to form soluble sodium aluminate(III), $NaAl(OH)_4$.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$$

Since the impurities in the ore, notably iron(III) oxide and the various trioxosilicates(IV), do not react with or dissolve in the alkali, they can be filtered off as a sludge. The filtrate which contains the aluminate(III) is then seeded with aluminium hydroxide crystals to induce the precipitation of aluminium hydroxide.

$$NaAl(OH)_4(aq) \rightarrow Al(OH)_3(s) + NaOH(aq)$$

Fig. 26.8 Extraction of aluminium



The aluminium hydroxide precipitate is then filtered off, washed, dried and heated strongly to yield pure aluminium oxide or alumina, Al_2O_3, while the sodium hydroxide is concentrated and used again.

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(l)$$

Electrolysis of alumina The electrolytic cell is an iron container lined with graphite. The graphite lining serves as the cathode while the anodes consist of graphite rods dipping into the electrolyte which is a solution of pure alumina in molten cryolite, Na_3AlF_6. The electrolyte is maintained at about 950 °C by the heating effect of a large current. This makes the process very expensive.

During the electrolysis of alumina, oxygen is given off at the anodes. As a result, the anodes are slowly burnt away as carbon(IV) oxide, and must be replaced continuously. This adds to the cost of the whole process. Molten aluminium collects at the bottom of the cell and is tapped off at intervals.

Table 26.8 *Electronic configurations and related properties of aluminium and boron.*

Metal		Electronic configuration	First ionization energy (kJ mol⁻¹)	Atomic radius (nm)
Boron	B	$1s^2\ 2s^2\ 2p^1$	800 (first)	0.080
Aluminium	Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	580 (first) 1 800 (second) 2 700 (third)	0.125

Chemistry of the reaction Alumina consists of aluminium and oxygen ions.

At the cathode The aluminium ions gain three electrons each at the cathode to become deposited as metallic aluminium.

$$Al^{3+} + 3e^- \rightarrow Al \qquad \textit{(Reduction)}$$

At the anode The oxygen ions donate two electrons each to form atomic oxygen, which then pair off to form gaseous molecules.

$$O^{2-} \rightarrow O + 2e^- \qquad \textit{(Oxidation)}$$

$$O + O \rightarrow O_2$$

Overall electrolytic reaction

$$4Al^{3+}(l) + 6O^{2-}(l) \rightarrow 4Al(s) + 3O_2(g)$$

Physical Properties

Appearance	Silvery-white solid
Relative density	2.7 (low)
Malleability and ductility	Very malleable and ductile; can be rolled into a foil
Tensile strength	Moderate, but high in alloys
Melting point	660 °C
Conductivity	Very good conductor of heat and electricity

Chemical Properties

Reaction with air When a piece of aluminium sheet is exposed to moist air, a thin, continuous coating of aluminium oxide is formed, which prevents further attack of the metal by atmospheric oxygen and water or steam under normal conditions. Aluminium sheets are, thus, said to be corrosion-free. If the aluminium sheet is heated to 800 °C and above, the remaining aluminium metal will react with air to form aluminium oxide, Al_2O_3, and the aluminium nitride, AlN.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

$$2Al(s) + N_2(g) \rightarrow 2AlN(s)$$

Reaction with non-metals Heated aluminium combines directly with the halogens, sulphur, nitrogen, phosphorus and carbon, with the evolution of heat. For example,

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

Reaction with acids Aluminium reacts slowly with dilute hydrochloric acid but more rapidly with the concentrated acid to displace hydrogen.

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

Aluminium does not react with dilute tetraoxosulphate(VI) acid. However, the hot concentrated acid oxidizes it to liberate sulphur(IV) oxide.

$$2Al(s) + 6H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

Aluminium does not react with trioxonitrate(V) acid at any concentration due to the formation of a protective layer of aluminium oxide. As a result, aluminium containers are frequently used to transport the acid.

Reaction with alkali Aluminium dissolves in both sodium and potassium hydroxides to form a soluble aluminate(III), with the evolution of hydrogen. For example,

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2NaAl(OH)_4(aq) + 3H_2(g)$$

Thus, washing soda is never used to clean aluminium vessels.

Reaction with iron(III) oxide Aluminium reduces iron(III) oxide to molten iron. This is the reaction used in the *thermit process*.

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$$

With aqueous ammonia Add a few drops of aqueous ammonia to the unknown salt solution. The formation of a white gelatinous precipitate which is insoluble in excess aqueous ammonia confirms the presence of aluminium ions.

$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$$

NOTE Lead(II) and zinc salts give similar reactions. However, lead(II) salts give a white precipitate with concentrated hydrochloric acid, while aluminium salts do not. Zinc salts give a white precipitate with aqueous ammonia but the precipitate dissolves in an excess of the reagent.

The above is the only valid test.

Experiment 26.2 To show that aluminium is a reducing agent.

Method Take some dry iron(III) oxide powder and test it with a magnet. Then mix the oxide with dry aluminium dust. Place the mixture on a tin lid and partially bury a piece of magnesium ribbon inside the mixture. Warm the mixture and light the magnesium strip (which acts as a fuse). When the reaction is over, allow the residue to cool and test with a magnet.

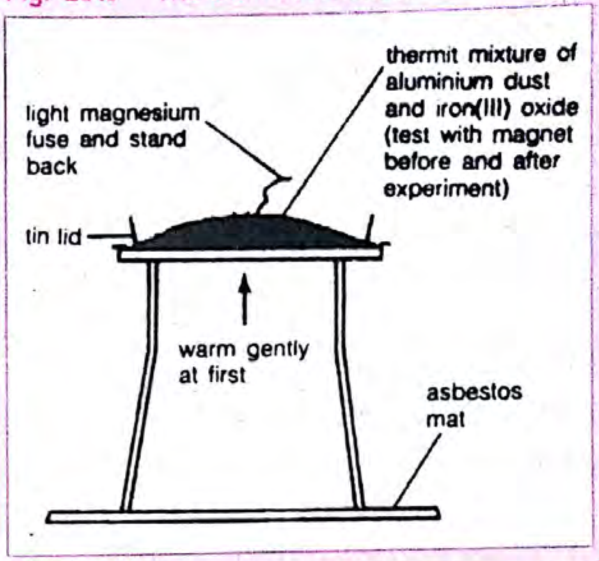
CAUTION This experiment should be done in a fume cupboard. Care must be taken as a lot of heat is generated during the reaction.

Result Iron(III) oxide is not magnetic. It is not attracted by the magnet. When ignited, the mixture melts and becomes white hot, giving off aluminium oxide as white smoke.

When the residue is tested with a magnet, some of the globules in the residue are attracted to the magnet, indicating the presence of iron.

Conclusion Aluminium is a reducing agent.

Fig. 26.9 The thermit reaction.



es

Aluminium is used in making cooking utensils because it is cheap, light and a good conductor of heat. The metal can be made more resistant to corrosion by anodizing, which produces a thicker and harder film of aluminium oxide on the surface of the metal.

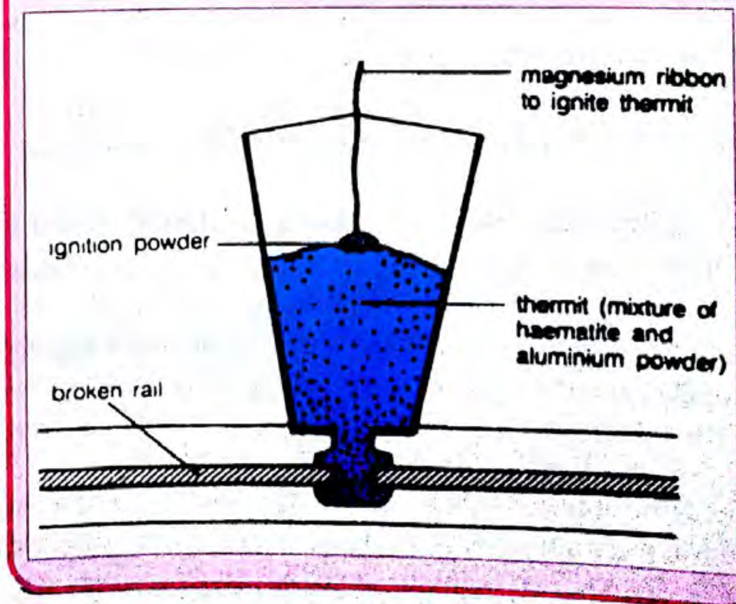
It is used in making overhead electric cables because it is light and has good electrical conductivity.

Aluminium powder suspended in oil is used in paints, and for mirrors and cars because of its high reflectivity.

Aluminium is used in making alloys such as duralumin (a mixture of Al, Cu, Mg, Mn), aluminium bronze (a mixture of Cu, Al) and magnalium (a mixture of Al, Mg), which are stronger and harder than pure aluminium but retain its properties of lightness and resistance to corrosion. These alloys are used in cars, ships, aircraft and the moving parts of machines.

Aluminium powder is used in the thermit process for welding together broken metallic parts of machines and equipment. For example, to weld together the broken ends of an iron rod, a mixture of aluminium powder and iron(III) oxide, known as thermit, is ignited. During this reaction, aluminium oxide and metallic iron are formed with the evolution of a large amount of heat. This heat melts the iron formed, which then welds together the two broken ends.

Fig. 26.10 Thermit welding — molten iron flows out from the bottom of the converter to weld together the parts of a broken rail.



$$Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(l)$$

If a chromium article is involved, chromium(III) oxide is used in place of iron(III) oxide.

$$Cr_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Cr(l)$$

Pure manganese and chromium can also be extracted from their oxides by this method.

6 Aluminium foils are widely used as packaging material.

7 Aluminium ions, Al^{3+}, are used as coagulating agents. For example, aluminium tetraoxosulphate(VI) is used in water treatment plants to remove colloidal organic matter.

COMPOUNDS OF ALUMINIUM

The compounds of aluminium are mainly covalent. In ionic compounds, such as aluminium fluoride, it exists as a trivalent aluminium ion, Al^{3+}. The hydrated aluminium ion is found in many compounds, e.g. $Al_2(SO_4)_3.18H_2O$, and in aqueous solution. Hydrated aluminium ions are usually acidic in aqueous solution.

Aluminium Oxide

Aluminium oxide, Al_2O_3, is commonly known as alumina. It occurs naturally as bauxite, corundum and *white sapphire*. It also occurs as *ruby*, *amethyst*, *topaz*, *blue sapphire* and *emerald*, the characteristic colours of which are due to other metallic oxides present as impurities. It is prepared by heating aluminium hydroxide or other aluminium compounds.

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g)$$

Aluminium oxide is a white crystalline powder which is almost insoluble in water. It reacts readily with dilute acids and strong alkalis to form salts, i.e. it is amphoteric. Its reactions with acids and alkalis depend on the oxide being prepared at the lowest temperature possible, otherwise it will exist in a form which is insoluble in both acids and alkalis.

Aluminium oxide is used as a source of aluminium and in making furnace linings, ceramics and synthetic gem stones. It is also used as an abrasive, for absorption in chromatography, and as a catalyst in the catalytic cracking of hydrocarbons.

Aluminium Hydroxide

Aluminium hydroxide, $Al(OH)_3$, is precipitated when sodium hydroxide is added to an aqueous solution of an aluminium salt.

$$Al^{3+}(aq) + 3NaOH(aq) \rightarrow Al(OH)_3(s) + 3Na^+(aq)$$

Aluminium hydroxide is amphoteric. In excess alkali, it gives tetrahydroxoaluminate(III) ion, and in acids, it forms salts.

$$Al(OH)_3(s) + NaOH(aq) \rightarrow NaAl(OH)_4(aq)$$

$$2Al(OH)_3(aq) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6H_2O(l)$$

Aluminium hydroxide is used in the dyeing industry. It is called a mordant as it helps the dye to stick to the cloth.

Aluminium Chloride

Aluminium chloride, $AlCl_3$, is prepared by heating aluminium foils in a stream of dry chlorine or hydrogen chloride. The ease with which the anhydrous salt hydrolyzes explains why hydrogen chloride fumes are evolved from it in damp air.

NOTE Sodium chloride and calcium chloride are electrovalent compounds which dissolve in water to give ions. Aluminium chloride, however, is a covalent compound which reacts with water.

Aluminium Tetraoxosulphate(VI)

Aluminium tetraoxosulphate(VI), $Al_2(SO_4)_3$, occurs naturally but can be manufactured by the action of hot concentrated tetraoxosulphate(VI) acid on aluminium oxide.

$$Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$$

It is a white crystalline solid which is moderately soluble in water. It forms double salts (alums) with other tetraoxosulphates(VI), and is used in the treatment of water and sewage, and in paper making.

Alums Alums are double tetraoxosulphates(VI) which ionize in solution to yield a monovalent cation (usually Na^+, K^+ or NH_4^+), a trivalent cation (usually Fe^{3+}, Al^{3+} or Cr^{3+}) and tetraoxosulphate(VI) ions. Their general formula can be written as follows:

$$M_2^ISO_4M_2^{III}(SO_4)_3.24H_2O \quad \text{or} \quad M^IM^{III}(SO_4)_2.12H_2O$$

where M^I and M^{III} are the monovalent and trivalent cations respectively.

All alums can be made by mixing equimolar masses of the tetraoxosulphates(VI) concerned. The alums crystallize out, each cation being associated with six molecules of water of crystallization. All alums have similar octahedral crystalline shapes.

Aluminium potassium tetraoxosulphate(VI)-dodecahydrate, $KAl(SO_4)_2.12H_2O$, or *potash alum*, is one of the commonest alums known. It is obtained by mixing hot solutions containing equimolar masses of potassium and aluminium tetraoxosulphates(VI). When the mixture is cooled, colourless crystals of the alum separate out.

Potash alum is usually used as a mordant in dyeing, i.e. it combines with and fixes the dyestuff onto the fibre in cases where the fibre cannot be dyed directly. Potash alum is also commonly used as a coagulant in water purification for removing colloidal suspension particles.

Aluminium Trioxonitrate(V)

Aluminium trioxonitrate(V), $Al(NO_3)_3$, may be prepared in the laboratory by dissolving aluminium oxide or aluminium hydroxide in dilute trioxonitrate(V) acid. The salt crystallizes out as nonahydrate crystals, $Al(NO_3)_3.9H_2O$.

$$Al_2O_3(s) + 6HNO_3(aq) \rightarrow 2Al(NO_3)_3(aq) + 3H_2O(l)$$

$$Al(OH)_3(s) + 3HNO_3(aq) \rightarrow Al(NO_3)_3(aq) + 3H_2O(l)$$

Aluminium Hydride

Aluminium hydride, AlH_3, is a white covalent solid. It can be prepared by reacting excess aluminium chloride with lithium hydride.

$$6LiH + Al_2Cl_6 \rightarrow 2AlH_3 + 6LiCl$$

With excess lithium hydride, lithium tetrahydridoaluminate(III) is obtained.

$$8LiH + Al_2Cl_6 \rightarrow 2LiAlH_4 + 6LiCl$$

Lithium tetrahydridoaluminate(III), $LiAlH_4$, and sodium tetrahydridoborate(III), $NaBH_4$, are strong reducing agents used in organic chemistry.

GROUP 4 ELEMENTS

Carbon, silicon, tin and lead are some common Group 4 elements. As we go down the group from carbon to lead, the elements become more metallic in character. The nature of the oxides change from acidic (e.g. carbon(IV) oxide) to basic (e.g. lead(II) oxide). Their reactivities also increase, as can be seen from the decrease in the ionization energies.

Carbon forms mainly covalent compounds in which it has a +4 oxidation state. All the four electrons (i.e. $2s^22p^2$) in the outermost shell of its atom are used in bonding. Tin and lead, however, form compounds in which they exist in the +2 and +4 oxidation states. In the +2 oxidation state, the two *s* electrons in the outermost shells of the tin and lead atoms do not take part in bonding. In lead, the +2 oxidation state is the more stable form.

TIN

Tin does not occur naturally as the free element. The

Table 26.9 Electronic configurations and related properties of Group 4 elements.

Metal		Electronic configuration	First ionization energy (KJ mol⁻¹)	Atomic radius (nm)
Carbon	C	$1s^2\ 2s^2\ 2p^2$	1 089	0.091 4
Silicon	Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$	787	0.132
Tin	Sn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$	708	0.162
Lead	Pb	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$	716	0.175

main source is the mineral *cassiterite* or *tin stone*, SnO_2, which is found as low grade ore in alluvial deposits in Malaysia, Bolivia and Indonesia.

In Nigeria, tin was one of the first minerals mined in 1903 in the Jos plateau. The ore was found mainly in the granite rocks and the alluvial beds of former river valleys. Today, Nigeria provides about 4% of the world's tin and is the seventh largest producer. About 13000 tonnes of tin is produced a year, most of which is exported.

Extraction

Tin ore, SnO_2, is crushed and washed with water. This is called concentration of ore. Then it is roasted in air to remove impurities like sulphur, arsenic and antimony as volatile oxides. The product is mixed with powdered charcoal and heated to 1 300 °C to reduce the oxide. Molten tin is then tapped off.

$$SnO_2(s) + 2C(s) \rightarrow Sn(l) + 2CO(g)$$

The tin obtained is impure. It is refined by heating it gently on a sloping surface. As molten tin flows down the surface, the impurities are exposed to air and become converted to oxides which are left behind as scum. This method of refinement gives tin with a purity of 99.9%.

Physical Properties

Appearance	Silvery-white solid with lustre
Relative density	Varies for different allotropes
Malleability	Very malleable metal; soft enough to be cut with a knife
Ductility	Not ductile enough to be drawn into wires
Tensile strength	Fairly strong
Melting point	232 °C
Conductivity	Good conductor of heat and electricity

Tin exists in three allotropic forms, which have different densities. At room temperature, tin exists as *white tin*.

$$\underset{5.76\ \text{g cm}^{-3}}{\text{grey tin}} \overset{13.2°\text{C}}{\rightleftharpoons} \underset{7.28\ \text{g cm}^{-3}}{\text{white tin}} \overset{161°\text{C}}{\rightleftharpoons} \underset{6.6\ \text{g cm}^{-3}}{\text{rhombic tin}}$$

Chemical Properties

Reaction with oxygen Tin is unreactive and only combines with oxygen above 1 200 °C. It does not corrode when exposed to the atmosphere. It also does not combine with nitrogen and carbon.

$$Sn(s) + O_2(g) \xrightarrow{1\,200\ °C} SnO_2(s)$$

Reaction with non-metals Tin combines with chlorine when heated to give tin(IV) chloride.

$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(s)$$

Reaction with acids Tin reacts slowly with dilute hydrochloric acid but rapidly with the concentrated acid to give tin(II) chloride.

$$Sn(s) + 2HCl(aq) \rightarrow SnCl_2(s) + H_2(g)$$

With dilute tetraoxosulphate(VI) acid, hardly any reaction is observed, but with the hot concentrated acid, sulphur(IV) oxide is evolved.

$$Sn(s) + 2H_2SO_4(aq) \rightarrow SnSO_4(aq) + SO_2(g) + 2H_2O(g)$$

The reaction of tin with trioxonitrate(V) acid depends on the concentration and temperature of the acid.

Reaction with alkalis Tin dissolves in concentrated solutions of alkalis to give trioxostannate(IV) salts and hydrogen.

$$Sn(s) + 2NaOH(l) + H_2O(l) \rightarrow Na_2SnO_3(aq) + 2H_2(g)$$

Tests for tin(II) ions

Hydrogen sulphide Pass hydrogen sulphide into a solution of the unknown salt acidified with dilute hydrochloric acid. Tin(II) ions are present if a brown precipitate which dissolves in yellow ammonium sulphide and in hot concentrated hydrochloric acid is obtained.

$$SnCl_2(aq) + H_2S(g) \rightarrow SnS(s) + 2HCl(aq)$$

Mercury(II) chloride Add a little mercury(II) chloride solution to the unknown salt solution. On standing, the formation of a white precipitate of mercury(I) chloride would indicate the presence of in(II) ions.

queous ammonia Tin(II) ions form a white precipitate of tin(II) hydroxide which is insoluble in excess queous ammonia.

$$nCl_2(aq) + 2NH_4OH(aq) \rightarrow Sn(OH)_2(s) + 2NH_4Cl(aq)$$

ses

The main use of tin is in coating steel to prevent its corrosion. The coating can be applied by dipping steel into molten tin and rolling it or by electrolytic deposition. Tin plating is especially useful in the canning of food and drinks because tin is not poisonous.

Tin is used in alloys together with lead, antimony and copper. Because of its low melting point and resistance to atmospheric corrosion, tin is used in making sheet glass.

OMPOUNDS OF TIN

n can combine with other atoms in two ways.

It can covalently share the two *p* electrons ($5p^2$) in the outermost shell of its atom to form tin(II) compounds. These compounds dissolve in water to give tin(II) ions, Sn^{2+}.

It can also covalently share all the four electrons ($5s^25p^2$) in the outermost shell of its atom.

Tin(II) compounds are strong reducing agents ince they can be readily oxidized to tin(IV) ompounds.

Tin(II) Oxide

Tin(II) oxide, SnO, can be made by heating tin(II) ethanedioate or tin(II) hydroxide in an inert atmosphere.

$$SnC_2O_4(s) \rightarrow SnO(s) + CO(g) + CO_2(g)$$

It is a grey solid which oxidizes readily to tin(IV) oxide when heated in air.

$$2SnO(s) + O_2(g) \rightarrow 2SnO_2(s)$$

Tin(II) oxide is amphoteric, giving tin(II) salts when it reacts with acids, and tetrahydroxostannates(II) when it reacts with alkalis.

$$SnO(s) + 2H^+(aq) \rightarrow Sn^{2+}(aq) + H_2O(l)$$
$$SnO(s) + 2OH^-(aq) + H_2O(l) \rightarrow Sn(OH)_4^{2-}(aq)$$

Tin(IV) Oxide

Tin(IV) oxide, SnO_2, occurs naturally as cassiterite and can be made by heating tin strongly in air, by dissolving tin in concentrated trioxonitrate(V) acid or by hydrolyzing tin(IV) chloride.

$$Sn(s) + 4HNO_3(aq) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$$
$$SnCl_4(l) + 2H_2O(l) \rightarrow SnO_2(s) + 4HCl(aq)$$

Tin(IV) oxide is a white solid that is insoluble in water and generally insoluble in acids. In fused alkalis, it forms hexahydroxostannates(IV).

$$SnO_2(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow Sn(OH)_6^{2-}(aq)$$

If tin(IV) oxide is freshly prepared, it is amphoteric and dissolves both in concentrated acids and alkalis.

$$SnO_2(s) + 2H_2SO_4(aq) \rightarrow Sn(SO_4)_2(aq) + 2H_2O(l)$$

Tin(IV) oxide is used industrially to make white enamel and tiles.

Tin(II) Hydroxide

When tin(II) salts are added to an alkali, tin(II) hydroxide is precipitated.

$$Sn^{2+}(aq) + 2OH^-(aq) \rightarrow Sn(OH)_2(s)$$

Tin(II) hydroxide is amphoteric and reacts with both alkalis and acids as shown.

$$Sn(OH)_2(s) + 2H^+(aq) \rightarrow Sn^{2+}(aq) + 2H_2O(l)$$
$$Sn(OH)_2(s) + 2OH^-(aq) \rightarrow Sn(OH)_4^{2-}(aq)$$

Tin(II) Chloride

Tin(II) chloride, $SnCl_2$, is prepared by heating tin in a stream of dry hydrogen chloride gas or by dissolving tin in concentrated hydrochloric acid. When acid is used, the salt is obtained as a dihydrate.

$$Sn(s) + 2HCl(g) \rightarrow SnCl_2(s) + H_2(g)$$

$$Sn(s) + 2HCl(aq) + 2H_2O(l) \rightarrow SnCl_2.2H_2O(aq) + H_2(g)$$

Anhydrous tin(II) chloride is a covalent white solid. Both the anhydrous chloride and the dihydrate dissolve readily in water. This solution soon turns milky due to hydrolysis and the formation of a basic salt.

$$SnCl_2(aq) + H_2O(l) \rightleftharpoons Sn(OH)Cl(s) + HCl(aq)$$

Hydrolysis of the chloride can be prevented by adding hydrochloric acid. A piece of tin is also added to this solution to prevent aerial oxidation to tin(IV) chloride.

Tin(II) chloride reduces iron(III) salts to iron(II) salts, copper(II) salts to copper(I) salts, and mercury(II) salts to the metal.

$$Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

(a) $2HgCl_2(aq) + SnCl_2(aq) \rightarrow Hg_2Cl_2(s) + SnCl_4(aq)$

(b) $Hg_2Cl_2(s) + SnCl_2(aq) \rightarrow 2Hg(s) + SnCl_4(aq)$

Tin(IV) Chloride

Tin(IV) chloride, $SnCl_4$, can be made by passing dry chlorine over heated tin. It is a colourless covalent liquid that fumes in moist air, due to hydrolysis, to form tin(IV) oxide.

$$Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)$$
$$SnCl_4(l) + 2H_2O(l) \rightarrow SnO_2(s) + 4HCl(g)$$

Tin(IV) Hydride

Tin(IV) hydride is unstable and decomposes at room temperature. It can be prepared by reacting tin(IV) chloride and lithium tetrahydridoaluminate(III) at low temperatures.

$$SnH_4(g) \rightarrow Sn(s) + 2H_2(g)$$
$$SnCl_4(l) + LiAlH_4(aq) \rightarrow SnH_4(g) + LiCl(aq) + AlCl_3(s)$$

LEAD

Lead was first mined in the first century A.D. Although it is not a very reactive metal, it occurs combined in nature. The principal ore of lead is *galena*, PbS, which is found in many parts of the world. Others include *cerussite*, $PbCO_3$, and *anglesite*, $PbSO_4$.

In Nigeria, small quantities of lead are found in Ogoja, Abakaliki and along the Benue River in Gongola State.

Extraction

Lead is extracted mainly from galena, PbS. The ore is first roasted in air to yield lead(II) oxide. The lead(II) oxide is then heated in a blast furnace together with some coke, limestone and scrap iron.

$$2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$$

The limestone forms a slag with the impurities and this can be tapped off separately, while the lead(II) oxide is reduced to lead by the carbon. Any unchanged lead(II) sulphide which might still be present is also reduced to lead by the iron.

$$2PbO(s) + C(s) \rightarrow 2Pb(s) + CO_2(g)$$
$$PbS(s) + Fe(s) \rightarrow Pb(s) + FeS(s)$$

Physical Properties

Appearance	Greyish-white solid with lustre
Relative density	11.3
Malleability	Very malleable metal; soft enough to be cut with a knife
Ductility	Not ductile enough to be drawn into wires
Tensile strength	Fairly strong
Melting point	327 °C
Conductivity	Good conductor of heat and electricity

Chemical Properties

Reaction with air Lead is attacked by moist air to form a thin white coating of lead(II) oxide, lead(II) hydroxide and lead(II) trioxocarbonate(IV) on the outside. On heating strongly in air, lead combines slowly with oxygen to yield yellow lead(II) oxide.

$$2Pb(s) + O_2(g) \rightarrow 2PbO(s)$$

However, continued heating in air to a temperature of about 450 °C results in the formation of red dilead(II) lead(IV) oxide.

$$3Pb(s) + 2O_2(g) \rightarrow Pb_3O_4(s)$$

Reaction with acids Lead does not dissolve in dilute hydrochloric or tetraoxosulphate(VI) acids due to the formation of an insoluble outer layer of lead(II) chloride or tetraoxosulphate(VI) which protects the metal from further attack. However, lead is attacked rapidly by hot concentrated hydrochloric acid and slowly by hot concentrated tetraoxosulphate(VI) acid to liberate hydrogen and sulphur(IV) oxide respectively.

$$Pb(s) + 2HCl(aq) \rightarrow PbCl_2(s) + H_2(g)$$
$$Pb(s) + 2H_2SO_4(aq) \rightarrow PbSO_4(s) + 2H_2O(l) + SO_2(g)$$

Lead is readily soluble in trioxonitrate(V) acid, reacting to form nitrogen(II) oxide with the dilute acid, and nitrogen(IV) oxide with the concentrated acid.

$$3Pb(s) + 8HNO_3(aq) \rightarrow 3Pb(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

$$Pb(s) + 4HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

Reaction with alkalis Lead, being fairly far down the activity series, has no action with alkalis.

Tests for lead(II) ions

Aqueous ammonia Add a few drops of aqueous ammonia to the unknown salt solution. The formation of a white precipitate, which does not dissolve in an excess of aqueous ammonia, indicates the presence of lead(II) ions.

$$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$$

NOTE A similar reaction is also given by aluminium salts. Use ammonia and KI as valid tests for Pb^{2+}.

Potassium tetraoxochromate(VI) or iodide Add some potassium tetraoxochromate(VI) or iodide solution to the unknown salt solution. The formation of a yellow precipitate in either case indicates the presence of lead(II) ions.

$$Pb^{2+}(aq) + K_2CrO_4(aq) \rightarrow PbCrO_4(s) + 2K^+(aq)$$
$$Pb^{2+}(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2K^+(aq)$$

Concentrated hydrochloric acid Add a few drops of concentrated hydrochloric acid to the unknown salt solution. The formation of a white precipitate, which dissolves when warmed but reappears on cooling, confirms the presence of lead(II) ions.

$$Pb^{2+}(aq) + 2HCl(aq) \rightarrow PbCl_2(s) + 2H^+(aq)$$

Uses

1 Lead is used for roofing, for making water and gas pipes, and for sheathing cables because of its resistance to corrosion, its flexibility, low melting point and cheapness. However, if it is used to make water pipes, there is a danger of lead poisoning because water containing dissolved oxygen attacks lead slowly to form lead(II) hydroxide which is slightly soluble. This poisonous effect can be avoided if the water is slightly hard, because the dissolved tetraoxosulphates(VI) and hydrogentrioxocarbonates(IV) will soon react with the lead to form a protective layer of insoluble salts.
2 It is used for making bullets, lead shots and weights because of its high density.
3 Lead is used for making lead accumulators.
4 Lead is used in making alloys such as type metal, pewter and plumber's solder.
5 Lead is used for making lead compounds, e.g. the oxides and lead(IV) tetraethyl.
6 Lead is used as a shield against X-rays and radioactive radiation because it is the cheapest of the very dense metals and has a high absorbing power.

COMPOUNDS OF LEAD

Lead forms stable electrovalent compounds where it is present as lead(II) ions. Lead(IV) compounds, which are covalent, are less stable and tend to be strongly oxidizing. Most lead compounds are generally insoluble in water.

Lead(II) Oxide

There are two forms of lead(II) oxide, PbO, with different densities and crystalline structures. The yellow form, known as *massicot*, is produced by heating lead in air at about 480 °C or by heating lead(IV) oxide, dilead(II) lead(IV) oxide and the trioxonitrate(V), trioxocarbonate(IV) or hydroxide of lead(II). The reddish-brown form, known as *litharge*, is obtained by heating lead in air at 900 °C.

Lead(II) oxide is insoluble in water. It is readily reduced to metallic lead by heating in hydrogen or carbon(II) oxide or with carbon. It behaves as a typical base, since its suspension in water turns red litmus blue. It is also amphoteric as it dissolves in both acids and alkalis to form lead(II) and plumbate(II) salts.

$$PbO(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l)$$
$$PbO(s) + 2NaOH(aq) + H_2O(l) \rightarrow Na_2Pb(OH)_4(aq)$$

Ionically, the reaction with an alkali can be represented as follows:

$$PbO(s) + 2OH^-(aq) + H_2O(l) \rightarrow \underset{\text{plumbate(II) ion}}{[Pb(OH)_4]^{2-}(aq)}$$

Although lead(II) oxide reacts readily with trioxonitrate(V) acid, its reactions with dilute tetraoxosulphate(VI) acid and hydrochloric acid are limited. This is due to the formation of protective outer layers of insoluble lead(II) tetraoxosulphate(VI) and lead(II) chloride respectively around the oxide.

Lead(II) oxide is used in making lead accumulators and lead glass. It is also used as a drier in paints, varnishes and glazes, where it catalyzes the process of atmospheric oxidation which hardens these materials.

Lead(IV) oxide, PbO_2, is made by treating dilead(II) lead(IV) oxide with trioxonitrate(V) acid or by heating a solution of lead(II) trioxonitrate(V).

$$Pb_3O_4(s) + 4HNO_3(aq) \rightarrow 2Pb(NO_3)_2(aq) + PbO_2(s) + 2H_2O(l)$$

Lead(IV) oxide is a dark brown solid which is insoluble in water and dilute acids, but dissolves in concentrated alkalis to form plumbate(IV) salts

$$PbO_2(s) + 2NaOH(aq) + 2H_2O(l) \rightarrow Na_2Pb(OH)_6(aq)$$

Ionically,

$$PbO_2(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow \underset{\text{plumbate(IV) ion}}{[Pb(OH)_6]^{2-}(aq)}$$

Lead(IV) oxide is a powerful oxidizing agent, giving off oxygen when heated alone. It oxidizes concentrated hydrochloric acid to chlorine and combines with sulphur(IV) oxide to form lead(II) tetraoxosulphate(VI). When heated with sulphur or red phosphorus, it causes their ignition. Therefore, lead(IV) oxide is used in match-heads. It is also used in lead accumulators.

$$2PbO_2(s) \xrightarrow{\text{heat}} 2PbO(s) + O_2(g)$$
$$PbO_2(s) + 4HCl(aq) \rightarrow PbCl_2(s) + 2H_2O(l) + Cl_2(g)$$
$$PbO_2(s) + SO_2(g) \rightarrow PbSO_4(s)$$

Dilead(II) Lead(IV) Oxide

Dilead(II) lead(IV) oxide, Pb_3O_4, is commonly known as *red lead oxide*. It is prepared by heating powdered lead(II) oxide in air at 400 °C. Care must be taken to control the temperature because the reaction reverses at 470 °C.

$$6PbO(s) + O_2(g) \underset{470\ ^\circ C}{\overset{400\ ^\circ C}{\rightleftharpoons}} 2Pb_3O_4(s)$$

Dilead(II) lead(IV) oxide is a red powder which is insoluble in water. It behaves chemically as a mixed oxide, $PbO_2.2PbO$. This is clearly seen in its reaction with dilute trioxonitrate(V) acid.

$$Pb_3O_4(s) + 4HNO_3(aq) \rightarrow 2Pb(NO_3)_2(aq) + PbO_2(s) + 2H_2O(l)$$

It is used in making lead glass, plumber's cement and priming paints.

Lead(II) Hydroxide

Lead(II) hydroxide, $Pb(OH)_2$, is formed when an alkali is added to a lead(II) salt solution.

$$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$$

The hydroxide is amphoteric and dissolves in both dilute trioxonitrate(V) acid and in aqueous alkali to form lead(II) trioxonitrate(V) and tetrahydroxoplumbates(IV) respectively.

$$Pb(OH)_2(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + 2H_2O(l)$$
$$Pb(OH)_2(s) + 2OH^-(aq) \rightarrow Pb(OH)_4{}^{2-}(aq)$$

Hydrochloric acid and tetraoxosulphate(VI) acid form precipitates of lead(II) chloride and lead(II) tetraoxosulphate(VI) with lead(II) hydroxide.

Lead(II) Chloride

Lead(II) chloride, $PbCl_2$, is prepared by the double decomposition reaction between a soluble lead(II) salt, e.g. lead(II) trioxonitrate(V), and any soluble chloride, e.g. sodium chloride. The lead(II) chloride is formed as a precipitate which can be obtained as a residue on filtration.

$$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$$

Lead(II) chloride is a white anhydrous solid with a partial ionic character. It is insoluble in cold water but fairly soluble in hot water. It reacts with concentrated hydrochloric acid to form tetrachloroplumbate(II) ions.

$$PbCl_2(s) + 2Cl^-(aq) \rightarrow PbCl_4{}^{2-}(aq)$$

Lead(IV) Chloride

Lead(IV) chloride, $PbCl_4$, is a yellow covalent liquid, obtained when concentrated hydrochloric acid reacts with lead(IV) oxide at 0 °C.

$$PbO_2(s) + 4HCl(aq) \xrightarrow{0\ °C} PbCl_4(l) + 2H_2O(l)$$

Above 0 °C, lead(IV) chloride decomposes to give lead(II) chloride and chlorine.

$$PbCl_4(l) \rightarrow PbCl_2(s) + Cl_2(g)$$

Lead(II) Trioxonitrate(V)

Lead(II) trioxonitrate(V), $Pb(NO_3)_2$, is prepared by the action of lead(II) oxide or lead(II) trioxocarbonate(IV) on dilute trioxonitrate(V) acid.

$$PbO(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l)$$

$$PbCO_3(s) + 2HNO_3(aq)$$
$$\rightarrow Pb(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

Lead(II) trioxonitrate(V) is a colourless crystalline solid which contains no water of crystallization. It is one of the few soluble salts of lead. On heating, it decrepitates and decomposes.

$$Pb(NO_3)_2(s) \xrightarrow{\Delta} PbO(s) + NO_2(g) + O_2(g)$$

SUMMARY

Metals - general

- Metals, with a few exceptions, have high melting and boiling points; they have relatively high densities and are good conductors of heat and electricity; they are shiny, malleable, ductile and have high tensile strength.
- (a) Metals tend to ionize by electron loss to form positive ions while non-metals tend to ionize by accepting electrons to form negative ions.

  (b) Most oxides of metals are basic while those of non-metals are acidic or neutral.

  (c) Metals which are more electropositive than hydrogen displace it from acids.
- Metals can be classed according to the activity series into very reactive, moderately reactive and least reactive metals.
- Most metals are found in combined forms as minerals. Ores contain minerals and earthy impurities.
- The reactive metals are extracted from their ores by electrolytic reduction. The less reactive metals are extracted by chemical and thermal reduction of their ores.

Group 1 elements

- Group 1 elements are all metals except for hydrogen. The metals are commonly known as alkali metals because they react with water to form alkalis.
- Group 1 metals have only one valence electron in each of their atoms, so they readily ionize to form univalent positive ions. As a result, they are very good reducing agents.
- Group 1 metals are soft and light with low melting points because the atoms in their crystal lattices are held together by weak metallic bonds.
- Chemically, the Group 1 metals are very reactive. As we go down the group, this reactivity increases as the ionization energy decreases.
- Group 1 metals and their ions give characteristic flame colours.

Sodium

- Sodium is a typical Group 1 metal. It is extracted by electrolytic reduction of the fused sodium chloride in the Downs cell.
- It is a soft, silvery metal with a relative density of 0.98 and a low melting point 97 °C.
- It is very reactive, readily combining with the atmospheric gases and has to be stored under oil. Sodium is used in street lamps and in the manufacture of compounds like sodium peroxide and sodamide.

Compounds of sodium and potassium

- Compounds of sodium and potassium are ionic solids with high melting points. They are soluble in water and are white unless the anion is coloured.
- (a) Sodium hydroxide or caustic soda is manufactured by electrolysis of brine.

(b) It is used to manufacture soap, rayon and paper; in purifying bauxite; and in refining petroleum.

(a) Sodium chloride is obtained from rock salt and sea-water.

(b) It is a dietary requirement and is a common food preservative. It is used in the manufacture of many compounds such as sodium, chlorine and sodium hydroxide.

(a) Sodium trioxocarbonate(IV) or washing soda is manufactured by the Solvay process from sodium chloride and calcium trioxocarbonate.

(b) It is used to make glass, caustic soda and soap, and as a water-softener.

Potassium trioxonitrate(V) or nitre is used in making explosives.

roup 2 elements

All Group 2 elements are metals. Known as alkaline earth metals, they have only two valence electrons in each of their atoms and ionize readily to form divalent positive ions.

They are reactive but less than the Group 1 metals. The metallic bonds in their crystal lattices are stronger than those in the Group 1 metals. The metals and their ions give characteristic flame colours.

alcium

Calcium occurs naturally as calcium trioxocarbonate(IV) in limestone, chalk and marble. It is extracted by electrolysis of the fused chloride.
Calcium reacts readily with water, and with carbon(IV) oxide and oxygen in the air. Calcium is an essential dietary requirement, needed for the development of healthy bones and teeth.

alcium compounds

Calcium oxide or quicklime is made by heating limestone. It is used to make slaked lime and calcium carbide; to treat acidic soils; and to neutralize acidic wastes in industry.

Calcium hydroxide or slaked lime is used to treat acidic soils and to make mortar, an important building material.

Calcium carbonate, as limestone, is a major raw material in chemical industry. It is used for the extraction of iron and for making glass, quicklime and cement. Cement and concrete (made from cement) are important building materials.

agnesium

Magnesium is extracted by electrolysis of the fused chloride.

It is used to prepare light but tough alloys.

Group 3 elements

All Group 3 elements except boron are metals.

Aluminium is a familiar Group 3 metal. It has three valence electrons in each atom and tends to form more covalent compounds than ionic ones.

Aluminium

Aluminium is found commonly as the oxide ore, bauxite. The metal is extracted by electrolysis of the molten oxide.

- (a) Aluminium reacts with oxygen in air to form an oxide which forms a thin continuous coating over the metal. This makes the metal corrosion-free and passive.

  (b) It is amphoteric and reacts with both acids and alkalis.

  (c) It reduces iron(III) oxide to molten iron. This reaction is used in the thermit process to weld broken metallic parts.
- Aluminium is used for making cooking utensils and overhead electric cables. Its alloys are used for making the body parts of aircraft.

Compounds of aluminium

- Aluminium oxide or alumina is prepared by heating aluminium hydroxide. It is amphoteric. It is used to make furnace linings and in the catalytic cracking of hydrocarbons.
- Aluminium hydroxide is used as a mordant in dyeing cloth.
- Aluminium tetraoxosulphate(VI) forms alums with other tetraoxosulphates(VI). It is used in the treatment of water and sewage, and in paper-making.

Group 4 elements

- Group 4 elements change from non-metals (carbon) to metals (tin and lead) as we go down the group. Since the atoms of these elements have four valence electrons, they tend to form covalent compounds.
- Carbon forms covalent compounds in which it has an oxidation state of +4. Tin and lead form compounds in which they exist in the +2 and +4 oxidation states. The stable compounds of lead are the lead(II) compounds which are mainly ionic.

Tin

- Tin occurs as the oxide ore, cassiterite. It is extracted by roasting the ore in air to remove impurities, and then heating the concentrated ore with powdered charcoal to reduce the tin(IV) oxide to the metal. The impure tin formed is purified by remelting.
- Tin is used to coat iron and steel to prevent them from rusting. It is important in the food canning industry for coating the cans since it is not poisonous.

Lead

- Lead occurs mainly as the sulphide ore, galena. The ore is roasted in air and then heated in a blast furnace with coke to extract the metal.
- Lead is used for roofing and for making gas pipes, bullets, lead accumulators and alloys. It is also used as a shield against X-rays and radioactive radiation.

Compounds of lead

- (a) Lead(II) oxide is amphoteric. It is used in making lead accumulators and lead glass, and as a drier in paints, varnishes and glazes.

  (b) Lead(IV) oxide is a powerful oxidizing agent. It is used in match-heads and in lead accumulators.

  (c) Dilead(II) lead(IV) oxide is a red powder used in priming paints and making lead glass and plumber's cement.

EXERCISES

1. Most metals exist in nature as
A crusts. B alloys.
C ores. D felspar.

Most metals are malleable with high densities and have high boiling and melting points except
A Zn B K
C Sn D Ca

Hydrogen differs from the rest of the common non-metals because
A it is an electron acceptor.
B it is an electron donor.
C it is monoatomic.
D it appears in free state.

Most reactive metals are extracted from their ores through electrolysis except
A Na B Ca
C Al D Mg

Method adopted in extracting a particular metal from its ore depends on
A the fragile nature of the metal.
B the location of the ore in the earth's crust.
C the stability of the ore which depends on the position of the ore in the E.C.S.
D the availability of power in the country.

Group I metals are good reducing agents because
A they are soft.
B they are light.
C they easily form unipositive ions.
D They have low melting points.

7. Potassium is difficult to extract even through electrolysis because
A it is soft.
B it is deliquescent.
C it evaporates fast.
D it is very reactive.

8. In Down's cells used for the extraction of sodium metal, the anode and the cathode are screened with gauze diaphragm in order to
A obtain screened products.
B obtain cheap products.
C separate the products from reacting.
D obey conventional rule of electrolysis.

9. The major function of calcium chloride in the sodium electrolyte is to
A obtain pure product.
B remove major impurities.
C extend the life span of Down's cell.
D depress the melting point of sodium chloride.

10. Corrosion of highly reactive metals is called
A rusting.
B temperature inhibitants.
C tarnishing.
D concentration of ores.

11. These are deliquescent except
A Pure NaCl B $FeCl_3$
C $CaCl_2$ D NaOH pellets.

12. The only by-product of the Solvay Process not used in the process is
A CO_2 B CaO
C $CaCl_2$ D NaCl

13. In the extraction of calcium, some calcium fluoride is introduced to
A obtain pure products.
B stabilize the electrodes.
C check the calcium from reacting with chlorine.
D act as a temperature depressant.

14. Calcium reacts directly with nitrogen to form
A Ca_3N_3 B Ca_2N_3
C Ca_3N_2 D Ca_3N

15. In the extraction of aluminium, some Na_3AlF_6 is added to the electrolyte, bauxite, to
A stabilize the products.
B increase the field of aluminium.
C lower the fusion point of the bauxite.

D elevate the boiling point of the molten electrolyte.

16. Aluminium reacts readily with all common mineral acids except

A HNO_3 B HCl
C H_2SO_4 D H_3PO_4

17. The great affinity of aluminium for oxygen at high temperatures is employed in the

A electrolytic process.
B thermit process.
C Haber process.
D lead chamber process.
E Solvay process.

18. Aluminium materials should not be exposed to alkalis because aluminium is

A basic.
B acidic.
C an oxidizing agent.
D a reducing agent.
E amphoteric.

19. The Solvay process cannot be employed in the production of potassium hydrogentrioxocarbonate(IV) because it is

A acidic. B basic.
C insoluble. D soluble.
E amphoteric.

20. Which of these compounds is not an alkali?

A Sodium hydroxide
B Aqueous ammonia
C Magnesium hydroxide
D Potassium hydroxide
E None of the above

21. (a) Give a definition of
(i) a metal, (ii) a non-metal.
(b) Compare the properties (both physical and chemical) of metals and non-metals.
(c) Discuss the reasons why some metals occur as free elements in nature while others occur in combined forms. Give two examples of each type.
(d) Name two metals which will not liberate hydrogen from dilute tetraoxosulphate(VI) acid.
(e) Name two metals which form both soluble trioxocarbonates(IV) and soluble tetraoxosulphates(VI).

22. (a) Draw the electrolytic cell for the extraction of sodium from sodium chloride.
(b) Describe and explain the reactions taking place at the electrodes.
(c) How is metallic sodium usually stored and explain why it is thus stored?

23. (a) How would you prepare caustic soda from washing soda? Give the experimental details and the equation of the reaction.
(b) How does sodium hydroxide react with metallic zinc and aluminium respectively? Give the equations of the reactions.
(c) Explain why the glass stoppers of caustic soda solutions get stuck in the bottles.
(d) What happens to
(i) washing soda
(ii) caustic soda pellets
when they are exposed to the atmosphere?

24. (a) What is the main source of aluminium in nature?
(b) Using a diagram and equations, explain how pure aluminium is extracted from the above source.
(c) With the aid of a diagram and the equation of the reaction, show how you would mend a broken iron rod by the thermit process.
(d) Why does iron but not aluminium corrode easily on exposure to air despite the fact that aluminium is above iron in the electrochemical series?

25. (a) With the help of equations of the reactions and a diagram, show how washing soda is manufactured industrially from common salt and other reagents.
(b) Why is it impossible to manufacture potassium trioxocarbonate(IV) by this process?

26. (a) Describe what happens when water is added drop by drop to quicklime. Give the equation of the reaction involved.
(b) Give four uses of quicklime.
(c) How would you obtain quicklime from sea-shells?
(d) Write notes on the following:
(i) Cement
(ii) Concrete and reinforced concrete
(iii) Milk of lime
(iv) Slaked lime
(v) Plaster of Paris

METALS AND THEIR COMPOUNDS (2)

27

TRANSITION ELEMENTS

ransition elements are all metals of economic mportance. They are found in the *d*-block of the eriodic Table between Groups 2 and 3. They occupy hree rows, with ten elements in each row. The term *ansition element* refers only to an element which as partially filled *d* orbitals.

First Transition Series

he first transition series from scandium to zinc is rticularly important in industry. This series of ten -block metals occurs in Period 4. Potassium and lcium are the *s*-block metals in this period. The ansition metals have very similar properties and are ite different from the reactive *s*-block metals of roups 1 and 2.

Electronic Configuration

The atoms of the metals in the first transition series have one or two 4*s* electrons like the Groups 1 and 2 metals in the same period (see fig. 27.2). In addition, they have partially filled 3*d* orbitals which are responsible for the special properties of the transition metals. Exceptions include

- zinc atom (Zn), zinc ion (Zn^{2+}), copper atom (Cu), and copper(I) ion (Cu^+) which have completely filled 3*d* orbitals, and
- scandium ion (Sc^{3+}) which does not have any electrons in its 3*d* orbitals.

Zinc and the forms of copper and scandium given above are usually considered as non-transitional.

Chromium and copper atoms have only one

ble 27.1 *The transition elements.*

irst transition series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Second transition series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Third transition series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Number of *d* electrons	1	2	3	5	5	6	7	8	10	10

Fig. 27.1 The *s*-block and *d*-block metals of Period 4.

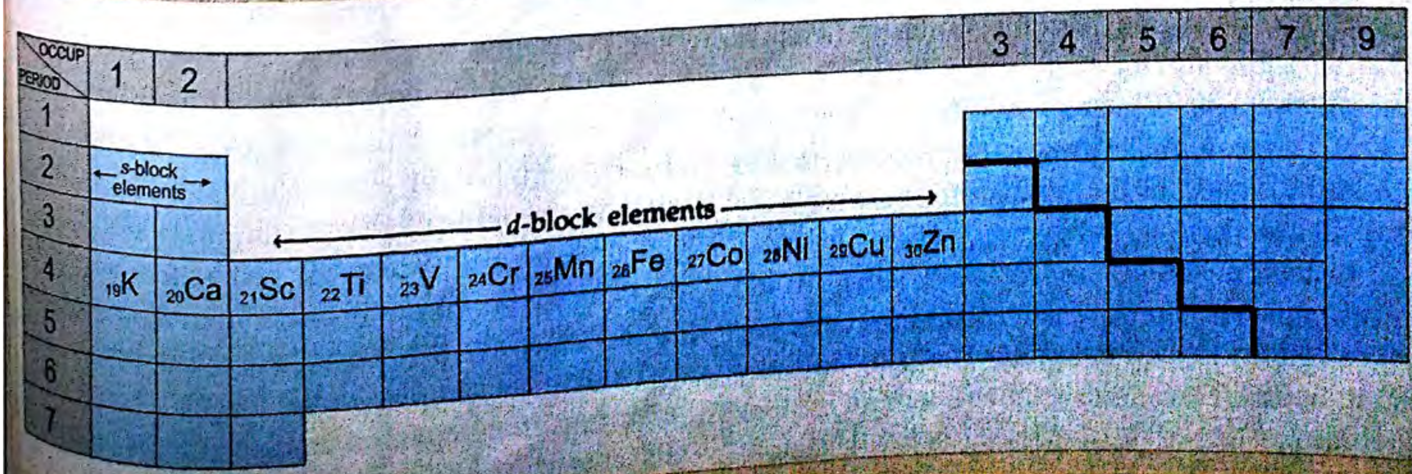


Fig. 27.2 Electronic configuration of the *s*-block and *d*-block metals of Period 4

Element	**Electronic configuration**										
***s*-block**	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*					4*s*
K	2	2	6	2	6						1
Ca	2	2	6	2	6						2
***d*-block**											
Sc	2	2	6	2	6	↓					2
Ti	2	2	6	2	6	↓	↓				2
V	2	2	6	2	6	↓	↓	↓			2
Cr	2	2	6	2	6	↓	↓	↓	↓	↓	1
Mn	2	2	6	2	6	↓	↓	↓	↓	↓	2
Fe	2	2	6	2	6	↓↑	↓	↓	↓	↓	2
Co	2	2	6	2	6	↓↑	↓↑	↓	↓	↓	2
Ni	2	2	6	2	6	↓↑	↓↑	↓↑	↓	↓	2
Cu	2	2	6	2	6	↓↑	↓↑	↓↑	↓↑	↓↑	1
Zn	2	2	6	2	6	↓↑	↓↑	↓↑	↓↑	↓↑	2

NOTE There are five 3*d* orbitals. Each of these can only accommodate two electrons with opposite spins.

electron in the 4*s* orbital. This is because a special stability is associated with the $3d^5$ and $3d^{10}$ electronic configurations, i.e. when all the five 3*d* orbitals are singly or doubly filled.

Physical Properties

Transition elements are typical metals with high boiling and melting points. They are hard, dense and lustrous. They are also good conductors of heat and electricity.

These properties of the transition metals indicate the presence of strong metallic bonding. This is because, in addition to the 4*s* electrons, the 3*d* electrons in the atoms of these metals are also available for bonding. The presence of these extra electrons makes the metallic bonds in the transition elements very strong. In comparison, the corresponding Groups 1 and 2 metals, potassium and calcium, are soft and have lower melting points. Their atoms have only one or two electrons in their outermost shells for forming metallic bonds. Thus, the metallic bonds in *s*-block metals are not as strong as those in *d*-block metals.

The atomic size of the *s*-block and *d*-block metals also affects their properties. Both groups have atoms with the same number of electron shells (*K*, *L*, *M*, *N*), but the atomic numbers of the transition metals are larger. As a result, the atoms of the transition metals are smaller than those of the *s*-block metals. For example, the nucleus of a copper atom with a charge of +29 will have a stronger attraction on its electrons and will pull them closer to it (thus decreasing the atomic size) than the nucleus of a potassium atom with a charge of +19. This difference in atomic sizes is reflected by the atomic radii of copper (0.12 nm) and potassium (0.20 nm).

Thus, we see that the strong metallic bonds and the small sizes and high charges of the atoms account for the high boiling and melting points, densities and tensile strengths of the transition metals.

The melting points of manganese and zinc are comparatively lower because their atoms have half-filled and fully-filled *d* orbitals respectively. Such *d* orbitals give stability to the atoms. Therefore, the *d* electrons in manganese and zinc do not contribute to the metallic bonding.

Table 27.2 *Some properties of the transition metals of the first series.*

PROPERTY \ ELEMENT	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	s-block		*d*-block									
Atomic number	19	20	21	22	23	24	25	26	27	28	29	30
Relative atomic mass	39.1	40.1	45.0	47.9	50.9	52.0	54.9	55.8	58.9	58.7	63.5	65.4
Melting point/ °C	63.5	850	1 400	1 720	1 710	1 900	1 250	1 530	1 490	1 450	1 083	419
Boiling point/ °C	775	1 490	2 700	3 200	3 500	2 480	2 000	2 730	2 900	2 840	2 350	907
Density/g cm^{-3}	0.86	1.55	3.1	4.5	6.1	7.1	7.2	7.9	8.7	8.9	9.0	7.1
Colour of M^{2+} (in solution)	–	–	–	Brown	Purple	Blue	Pink	Green	Pink	Green	Blue	—
Valencies (commonest in bold)	+1	+2	+3	+2,+3,+4	+2,+3,+4,+5	+2,+3,+6	+2,+3,+4,+6,+7	+2,+3	+2,+3	+2,+3	+1,+2	+2
Atomic radius/nm	0.20	0.17	0.14	0.13	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.13
Ionic radius/nm												
M^{+}	0.130											
M^{2+}		0.094		0.090	0.088	0.084	0.080	0.076	0.074	0.072	0.070	0.074
M^{3+}			0.081	0.076	0.074	0.069	0.066	0.064	0.063	0.062		

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The densities of the transition metals increase across the series because their relative atomic masses increase progressively while their atomic sizes remain fairly constant. The densities of potassium and calcium, however, are lower than those of the transition metals since the latter have higher atomic masses and smaller atomic sizes.

Chemical Reactivity

In the *s*-block and *p*-block, the chemical properties of the elements in the same period vary, often quite markedly, from left to right. This does not happen with the transition metals because electrons are added progressively to the inner *d* orbitals, not the outermost orbitals, as in the *s*-block and *p*-block elements.

The nuclei of the transition metals exert a greater attraction on their electrons than the nuclei of the *s*-block metals. So the *s*-block metals have a lower ionization energy and are more reactive than the transition metals.

In general, transition metals are moderately reactive. Their reactivities decrease across the series due to a corresponding increase in the values of their ionization energies.

Variable Oxidation States

Transition metals have variable oxidation states because the 3*d* electrons are available for bond formation. For example, manganese with the following electronic configuration

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$$

can lose

- two 4*s* electrons to give a +2 oxidation state as in MnO,
- two 4*s* and two 3*d* electrons to give a +4 oxidation state as in MnO_2,
- two 4*s* and four 3*d* electrons to give a +6 oxidation state as in MnO_4^{2-},
- two 4*s* and five 3*d* electrons to give a +7 oxidation state as in MnO_4^-.

In addition, the differences in the successive ionization energies of a transition metal are small. This allows the formation of stable ions at each stage. For example

	$Mn \rightarrow Mn^+$	$\rightarrow Mn^{2+}$	$\rightarrow Mn^{3+}$
Ionization energy (kJ mol^{-1})	720	1 510	3 260

Non-transition metals usually have one stable oxidation state. Successive oxidations show large differences in the ionization energies. For example, in calcium, the +1 oxidation state is transient, the +2 state is the stable state while the +3 state does not exist naturally since the ionization energy needed for its formation is very large.

	$Ca \rightarrow Ca^+$	$\rightarrow Ca^{2+}$	$\rightarrow Ca^{3+}$
Ionization energy (kJ mol^{-1})	580	1 140	5 000

The lower oxidation states of the transition metals occur in ionic compounds and tend to form

- reducing agents, e.g. chromium(II) salts, and
- basic oxides, e.g. manganese(II) oxide.

The higher oxidation states are found in covalent compounds and tend to form

- oxidizing agents, e.g. potassium heptaoxodichromate(VI) and potassium tetraoxomanganate(VII), and
- acidic oxides, e.g. manganese(VII) oxide.

Compounds of transition metals with intermediate oxidation states form amphoteric oxides.

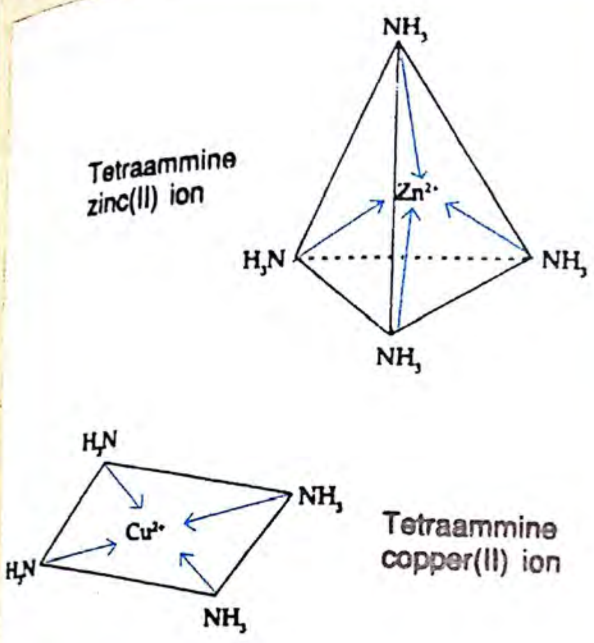
Complex Ion Formation

Transition metals have an outstanding ability to form complex ions. A complex ion has a central positive ion linked to several other atoms, ions or molecules called *ligands*. The bonding between the central metal ion and the ligands may be either predominantly electrovalent or predominantly coordinate.

An example of a complex ion is the blue tetraammine copper(II) ion, $[Cu(NH_3)_4]^{2+}$, in which the central copper(II) ion is linked by coordinate bonding to four ammonia molecules.

Transition metal complex ions usually have four or six ligands. When the complex ion has six ligands, the ligands are arranged octahedrally around the central metal ion as in the case of hexacyanoferrate(III) ion, $[Fe(CN)_6]^{3-}$ (see page 60). When four ligands are

Fig. 27.3 Some examples of complex ions.



present, they may be arranged tetrahedrally as in tetraammine zinc(II) ion, $[Zn(NH_3)_4]^{2+}$, or at the corners of a square as in tetraammine copper(II) ion.

The electrons donated by the ligands usually fill up the incomplete *d* orbitals, and the 4*s* and 4*p* orbitals in the central transition metal ion.

All transition metal ions tend to form complex ions with water. These hydrated ions are usually unstable.

Colour of Transition Metal Ions

Transition metallic ions are usually coloured which serve as a useful guide in identifying a compound. The colours are associated with partially filled 3*d* orbitals (i.e. $3d^1$ to $3d^9$). Zinc and scandium ions are colourless since they do not have partially filled 3*d* orbitals. In the complex ions, the nature of the ligands also contribute to the colour.

Catalytic Activity

The ease with which ions of transition metals change their oxidation states enables them to act as catalysts. For example, in the catalytic decomposition of hydrogen peroxide, H_2O_2, to oxygen and water, the catalyst used to speed up the reaction is manganese(IV) oxide. The Haber process, the Contact process and the hydrogenation of vegetable oil are examples of industrial processes where transition metals are used as catalysts. Iron with aluminium and potassium oxides, vanadium(V) oxide and nickel are the catalysts used in the three processes respectively.

Table 27.3 The colours of some transition metal ions in aqueous solution.

Ion	*d* electrons	Colour
Sc^{3+}	$3d^0$	Colourless
Ti^{3+}	$3d^1$	Purple
V^{3+}	$3d^2$	Green
Cr^{3+}	$3d^3$	Violet
Mn^{3+}	$3d^4$	Violet
Mn^{2+}	$3d^5$	Pink
Fe^{3+}	$3d^5$	Yellow
Fe^{2+}	$3d^6$	Green
Co^{2+}	$3d^7$	Pink
Ni^{2+}	$3d^8$	Green
Cu^{2+}	$3d^9$	Blue
Zn^{2+}	$3d^{10}$	Colourless

IRON

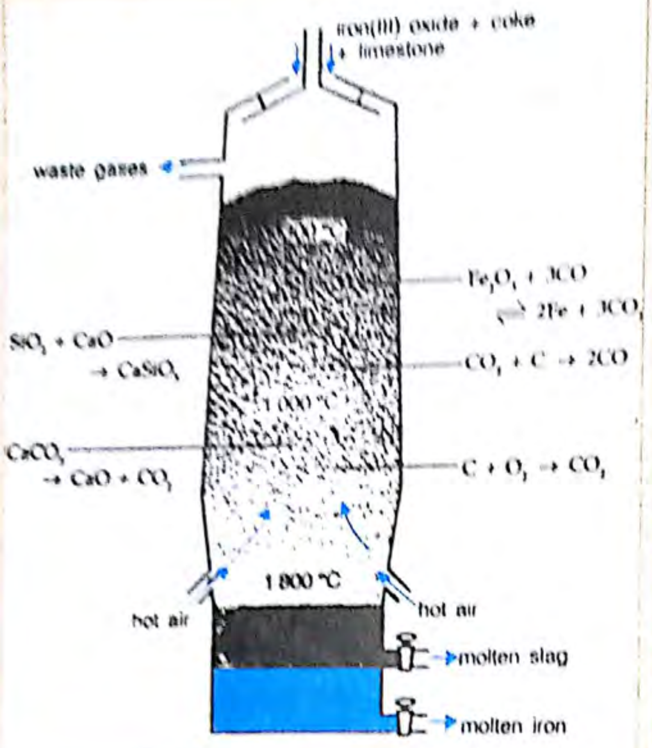
Iron is the second most abundant metal found in the earth's crust after aluminium. It is not found in the free metallic state except in meteorites. The most common iron ores are *haematite*, Fe_2O_3, *magnetite*, Fe_3O_4, *iron pyrites*, FeS_2, *siderite* or *spathic iron ore*, $FeCO_3$, and *limonite*, $Fe_2O_3.H_2O$. Iron is also present as trioxosilicates(IV) in clay soils. It is a constituent of the pigments haemoglobin in animals and chlorophyll in plants.

Iron ores are available in commercial quantities in Anambra and Edo States. However, the most important iron ore areas are in Itakpe, Ajaokuta, Jebba and Lokoja in Kogi State. Ore from these areas provide raw materials for the National Iron and Steel Industry of Nigeria. Two new steel-works have been set up at Aladja in Edo State and at Ajaokuta in Kogi State.

Extraction

The iron ore is first roasted in air so that iron(III) oxide is produced. The iron(III) oxide is then mixed with coke and limestone and heated to a very high

Fig. 27.4 Extraction of iron



temperature in a blast furnace. The ingredients are loaded into the furnace from the top while a blast of hot air is introduced into it from the bottom through small pipes known as tuyéres.

The temperature inside the furnace varies from about 2 000 °C near the bottom to about 200 °C at the top. In the lower part, the white-hot coke is oxidized by the oxygen in the hot air blast to liberate carbon(IV) oxide. The reaction is exothermic and a lot of heat is evolved.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

As the gas mixture moves up, the oxygen in the air lessens and the carbon(IV) oxide becomes reduced by the white-hot coke to carbon(II) oxide. The carbon(II) oxide then reacts with the iron(III) oxide, reducing it to iron.

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$
$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

The limestone present decomposes at this high temperature to yield calcium oxide, which then combines with the silicon(IV) oxide (impurity) to form calcium trioxosilicate(IV).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
$$SiO_2(s) + CaO(s) \rightarrow CaSiO_3(s)$$

The molten iron formed sinks to the bottom of the furnace, and is tapped off. It is run into moulds where it sets as pig iron. It may also be used directly to make steel, or further purified to produce and wrought iron. The calcium trioxosilicate(IV) and other earthy impurities form a molten slag which floats on the molten iron and can be tapped off separately. The waste gas mixture which comes out of the furnace contains mainly nitrogen with about 30% carbon(II) oxide and 10% carbon(IV) oxide, and is used for pre-heating the air blast and iron ore.

The whole process is continuous, and a blast furnace is normally kept going continuously for months or years until the lining needs to be replaced.

Types of Iron and Their Uses

Pig iron

Pig iron is obtained directly from the blast furnace, and is quite impure. It contains up to 5% of carbon, which is present both as graphite and as iron carbide, Fe_3C, together with impurities like phosphorus, sulphur, silicon and manganese in varying proportions, depending on the ores used and the operating temperature. The presence of these impurities lowers the melting point of the iron from 1 530 °C to about 1 200 °C. Pig iron is hard and brittle and has limited industrial uses.

Cast iron

Cast iron is obtained from pig iron which has been re-melted with some scrap iron and then cooled in moulds of required shapes. Cast iron has a slightly lower percentage of impurities than pig iron and like the latter, it is brittle and cannot be welded or forged. It is used for making objects which do not require high tensile strength, e.g. cookers, stoves, radiators, lamp posts, railings, the base of Bunsen burners and certain heavy machinery. Cast iron is easy to melt and expands slightly when cooled.

Wrought iron

Wrought iron, the purest form of commercial iron, contains only about 0.1% carbon. It is obtained by heating cast iron in a furnace with haematite, Fe_2O_3. During this process, carbon and sulphur are oxidized nd removed as gaseous oxides. Any phosphorus and silicon(IV) oxide present are also oxidized and emoved as slag from the semi-molten mass of iron.

$$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(s) + 3CO_2(g)$$
$$2Fe_2O_3(s) + 3S(s) \rightarrow 4Fe(s) + 3SO_2(g)$$

Wrought iron is soft but very tough and malleable. t can be shaped by hammering at about 1000 °C bout 500 °C below its melting point). It can be easily elded and forged. It is used for making nails, chains, on rods and sheets, horse shoes, agricultural plements and the cores of electromagnets.

eel and Its Uses

bout 90% of the pig iron produced is convered into eel. Ordinary steel is an alloy of iron with about 1-1.5% of carbon, while the alloy steels contain rying proportions of other elements, e.g. nickel and romium, depending on their intended use.

Steel is hard, tough and strong. Its properties pend on its carbon content, the heat treatment it ceives (tempering) and the presence of other metals. rdness and brittleness increase as the carbon content the steel increases. For example, mild steels contain 1–0.25% carbon and are soft, malleable and ductile. ey are used for general engineering purposes such in the making of tin-plates, corrugated sheets, car dies, nails, screws, steel pipes, etc. Medium steels 25–0.6% carbon) and hard steels (0.6–1.5% carbon) e harder than mild steels. They are used for making ols and most alloy steels.

Medium and hard steels can be heat-treated to oduce steels with different degrees of hardness by ating the steel to red heat and cooling it suddenly. he steel obtained is very hard and brittle. To remove e brittleness and increase its tensile strength, the eel is reheated to certain carefully regulated mperatures and allowed to cool. This is known as *mpering*. The hardness and tensile strength of the teel depends on the temperature to which it is heated nd the rate at which it is heated and cooled during empering. The steel thus obtained is known as *empered steel* and can be used for making razor blades nd tools.

Alloy steels are made by adding other metals to teel. These metals give the steel various desired roperties. The incorporation of chromium and nickel gives stainless steel which resists rusting and is used for making cutlery, scissors, saws and machinery; cobalt gives a highly magnetic steel used for making permanent magnets; tungsten gives very hard steels for making cutting and drilling tools; manganese gives manganese steels that are hard and tough and are used in rock drills; silicon gives spring steels; and molybdenum gives molybdenum steels which can resist acid corrosion.

Steel Making Process

There are several methods of making steel, the more important of which are the *Bessemer process*, the *open-hearth process*, the *electric-arc furnace process* and the *direct-reduction process*. However, they are all based on the same general principle, which is

- remove all the impurities from molten pig iron by oxidation, and
- add known quantities of carbon and other elements to the molten iron to obtain steel of the desired composition.

Pig iron, scrap iron and scrap steel are the raw materials that are used for making steel.

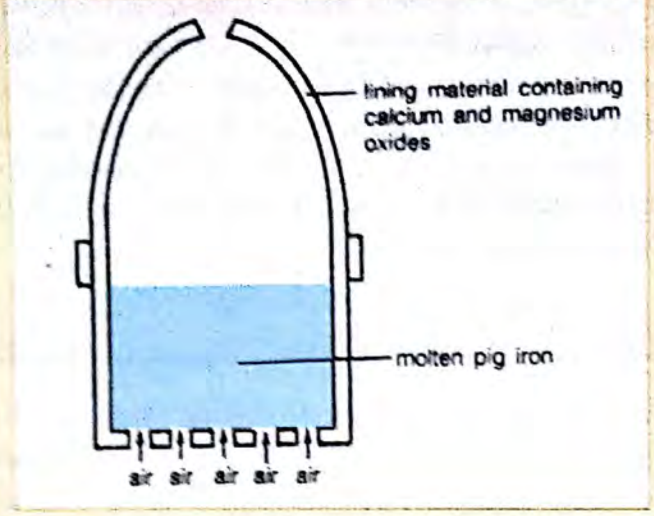
Bessemer process

A Bessemer converter is a huge vessel which can be rotated into various positions to enable materials to be loaded and unloaded. The converter is lined on the inner side with materials containing calcium and magnesium oxides.

Molten pig iron from the blast furnace is run into the converter. Air is blown into the molten iron from the bottom to oxidize impurities like carbon and sulphur to gaseous oxides. The remaining impurities such as silicon, phosphorus and manganese react with the lining of the converter to form slag which is tapped off. Then, required amounts of carbon and other metals are added to the molten iron to form the various types of steels.

The Linz–Donawitz (L-D) Process or Basic Oxygen Process which uses a modified Bessemer converter is now more commonly used. Here, a high speed jet of oxygen is blown vertically down onto the molten pig iron from a water-cooled oxygen lance. Heat liberated by the oxidizing reactions maintains the iron in a molten state.

Fig. 27.5 Original Bessemer converter.



This process is more economical since the time needed to produce steel is greatly reduced. The quality of steel produced is also better since, in the old process, the nitrogen in the air tends to make steel brittle.

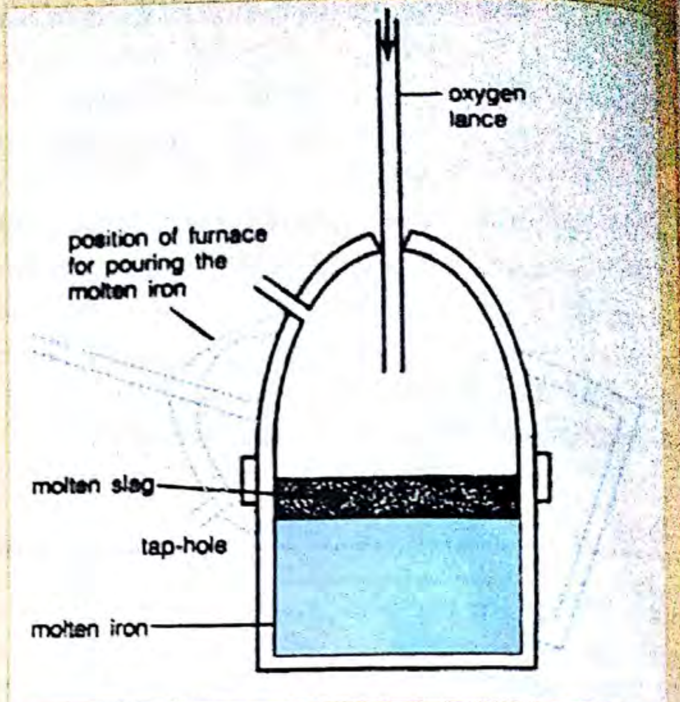
Open-hearth process

In the open-hearth process, the furnace has a broad shallow hearth. Flames from burning gas or oil melt the raw materials in the furnace. Solid oxygen-rich iron containing materials, such as iron ore, are loaded into the furnace to provide the oxygen for oxidizing the impurities. Limestone may be added to remove other unwanted elements as slag. The required amounts of carbon and other alloying materials are added for steel making. When the chemical content of the steel is correct, the molten steel is tapped off from the furnace, after the slag that floats on the steel is drawn off.

Electric-arc furnace process

The electric-arc furnace has a cylindrical shallow hearth with a removable lid through which three graphite electrodes project. Scrap iron is deposited in the furnace and the lid is swung into place. Electric current from the electrodes provides heat to melt the scrap. A very high temperature (as high as 1 900 °C) is reached as the electric arcs are struck. Limestone and oxygen are added through doors on the side of the furnace. Alloying materials needed for steel making are also added in the same way. The furnace is tipped to drain off the slag first, then the molten steel is poured out. This process is very expensive but it produces high quality steel. The Ovwian–Aladja steel-works has several electric-arc furnaces.

Fig. 27.6 Modified Bessemer converter.



Direct-reduction process

The construction of a blast furnace to reduce iron ore involves a very high capital cost. In the Aladja steel-works, a direct-reduction process is used to reduce iron ore and produce steel in the same furnace. The process uses a stream of reducing gases, consisting of hydrogen and carbon(II) oxide, to reduce the iron ore to iron.

$$Fe_2O_3(s) + CO(g) + 2H_2(g) \rightarrow 2Fe(s) + CO_2(g) + 2H_2O(g)$$

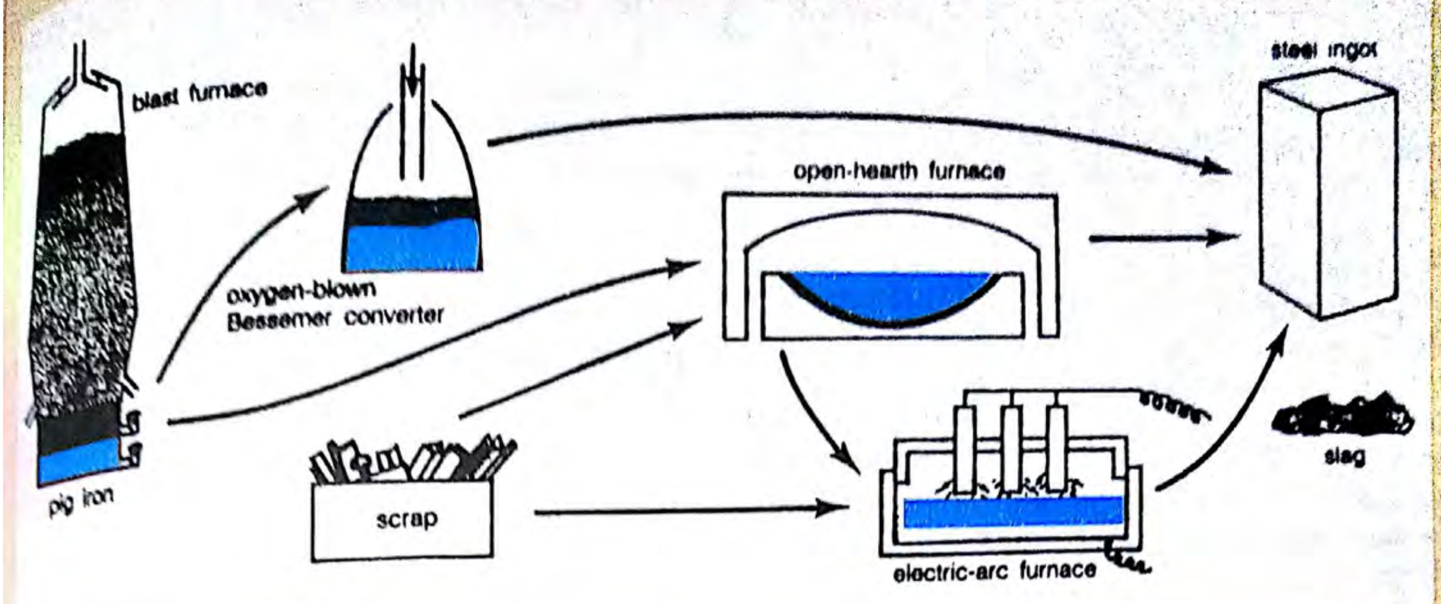
By regulating the flow of reducing gases, the iron obtained can be converted to various grades of steel in the same furnace.

$$3Fe(s) + CO(g) + 2H_2(g) \rightarrow Fe_3C(s) + H_2O(g)$$

The advantages of the direct-reduction process include

- the low capital cost involved;
- the low production cost that arises from the cheap source of reducing gases (which are readily produced from natural gas); and
- the ability to produce all grades of steels.

ig. 27.7 Conversion of iron to steel by the three common processes.



ron- A Transition Element

ron is a transition element with all the properties that haracterize this particular group. Besides having oloured ions, iron can form complexes ions by oordinate bonding. It also exhibits variable oxidation tates, the most stable being the +2 and +3 states.

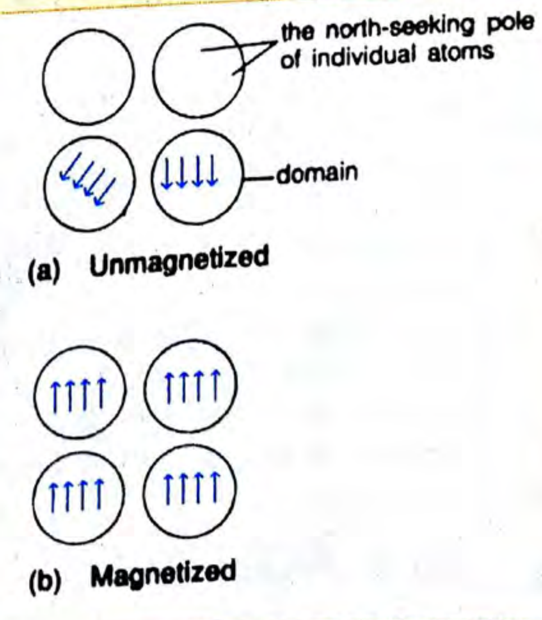
Iron is important in biological systems because of s ability to form complexes and to exist in different xidation states. The blood pigment haemoglobin ontains iron, which is able to become reversibly onded (by forming coordinate bonds) with oxygen nolecules. This allows haemoglobin to transport xygen to all parts of our body and release it where t is needed. Iron-sulphur proteins found in mitochondria and chloroplasts act as electron carriers (iron functions by changing its oxidation state).

Physical Properties

Appearance	Silvery solid with lustre
Relative density	7.9
Malleability	Very malleable
Ductility	Ductile
Tensile strength	High tensile strength
Melting point	1 530 °C
Conductivity	Good conductor of heat and electricity
Special property	Can be magnetized easily

Magnetism This is associated with the spinning o inner electrons about their axes. Atoms or ions having only paired electrons exhibit *diamagnetism*, i.e. they are repelled by a magnetic field. Those having one or more unpaired electrons are attracted into a magnetic field, i.e. they exhibit *paramagnetism*. Iron atom has four unpaired 3*d* electrons (see page 473). However, the attraction of iron objects into a magnetic field is far stronger than can be explained by the unpaired electrons. The special magnetic property of iron and certain magnetic metals and alloys is called *ferromagnetism*. In the solid state of these metals the atoms are thought to be grouped into small regions

Fig. 27.8 Ferromagnetism.



(a) Unmagnetized

(b) Magnetized

Table 27.4 The electronic configurations and some properties of the iron atom and its ions.

		Electronic configuration	Oxidation state	Colour of ions	Metal ion complex	Industrial catalyst
Iron	Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$	–	–	–	**In the Haber process**
Iron(II)	Fe^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$	+2	**Green**	$[Fe(CN)_6]^{4-}$	
Iron(III)	Fe^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$	+3	**Yellow**	$[Fe(CN)_6]^{3-}$	

called domains containing a large number of atoms. Within each domain, the individual atoms are all directed in the same way producing a magnetic effect. However, in an unmagnetized piece of iron the domains are directed in different directions, so that the magnetic effects are cancelled. When the piece of iron is placed in a magnetic field, the domains become aligned in one direction, producing a strong magnetic effect.

Chemical Properties

Reaction with air When iron is exposed to moist air, it gradually rusts, due to the formation of hydrated iron(III) oxide, $Fe_2O_3.xH_2O$.

$$4Fe(s) + 3O_2(g) + 2xH_2O(l) \rightarrow 2Fe_2O_3.xH_2O(s)$$

Unlike the oxide layers formed on exposure to air by metals such as zinc and aluminium, the iron rust layer is porous and does not prevent further corrosion. Thus the process of rusting continues until all the iron has been converted to the oxide.

If finely divided iron, e.g. iron filings, is heated in air, it will combine with oxygen to form iron(II) diiron(III) oxide, Fe_3O_4 (magnetic oxide of iron)

$$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s)$$

Reaction with steam When steam is passed over red-hot iron filings, iron(II) diiron(III) oxide and hydrogen are produced. This reaction is reversible.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Reaction with non-metals When heated, iron readily combines with chlorine to give iron(III) chloride and with sulphur to give iron(II) sulphide. It also combines directly with phosphorus and carbon but not with nitrogen.

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$
$$Fe(s) + S(s) \rightarrow FeS(s)$$

Reaction with acids Iron dissolves readily in dilute hydrochloric and tetraoxosulphate(VI) acids to give iron(II) salts and hydrogen.

$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$

With dilute trioxonitrate(V) acid, it yields several products including iron(II) trioxonitrate(V), ammonium trioxonitrate(V) and the oxides of nitrogen. No reaction is observed when concentrated trioxonitrate(V) acid is added to iron, probably because the acid oxidizes the iron to form a protective layer of oxide. Thus, concentrated trioxonitrate(V) acid is stored in iron containers.

Tests for iron(II) ions

Soluble iron(II) salts usually dissolve to form green solutions.

Sodium hydroxide Add a few drops of sodium hydroxide to the unknown salt solution. The formation of a dirty-green gelatinous precipitate, which is insoluble in excess sodium hydroxide, indicates the presence of iron(II) ions. If this precipitate turns reddish-brown iron(III) ions on exposure to air, the presence of iron(II) ions is confirmed.

In this reaction, the dirty green iron(II) hydroxide precipitated is oxidized by atmospheric oxygen to form reddish-brown iron(III) hydroxide.

NOTE Similar results are obtained if aqueous ammonia is used instead of sodium hydroxide.

$$Fe^{2+}(aq) + 2NaOH(aq) \rightarrow \underset{\substack{\text{dirty-green}\\ \text{precipitate}}}{Fe(OH)_2(s)} + 2Na^+(aq)$$

$$4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightarrow \underset{\substack{\text{reddish-brown}\\ \text{precipitate}}}{4Fe(OH)_3(s)}$$

Table 27.

REAGENT / TYPE OF SALT	Iron(II) salt	Iron(III) salt
Sodium hydroxide solution	Green precipitate of $Fe(OH)_2$	Reddish-brown precipitate of $Fe(OH)_3$
Aqueous ammonia	Green precipitate of $Fe(OH)_2$	Reddish-brown precipitate of $Fe(OH)_3$
Potassium hexacyanoferrate(II) solution	White or light blue precipitate	Deep blue precipitate
Potassium hexacyanoferrate(III) solution	Deep blue precipitate	Brown colouration
Potassium thiocyanate solution	No action	Blood-red coloration

Hexacyanoferrate(III) Add a few drops of potassium hexacyanoferrate(III) to the unknown salt solution. The formation of a dark blue precipitate confirms the presence of iron(II) ions.

$$Fe^{2+}(aq) + K_3Fe(CN)_6(aq) \rightarrow \underset{\text{dark blue precipitate}}{KFe^{II}[Fe^{III}(CN)_6](s)} + 2K^+(aq)$$

Tests for iron(III) ions

Soluble iron(III) salts usually dissolve to give yellow or brown solutions.

Sodium hydroxide Add a few drops of sodium hydroxide solution to the unknown salt solution. The formation of a reddish-brown gelatinous precipitate, which is insoluble in excess sodium hydroxide, indicates the presence of iron(III) ions.

NOTE Similar results are obtained if aqueous ammonia is used instead of sodium hydroxide.

$$Fe^{3+}(aq) + 3NaOH(aq) \rightarrow \underset{\text{reddish-brown precipitate}}{Fe(OH)_3(s)} + 3Na^+(aq)$$

Hexacyanoferrate(II) Add a few drops of potassium hexacyanoferrate(II) solution to the unknown salt solution. The formation of a blue precipitate confirms the presence of iron(III) ions.

$$Fe^{3+}(aq) + K_4Fe(CN)_6(aq) \rightarrow \underset{\text{blue precipitate}}{KFe^{III}[Fe^{II}(CN)_6](s)} + 3K^+(aq)$$

Thiocyanate Add a few drops of potassium thiocyanate solution to the unknown salt solution. The formation of a blood-red solution confirms the presence of iron(III) ions.

$$Fe^{3+}(aq) + 3KSCN(aq) \rightarrow \underset{\text{blood-red solution}}{Fe(SCN)_3(aq)} + 3K^+(aq)$$

COMPOUNDS OF IRON

The iron atom can lose two 4*s* electrons to form iron(II) compounds, where it has an oxidation state of +2. It can also lose two 4*s* electrons and one 3*d* electron, i.e. a total of three electrons, to form iron(III) compounds, where it has an oxidation state of +3. The iron(III) ion, Fe^{3+}, is more stable than the iron(II) ion, Fe^{2+}. This is because all the five 3*d* orbitals are singly filled ($3d^5$), and this electronic configuration gives the iron(III) ion a special stability. Iron(II) compounds are easily oxidized to iron(III) compounds. Thus, iron(II) compounds are good reducing agents, while iron(III) compounds are good oxidizing agents.

Iron salts of strong acids, like the chlorides, tetraoxosulphates(VI) and trioxonitrates(V), dissolve in water to form acid solutions.

Iron(II) Oxide and Iron(III) Oxide

Iron(II) oxide, FeO, is unstable and is immediately oxidized to give iron(III) oxide, Fe_2O_3. Iron(III) oxide occurs naturally as *haematite* and as the hydrate, *limonite*. It is widely distributed, being responsible for the reddish-brown colour of soil in many areas. It is obtained in the laboratory by strongly heating iron(II) tetraoxosulphate(VI) or iron(III) hydroxide.

$$2FeSO_4(s) \rightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g)$$
$$2Fe(OH)_3(s) \rightarrow Fe_2O_3(s) + 3H_2O(g)$$

Iron(III) oxide is basic but reacts only slowly with acids to form iron(III) salts. It also reacts with fused alkalis to give ferrates(III) containing $Fe(OH)^-_4$ or FeO_2^- ions. It can be reduced to metallic iron by heating in the presence of hydrogen or carbon(II) oxide.

The oxide can exist in a number of coloured forms, varying from purple to red. It is used in cosmetics, as a mild abrasive for polishing jewellery (jeweller's rouge) and as a red pigment.

Iron(II) Diiron(III) Oxide

Iron(II) diiron(III) oxide, Fe_3O_4, is sometimes referred to as the magnetic oxide of iron. It occurs naturally as *magnetite* or *lodestone* and can be prepared by the action of steam on red-hot iron.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Iron(II) diiron(III) oxide is a black solid. It is fairly inert, and concentrated trioxonitrate(V) acid has no action on it. It is easily reduced when heated with carbon or carbon(II) oxide. In chemical reactions, it functions as a mixed oxide, ($FeO + Fe_2O_3$), reacting with acids to give a mixture of iron(II) and iron(III) salts.

$$\begin{aligned} &Fe_3O_4(s) + 8HCl(aq) \\ &\qquad \rightarrow FeCl_2(aq) + 2FeCl_3(aq) + 4H_2O(l) \end{aligned}$$

Iron(II) Chloride

Anhydrous iron(II) chloride, $FeCl_2$, is prepared by passing a stream of dry hydrogen chloride over a heated iron coil.

$$Fe(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2(g)$$

The product formed is a white deliquescent solid. If the iron coil is dissolved in dilute hydrochloric acid in the absence of air, a pale green solution is obtained from which the tetrahydrate, $FeCl_2.4H_2O$, can be crystallized out. A solution of this hydrate will react with an alkali to form a dirty green precipitate of iron(II) hydroxide. This reaction is common to all aqueous solutions of iron(II) salts.

$$FeCl_2(aq) + 2NaOH(aq) \rightarrow \underset{\text{(green precipitate)}}{Fe(OH)_2(s)} + 2NaCl(aq)$$

Ionically,

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$

Iron(III) Chloride

Anhydrous iron(III) chloride, $FeCl_3$, is prepared by heating an iron coil in a stream of dry chlorine gas. The chloride which sublimes at 315 °C condenses as very dark green crystals in the cooled receiver.

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

Anhydrous iron(III) chloride is very deliquescent and should be stored in an air-tight container. The iron(III) chloride vapour exists as a dimer, Fe_2Cl_6, at low temperatures. At higher temperatures, the dimer dissociates to form iron(II) chloride and chlorine.

The dark green crystals of iron(III) chloride can be dissolved in water and recrystallized as a brownish-yellow hexahydrate, $FeCl_3.6H_2O$. This hydrated chloride can also be obtained by the action of dilute hydrochloric acid on iron(III) oxide or hydroxide.

Iron(III) chloride is a covalent compound which also hydrolyzes in excess water just like aluminium chloride. The product is a colloidal acidic solution, containing hydrated iron(III) hydroxide. This reaction can be written simply as follows:

$$FeCl_3(s) + 3H_2O(l) \rightarrow Fe(OH)_3(s) + 3HCl(aq)$$

Iron(III) chloride can be reduced to the iron(II) state by iodide ions.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(g)$$

Iron(II) Tetraoxosulphate(VI)

Iron(II) tetraoxosulphate(VI), $FeSO_4$, is prepared in the laboratory by the action of dilute tetraoxosulphate(VI) acid on metallic iron. It crystallizes out as the heptahydrate, $FeSO_4.7H_2O$, known commonly as *green vitriol*.

$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$

Commercially, it is prepared from solutions remaining after tetraoxosulphate(VI) acid has been used to clean steel, or by the action of air and water on iron(II) disulphide, FeS_2.

On heating, the green iron(II) tetraoxosulphate(VI) crystals are converted into a dirty-yellow anhydrous solid, which decomposes on stronger heating to iron(III) oxide, sulphur(IV) oxide and sulphur(VI) oxide. Iron(II) tetraoxosulphate(VI) is usually acidified with dilute tetraoxosulphate(VI) acid to prevent hydrolysis.

Iron(II) tetraoxosulphate(VI) is used in [illegible] inks, pigments and tonics (used for treating [illegible]

Iron(III) Tetraoxosulphate(VI)

Iron(III) tetraoxosulphate(VI), $Fe_2(SO_4)_3$, is prepared by the oxidation of a solution of acidified iron(II) tetraoxosulphate(VI) with concentrated trioxonitrate(V) acid or hydrogen peroxide.

$$2FeSO_4(aq) + H_2SO_4(aq) + H_2O_2(aq) \rightarrow Fe_2(SO_4)_3(aq) + 2H_2O(l)$$

On crystallizing the salt solution, the nonahydrate, $Fe_2(SO_4)_3.9H_2O$, is obtained. On careful heating, it yields a white anhydrous salt which decomposes at a higher temperature to iron(III) oxide and sulphur(VI) oxide.

$$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g)$$

A solution of iron(III) tetraoxosulphate(VI) undergoes hydrolysis readily to form an acidic solution. It readily forms alums such as $KFe(SO_4)_2.12H_2O$ and $(NH_4)Fe(SO_4)_2.12H_2O$ which are used as mordants in dyeing.

COPPER

Copper is one of the less reactive metals and belongs to a group of elements known as the *noble metals* which include silver and gold. It is very stable in air and can be found in the free metallic form in a few places. However, the principal source of the metal is *copper pyrites*, $CuFeS_2$. Copper also exists in the combined state as *cuprite*, Cu_2O, *malachite*, $CuCO_3.Cu(OH)_2$, *chalcocite*, Cu_2S, and *bornite*, $Cu_2S.CuS.FeS$.

Extraction

Copper is usually extracted from sulphide ores, such as copper pyrites, $CuFeS_2$. The ore is concentrated by froth flotation. Then it is roasted in a limited supply of air to oxidize the iron and some of the sulphur in the ore to iron(II) oxide and sulphur(IV) oxide respectively.

$$2CuFeS_2(s) + 4O_2(g) \rightarrow Cu_2S(s) + 2FeO(s) + 3SO_2(g)$$

Silicon(IV) oxide is added and the mixture is heated in the absence of air to convert the iron(II) oxide to iron(II) trioxosilicate(IV). The latter floats on copper(I) sulphide as slag and is removed.

$$FeO(s) + SiO_2(s) \rightarrow FeSiO_3(s)$$

The copper(I) sulphide that remains is heated in a controlled amount of air to produce copper with a purity of about 97–99%.

$$Cu_2S(s) + O_2(g) \rightarrow 2Cu(s) + SO_2(g)$$

Where copper of high purity (99.95%) is required, the crude copper is made into anodes in an electrolytic cell containing pure copper cathodes and a copper(II) tetraoxosulphate(VI) solution and refined by electrolysis (see page 209). During the process, the metallic copper atoms at the anodes ionize to form copper ions which move to the cathodes where they accept electrons and become deposited as pure copper metal. The anodes thus become depleted while the cathodes increase in size. Valuable impurities, e.g. silver and gold, are collected as anode slime.

Copper - A Transition Element

Copper is the most electronegative element in the first row of transition elements. It has a large positive electrode potential and is found low in the activity series. Thus, copper is relatively unreactive.

The electronic configuration of the copper atom shows that it has completely filled 3*d* orbitals ($3d^{10}$). This also explains the unreactive and stable nature of copper.

Table 27.6 Electronic configuration and some properties of the copper atom and its ions.

		Electronic configuration	Oxidation state	Colour of ions	Metal ion complex	Industrial catalyst
Copper	Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$	–	–	–	In the oxidation of methanol to methanal
Copper(I)	Cu^+	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$	+1	–	$[Cu(CN)_4]^{3-}$	
Copper(II)	Cu^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$	+2	Blue	$[Cu(NH_3)_4]^{2+}$ tetraamine copper(II) ion	

Physical Properties

Appearance	A soft, red solid with lustre
Relative density	8.95
Malleability	Very malleable
Ductility	Very ductile
Tensile strength	Relatively high tensile strength
Melting point	1 080 °C
Conductivity	Excellent conductor of heat and electricity

Chemical Properties

Reaction with air Copper, which is very low in the activity series, is very stable in pure air. In moist air, however, it gradually becomes covered with a green coating of basic copper(II) tetraoxosulphate(VI), $CuSO_4.3Cu(OH)_2$, and trioxocarbonate(IV). A coating of basic chloride is formed if it is exposed to moist sea air. On heating in air, copper is readily oxidized to give black copper(II) oxide.

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s)$$

Reaction with acids Being lower than hydrogen in the electrochemical series, copper is not capable of displacing hydrogen from dilute acids. It does not react with dilute tetraoxosulphate(VI) acid or hydrochloric acid at any concentration. However, copper is attacked by oxidizing acids.

With hot concentrated tetraoxosulphate(VI) acid, sulphur(IV) oxide is liberated.

$$Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

With trioxonitrate(V) acid, the products formed depend on the concentration of the acid. Nitrogen(II) oxide is given off by the dilute acid, while nitrogen(IV) oxide is liberated by the hot concentrated acid.

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

Displacement reaction Copper is displaced from solutions of its salts by most metals since it is nearly at the bottom of the activity series.

Tests for copper(II) ions

All common hydrated copper(II) salts are green or blue in colour, and they dissolve in water to form blue solutions.

Flame test All copper(II) salts impart a characteristic bluish-green colour to a non-luminous flame.

Sodium hydroxide Add a few drops of sodium hydroxide solution to a solution of the unknown salt. The formation of a blue gelatinous precipitate which is insoluble in excess sodium hydroxide confirms the presence of copper(II) ions.

$$Cu^{2+}(aq) + 2NaOH(aq) \rightarrow \underset{\text{blue precipitate}}{Cu(OH)_2(s)} + 2Na^+(aq)$$

Aqueous ammonia Add a few drops of aqueous ammonia to the unknown salt solution. If copper(II) ions are present, a blue precipitate of copper(II) hydroxide which dissolves in excess aqueous ammonia to give a deep blue solution will be formed.

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$$

$$Cu(OH)_2(s) + 4NH_4^+(aq) + 4OH^-(aq) \rightarrow \underset{\substack{\text{deep-blue}\\ \text{coloured ion}}}{Cu(NH_3)_4^{2+}(aq)} + 2OH^-(aq) + 4H_2O(l)$$

Uses

1 Copper is widely used for making electric wires because it is very ductile and, after silver, is the best metallic conductor of electricity.

2 It is used in metalwork because it is easy to work with, has an attractive appearance, and is resistant to corrosion. It is also used in plumbing and roofing.

3 It is used in producing a wide range of important alloys such as bronze (a mixture of Cu, Sn), brass (a mixture of Cu, Zn) and cupronickel (a mixture of Cu, Ni).

COMPOUNDS OF COPPER

Copper can form copper(I) and copper(II) compounds by sharing or losing one and two electrons respectively. However, the +2 oxidation state is more common. In aqueous solution, copper(I) ion is unstable with respect to the copper(II) ion and metal. This can be seen from their standard electrode potentials.

$Cu^{2+} + 2e \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V
$Cu^{+} + e \rightleftharpoons Cu$ $\quad E^\ominus = +0.52$ V
$Cu^{2+} + e \rightleftharpoons Cu^{+}$ $\quad E^\ominus = +0.15$ V

Thus, in aqueous solution, copper(I) ions are readily converted to copper(II) ions and the metal by simultaneous oxidation and reduction. This process is called *disproportionation*.

$$2Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

Copper(I) Oxide

opper(I) oxide, Cu_2O, is obtained as a red precipitate y reducing an alkaline solution of a copper(II) salt. This is the reaction that is used to identify reducing ugars in the Fehling's and the Benedict's tests.

Copper(I) oxide reacts with dilute tetraoxoulphate(VI) acid to form copper(II) tetraoxoulphate(VI) and copper. In this reaction, the copper s reduced and oxidized.

$$u_2O(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$$

onically,

$$2Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

Copper(I) oxide dissolves in concentrated ydrochloric acid to form a complex ion.

Copper(II) Oxide

Copper(II) oxide, CuO, commonly known as black copper oxide, is obtained by heating the metal in air or oxygen, or by heating the trioxonitrate(V) or trioxocarbonate(IV).

$$CuCO_3(s) \xrightarrow{heat} CuO(s) + CO_2(g)$$
$$2Cu(NO_3)_2(s) \xrightarrow{heat} 2CuO(s) + 4NO_2(g) + O_2(g)$$

Copper(II) oxide is a hygroscopic black solid which is insoluble in water. It is a basic oxide, forming copper(II) salts with acids. It decomposes above 1 000°C into copper(I) oxide and oxygen.

$$4CuO(s) \rightleftharpoons 2Cu_2O(s) + O_2(g)$$

Heated copper(II) oxide is readily reduced to metallic copper by hydrogen and carbon(II) oxide.

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$$
$$CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)$$

Copper(II) oxide also reacts with acids to form blue salts.

$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$

Copper(II) oxide is used in organic analysis, and as a catalyst in the thermal decomposition of potassium trioxochlorate(V).

Copper(II) Hydroxide

When an alkali is added to a copper(II) salt solution, copper(II) hydroxide is precipitated.

$$CuSO_4(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$$

Copper(II) hydroxide dissolves in excess aqueous ammonia to form a deep blue tetra-ammine copper(II) complex ion. This solution is used to dissolve cellulose. On further processing, artificial silk is obtained.

$$Cu(OH)_2(s) + 4NH_3(aq) \rightarrow \underset{\text{deep-blue ion}}{Cu(NH_3)_4^{2+}(aq)} + 2OH^{-}(aq)$$

Copper(I) Chloride

Copper(I) chloride, CuCl, is prepared by passing sulphur(IV) oxide through a solution of copper(II) tetraoxosulphate(VI) and sodium chloride.

$$2Cu^{2+}(aq) + 2Cl^{-}(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2CuCl(s) + SO_4^{2-}(aq) + 4H^{+}(aq)$$

Copper(I) chloride is a white covalent solid which is readily oxidized to green copper(II) chloride in moist air.

Copper(II) Tetraoxosulphate(VI)

Copper(II) tetraoxosulphate(VI), $CuSO_4$, is prepared by

- the action of dilute tetraoxosulphate(VI) acid on copper(II) oxide or trioxocarbonate(IV), or
- the oxidation of copper turnings with concentrated tetraoxosulphate(VI) acid.

On crystallization, the salt is obtained as blue pentahydrate crystals, $CuSO_4.5H_2O$, commonly known as *blue vitriol*.

$$Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

The pentahydrate loses four molecules of water of crystallization at about 100 °C, and the white, anhydrous salt is formed at temperatures above 300 °C. The anhydrous salt readily absorbs water to reform the coloured hydrate. This provides a convenient test to detect the presence of water.

$$CuSO_4.5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(l)$$

Copper(II) tetraoxosulphate(VI) is used mainly as a fungicide for spraying vines, citrus trees and potatoes. It is also used in electroplating, as a timber preservative, in dyeing and in the preparation of the other copper compounds.

Copper(II) Trioxonitrate(V)

Copper(II) trioxonitrate(V), $Cu(NO_3)_2$, is prepared by the action of copper on concentrated trioxonitrate(V) acid. The salt is obtained as blue deliquescent trihydrate crystals, $Cu(NO_3)_2.3H_2O$. Hexahydrate and nonahydrate crystals are also known.

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

On heating, copper(II) trioxonitrate(V) decomposes into copper(II) oxide, oxygen and nitrogen(IV) oxide.

Copper(II) Trioxocarbonate(IV)

Copper(II) trioxocarbonate(IV), $CuCO_3$, only exists as a basic salt and occurs naturally as *malachite*, $CuCO_3.Cu(OH)_2$ and *azurite*, $Cu(OH)_2.2CuCO_3$.

The basic trioxocarbonate(IV) of copper, $CuCO_3.Cu(OH)_2$, is precipitated when sodium trioxocarbonate(IV) is added to any copper(II) salt solution. It is a blue-green, insoluble solid which decomposes into copper(II) oxide and carbon(IV) oxide on heating. It is also attacked by dilute acids to produce carbon(IV) oxide.

ZINC

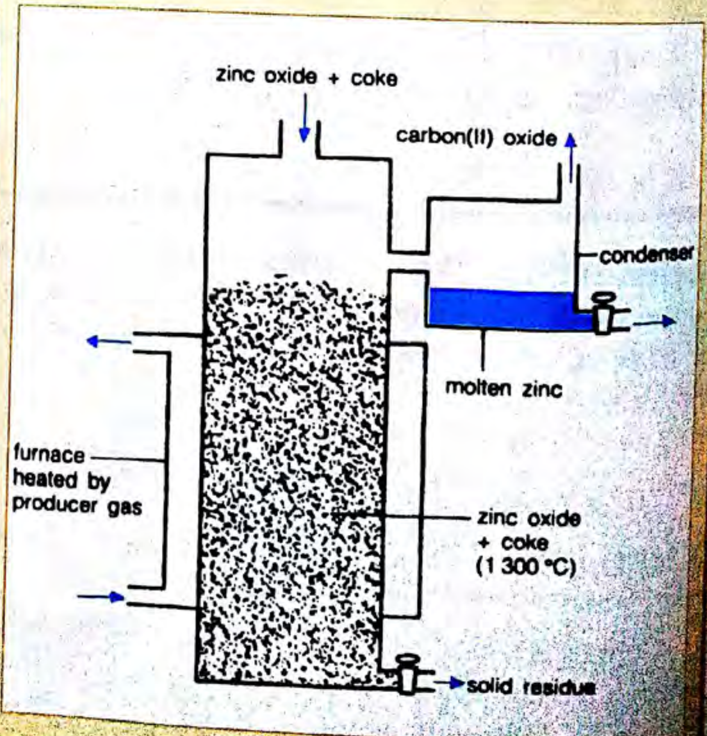
Zinc is a moderately reactive metal. It does not occur free in nature but is found mainly as *calamine*, $ZnCO_3$, and *zinc blende*, ZnS. Small amounts of zinc are found in Ogoja, Abakaliki and along the Benue river in Taraba State.

Extraction

The zinc ores are concentrated and then roasted in air to yield zinc oxide. The oxide is mixed with coke and heated to about 1 300 °C in a fire-clay retort to yield zinc and carbon(II) oxide. The zinc distils over as a vapour and condenses to a liquid in a receiver. The carbon(II) oxide also helps in the reduction.

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$
$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$
$$ZnO(s) + C(s) \rightarrow Zn(g) + CO(g)$$
$$ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2(g)$$

Fig. 27.9 Extraction of zinc.



This zinc contains traces of lead, cadmium and iron. It is purified by re-distillation or electrolysis. Granulated zinc is obtained by running molten zinc into water.

Zinc - A Transition Element

Zinc does not possess many of the properties that characterize the transition metals. For instance,

- it has only one oxidation state of +2;
- its metallic ions are not coloured;
- it is not used as a catalyst.

However, zinc does form complexes like the other transition metals.

The non-transition metal properties of zinc are due to its electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$. The five $3d$ orbitals are all completely filled even when it exists as an ion.

Physical Properties

Appearance	Bluish-white solid with lustre
Relative density	7.1
Malleability and ductility	Malleable and ductile between 100–150 °C, brittle at room temperature and at temperatures above 200 °C
Tensile strength	High tensile strength
Melting point	419 °C
Conductivity	Good conductor of heat and electricity

Chemical Properties

Reaction with air On prolonged exposure to moist air, zinc tarnishes because it undergoes gradual oxidation to become coated with a layer of zinc oxide and basic zinc trioxocarbonate(IV). This layer prevents further action on the metal by the atmospheric gases. When heated, zinc will burn in air with a bluish-green flame to form the oxide.

$$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$$

Reaction with water Zinc does not react with cold water but it reacts with steam at red heat, liberating hydrogen.

$$Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$$

Reaction with non-metals When heated, zinc combines directly with the halogens, phosphorus and sulphur, but not with nitrogen.

$$Zn(s) + Cl_2(g) \rightarrow ZnCl_2(s)$$

Reaction with acids Zinc displaces hydrogen from dilute acids. The rate of this reaction is greatly increased by small amounts of impurities such as copper or arsenic.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

With oxidizing acids like hot concentrated tetraoxosulphate(VI) and trioxonitrate(V) acids, zinc becomes oxidized while sulphur(IV) oxide and nitrogen(II) oxide are liberated respectively.

$$Zn(s) + 2H_2SO_4(aq) \rightarrow ZnSO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$3Zn(s) + 8HNO_3(aq) \\ \rightarrow 3Zn(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

Reaction with alkalis Zinc, being amphoteric, also reacts with hot concentrated alkalis to form a zincate(II) and hydrogen.

$$Zn(s) + 2NaOH(aq) + 2H_2O(l) \\ \rightarrow Na_2Zn(OH)_4(aq) + H_2(g)$$

Ionically,

$$Zn(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow Zn(OH)_4^{2-}(aq) + H_2(g)$$

Tests for zinc ions

All common zinc salts are white.

Sodium hydroxide Add some sodium hydroxide solution drop by drop to the unknown salt solution. The presence of zinc ions results in the formation of a white gelatinous precipitate which dissolves in excess sodium hydroxide solution.

$$Zn^{2+}(aq) + 2NaOH(aq) \rightarrow Zn(OH)_2(s) + 2Na^+(aq)$$
$$Zn(OH)_2(s) + 2NaOH(aq) \rightarrow Na_2Zn(OH)_4(aq)$$

Similar reactions are given by lead(II) and aluminium salts. However, these salts can be distinguished from zinc salts by the next test.

Aqueous ammonia Add a few drops of aqueous ammonia to the unknown salt solution. The formation of a white gelatinous precipitate which is soluble in excess aqueous ammonia confirms the presence of zinc ions.

(a) $Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s)$
(b) $Zn(OH)_2(s) + 4NH_4^+(aq) + 4OH^-(aq)$
$\rightarrow Zn(NH_3)_4^{2+}(aq) + 2OH^-(aq) + 4H_2O(l)$

Lead(II) and aluminium salts also form white precipitates when treated with aqueous ammonia but these are insoluble in excess aqueous ammonia.

Uses

1 Zinc is widely used for galvanizing iron and steel to prevent rusting. The layer of zinc can be applied electrolytically, by spraying or by dipping the article into molten zinc. However, galvanized vessels cannot be used for storing food because of the danger of zinc poisoning.
2 Zinc is used in making alloys such as brass (a mixture of Cu, Zn) and coinage bronze (a mixture of Cu, Sn, Zn).
3 Zinc is also used in making dry cells, lithographic plates and foil for packing, and as a reducing agent.

COMPOUNDS OF ZINC

Many compounds of zinc, like zinc chloride, are partially covalent. The zinc ion, Zn^{2+}, is readily hydrated. Zinc forms complexes with ammonia, cyanide ions and halide ions

Zinc Oxide

Zinc oxide, ZnO, is usually prepared by burning zinc in air or by heating the trioxocarbonate(IV), hydroxide or trioxonitrate(V).

$$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$$
$$2Zn(NO_3)_2(s) \rightarrow 2ZnO(s) + 4NO_2(g) + O_2(g)$$

It is a white, insoluble powder which turns yellow on heating. Being amphoteric, it dissolves in both acids and alkalis. It is used as a white pigment in paints and as a filler for rubber. The very pure form is used in cosmetic powders and creams, and in medicinal ointments and lotions.

Zinc Hydroxide

Zinc hydroxide, $Zn(OH)_2$, is precipitated when a little sodium hydroxide solution is added to an aqueous solution of a zinc salt. It is an insoluble, white, gelatinous solid which is amphoteric like the oxide. Thus, it reacts with both dilute acids and alkalis.

$$Zn(OH)_2(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + 2H_2O(l)$$
$$Zn(OH)_2(s) + 2OH^-(aq) \rightarrow \underset{\text{zincate(II) ion}}{Zn(OH)_4^{2-}(aq)}$$

Zinc hydroxide is also soluble in excess ammonia solution, forming an ammine complex ion.

$$Zn(OH)_2(s) + 4NH_3(aq)$$
$$\rightarrow Zn(NH_3)_4^{2+}(aq) + 2OH^-(aq)$$

Zinc Tetraoxosulphate(VI)

Zinc tetraoxosulphate(VI), $ZnSO_4$, is prepared in the laboratory by the action of dilute tetraoxosulphate(VI) acid on metallic zinc, zinc oxide or zinc trioxocarbonate(IV).

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

On crystallizing the salt solution, the heptahydrate, $ZnSO_4.7H_2O$, known as *white vitriol*, is obtained. At higher temperatures, other hydrates are obtained. At 450 °C, the anhydrous salt is formed. This decomposes on stronger heating.

Zinc tetraoxosulphate(VI) is used in the treatment f certain skin diseases, in making rayon, organo- c compounds and agricultural sprays. It is also ixed with barium tetraoxosulphate(VI) in the making f white paint, and with boric acid as an eye lotion.

inc Trioxonitrate(V)

c trioxonitrate(V), $Zn(NO_3)_2$, may be prepared by e action of zinc oxide on dilute trioxonitrate(V) acid.

$$ZnO(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2O(l)$$

Zinc trioxonitrate(V) forms white, hexahydrate ystals, $Zn(NO_3)_2.6H_2O$, which are deliquescent. The hydrous salt is unknown because it is easily ecomposed to give zinc oxide, oxygen and itrogen(IV) oxide.

ALLOYS

Pure metals are not used widely because many of heir properties such as hardness, tensile strength, esistance to corrosion and lustre can be improved by ixing them with other elements. These mixtures are nown as alloys.

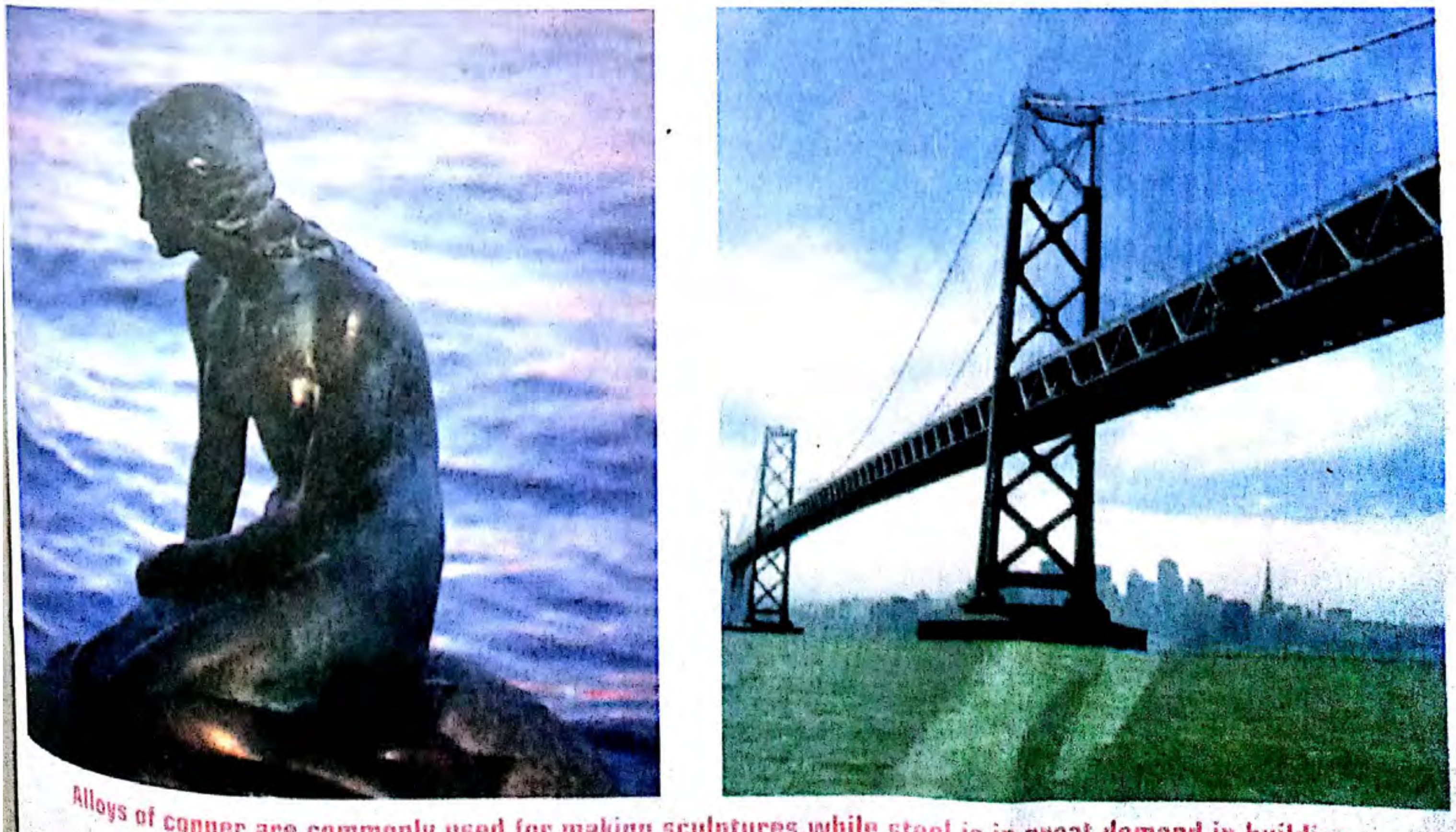
An alloy is a substance prepared by adding one or more elements to a base or parent metal to obtain desirable products. The added elements are usually metals or carbon.

A true alloy can be considered as a uniform mixture. It is usually made by melting the components together and solidifying the mixture. The components must be soluble in each other when molten and should not separate into distinct layers when the mixture solidifies. They should not undergo any chemical changes during the process of alloying. The percentage composition of the component elements in an alloy may vary according to the desired qualities.

Sometimes, the metals in an alloy mixture are only partially soluble, e.g. in certain types of brass.

In some alloys, the metals combine to form intermetallic compounds. For example, in an aluminium-copper alloy, some of the copper combines with aluminium while the rest form a solid solution with it.

Alloys are economically important since most of the things we use are made of alloys rather than pure metals.



Alloys of copper are commonly used for making sculptures, while steel is in great demand in building and bridge construction.

Table 27.7 *Some alloys, their compositions and uses.*

Alloy	Composition	Advantages	Uses
Brass	60–80% Cu 20–40% Zn	Stronger and more malleable than copper; greater workability because of lower melting point; more attractive appearance; does not corrode easily	For making moving parts of clocks and watches, nuts, bolts, rods, tubes, musical instruments, ornaments and for general metalwork
Bronze	90% Cu 10% Sn	Stronger than copper; greater resistance to chemical attack; more attractive appearance	For making coins and medals; sculptures and for general metalwork
Duralumin	95% Al 3% Cu 1% Mg 1% Mn	Very light but stronger than aluminium	Construction of aircraft, ships, cars and machinery
Steel	99.8% Fe 0.2%C	More malleable and ductile than iron; harder and stronger; can withstand great stress and strain	Construction of bridges, ships, cars and machinery
Stainless steel	60–80% Fe 10–20% Cr 8–20% Ni	Hard; resistant to corrosion; very attractive in appearance	For making cutlery, tools and surgical instruments
Permallory	22% Fe 78% Ni	Strongly magnetized by electric current	For making electromagnets
Alnico	23–25% Fe 6–12% Al 14–30% Ni 5–35% Co	Strongly magnetic	For making permanent magnets
Soft solder	50–70% Pb 30–50% Sn	Low melting point; high tensile strength when cold	For welding and plumbing
	70–75% Pb 16–20% Sb 8–10% Sn	Low melting point; tough; does not wear out easily	For printing

SUMMARY

General properties of transition metals

Transition metals are found in the *d*-block of the Periodic Table between Groups 2 and 3. They are all metals.

A transition element may be defined as an element with partially filled *d* orbitals.

The first transition series is found in Period 4. The atoms of these metals have one or two electrons in the 4*s* orbital. and partially filled 3*d* orbitals.

Transition metals have few properties in common with the *s*-block metals, but they are remarkably similar among themselves.

(a) In transition metals, the 3*d* electrons and 4*s* electrons contribute to the metallic bonding in the crystal lattices of the metals. Thus, the transition metals have stronger metallic bonds than the corresponding *s*-block metals. This makes them harder and stronger with higher melting points than the *s*-block metals.

(b) Transition metals have smaller atoms than the corresponding *s*-block metals. These atoms are closely packed in the crystal lattices because of the stronger metallic bonding, making these metals very dense.

(c) Chemically, transition metals are moderately active while the *s*-block metals are very reactive. This is because transition metals have higher ionization energies (due to their comparatively smaller atomic sizes and larger positive charges) than the *s*-block metals.

(d) In addition, the electrons in the *d* orbitals are responsible for the following characteristic properties of transition metals.
   (i) Variable oxidation states
   (ii) Ability to form complex ions
   (iii) Presence of coloured ions
   (iv) Ability to act as catalysts

ron

Iron is mainly extracted from its ores by chemical and thermal reduction in a blast furnace. It is also extracted by a direct reduction process which is used at the Aladja steel-works.

(a) Steel is an important alloy of iron that is used for many purposes such as making machine parts, car bodies, tools and magnets, and in the building construction industry.

(b) It is made by adding 0.1–1.5% carbon to iron. Steels for specific purposes are made by adding small quantities of other metals.

(c) Steel is made by the Bessemer process, the open-hearth process and the electric-arc furnace process.

Iron is a typical transition metal which exhibits +2 and +3 oxidation states in its compounds. The +3 state is more stable because of the half-filled *d* orbitals in the iron(III) ions.

Pure iron is a fairly soft malleable metal which is magnetic.

In the presence of moist air, iron rusts due to the formation of a reddish-brown hydrated iron(III) oxide. This oxide forms a porous layer over the metal, so that rusting continues until all the metal is changed to the oxide. Rusting is prevented by painting the metal or coating it with other metals like tin or zinc.

- An aqueous solution of iron(II) ion is pale green in colour, while iron(III) ion is yellow.
- Iron forms many coloured complex ions. Iron(II) and iron(III) ions form hydrated complexes in an aqueous solution.
- Iron and steel are used extensively in the building and construction industry and in making body parts of vehicles, machinery and tools.

Copper

- Copper is extracted from its ores by chemical and thermal reduction. The metal is purified by electrolysis.
- Copper is a reddish-brown, extremely malleable metal which is a good conductor of heat and electricity.
- Copper is not a reactive metal. In moist air, the metal becomes covered with a green coating of basic copper(II) tetraoxosulphate(VI) and trioxocarbonate(IV).
- Copper exhibits +1 and +2 oxidation states in its compounds. The +2 state is more stable.
- In aqueous solution, the ions are extensively hydrated. The hydrated copper(II) ions are blue in colour. Copper ions also form many coloured complexes with other ions and molecules.
- Copper(I) ions undergo disproportionation in aqueous solution to give copper(II) ions and metallic copper.
- Copper is used for making electrical wires and ornamental objects. Bronze and brass are important alloys of copper.

Zinc

- Zinc ores are roasted in air and heated with coke to extract the metal, which is purified by re-distillation or electrolysis.
- Zinc does not possess many transition metal properties because its five 3*d* orbitals are completely filled even when it exists as an ion.
- Zinc reacts with moist air to form zinc oxide and basic zinc trioxocarbonate(IV), both of which form a continuous layer over the metal, making it passive.
- Zinc is amphoteric and reacts with both acids and alkalis.
- Zinc compounds are partially covalent. The zinc ion is readily hydrated. It also forms complexes with other ions and molecules.
- Zinc is used for galvanizing iron and steel to prevent them from rusting. It is also used for making alloys.

Alloys

- An alloy is a substance prepared by adding one or more elements to a base metal to give it certain desirable qualities. Common alloys include brass, bronze, duralumin and steel.

All *d*-block elements are referred to as transition elements. This name is true for

A the three rows of elements.
B 1^{st} row of elements.
C elements with partially filled d-orbitals.
D elements which are coloured.

These are not true transition elements except

A Zn B Cu
C Sc D Ni

Orbitals acquire special stability when they

A contain a single electron.
B they contain two elections in their entire orbitals.
C they are singly or doubly filled.
D have a vacant orbital.

The following are characteristics of the transition metals with the exception of

A variable oxidation states.
B coloured ions.
C complex ion formation.
D high tendency to catenate.

Conversion of coke to carbon II oxide in a furnace is

A exothermic. B endothermic.
C isothermic. D hyperthermic.

Wrought iron is the

A purest form of iron.
B most brittle form of iron.
C most impure.
D form of iron containing no carbon.

Steel is an alloy of iron containing only

A carbon.
B carbon and other elements depending on the strength desired.
C carbon and nickel.
D carbon and chromium.

Ability of the blood haemoglobin (iron) to transport oxygen is because

A iron is a transition metal.
B iron is the most stable with oxygen.
C iron co-ordinates reversibly with blood oxygen.
D iron also purifies the blood.

9. Iron is paramagnetic because

A its orbitals have few unpaired electrons.
B its orbitals have only paired electrons.
C iron has large number of unpaired electrons.
D it is ferromagnetic.

10. Corrosion in iron is called

A rusting. B tarnishing.
C galvanization. D dimerization.

11. Unreactive nature of copper is as a result of having

A partly filled orbitals.
B partly filled orbitals and contains some inert impurities.
C completely filled 3 *d*-orbitals.
D a low position in the E.C.S.

12. The main reducing agent in the extraction of metal by reduction is

A coke.
B carbon IV oxide.
C carbon II oxide.
D graphite

13. Zinc is not regarded as a transition metal even though it is a *d*-block element because

A it has no electron in 3 *d*-orbital.
B it has all 3 *d*-orbitals completely filled.
C it blends with other neighbouring elements.
D it does not form complex like others.

14. Which one is the most common iron ore?

A Magnetite
B Haematite
C Spathic iron ore
D Carnallite
E Dolomite

15. Bronze and solder are both metallic alloys. Which of these constituents is common to both alloys?

A Copper B Tin
C Lead D Zinc
E Silver

16. Metallic elements that give coloured salts in aqueous solution are called

A transition elements.
B alkali metal.
C alkaline earth metal.
D noble metal.
E *s*-block metals.

17. Describe the essential features of transition metals and their compounds, using examples from the first transition series.

18. Transition metals are characterized by variable oxidation state, coloured ions, catalytic activity and the formation of complexes. Illustrate this statement using two transition metals as examples.

19. (a) What is the electronic configuration of iron?
(b) Iron forms the iron(II) ion, Fe^{2+}, and the iron(III) ion, Fe^{3+}. What are the electronic configurations of these ions? Which is more stable? Why?
(c) Iron readily reacts with both chlorine gas and hydrogen chloride gas. What products are formed in each case? Describe the appearance of each compound and give the equations of the reactions.

20. (a) The oxidation number of copper in its compounds is either +1 or +2. Give the name and formula of a compound in which copper has
(i) +1 oxidation state,
(ii) +2 oxidation state.
(b) To a solution of copper(II) ions, aqueous ammonia is added drop by drop. Describe what happens when
(i) a few drops are added,
(ii) an excess is added.

In each case write the ionic equations for the changes that occur.

21. (a) What is a complex ion? Name two metals that form complex ions, giving an example in each case.
(b) Give the electronic configurations of the zinc atom and ion. Explain why zinc does not exhibit typical transition metal properties.

22. (a) Using diagrams and equations, explain how iron is extracted from its ores.
(b) What is the chemical nature of iron rust? How would you attempt to determine by a series of chemical reactions that iron rust contains iron? Give the equations of the reactions where necessary.

23. (a) What are the conditions necessary for iron to rust? Carry out an experiment to determine these conditions.
(b) Explain why the middle portion of a ship shows more rust than either the top-most or the bottom-most portion.
(c) Give three everyday uses of iron.
(d) Write short notes on the following.
(i) Cast iron
(ii) Wrought iron
(iii) Pig iron
(iv) Steel

24. (a) Give the equations for two reactions in which copper behaves as a reducing agent.
(b) Using equations, describe what happens when potassium hexacyanoferrate(II) is added to a solution of an iron(II) salt.
(c) Give the formula of the zincate(II) ion.

25. (a) What are alloys? Explain why alloys are usually used in preference to the pure metals.
(b) Give the composition and uses of the following.
(i) Duralumin
(ii) Soft solder
(iii) Bronze
(iv) Type metal

SECTION FOUR

ORGANIC CHEMISTRY

8 HYDROCARBONS AND CRUDE OIL

9 ORGANIC CHEMISTRY (1)

0 ORGANIC CHEMISTRY (2)

28 HYDROCARBONS AND CRUDE OIL

HYDROCARBONS

Hydrocarbons are organic compounds composed only of two elements — *carbon* and *hydrogen* — hence their name. The main source of hydrocarbons is crude oil.

There are hundreds of different hydrocarbons. They can be put into two main classes — *aliphatic* and *aromatic hydrocarbons*.

Aliphatic hydrocarbons are composed of carbon chains. In acyclic compounds, the carbon chains are straight or branched. Important families that belong to this group are the alkanes, alkenes and alkynes. In cyclic aliphatic compounds, the end carbon atoms of an acyclic carbon chain join together to form a ring.

Aromatic hydrocarbons are all cyclic compounds. The basic cyclic structure is the benzene ring.

CRUDE OIL

The chief source of hydrocarbons is crude oil or *petroleum*. Petroleum, which means *rock oil* in Latin, occurs as a dark, sticky, viscous liquid. It is found in huge underground deposits in many parts of the world. Natural gas is usually found together with it.

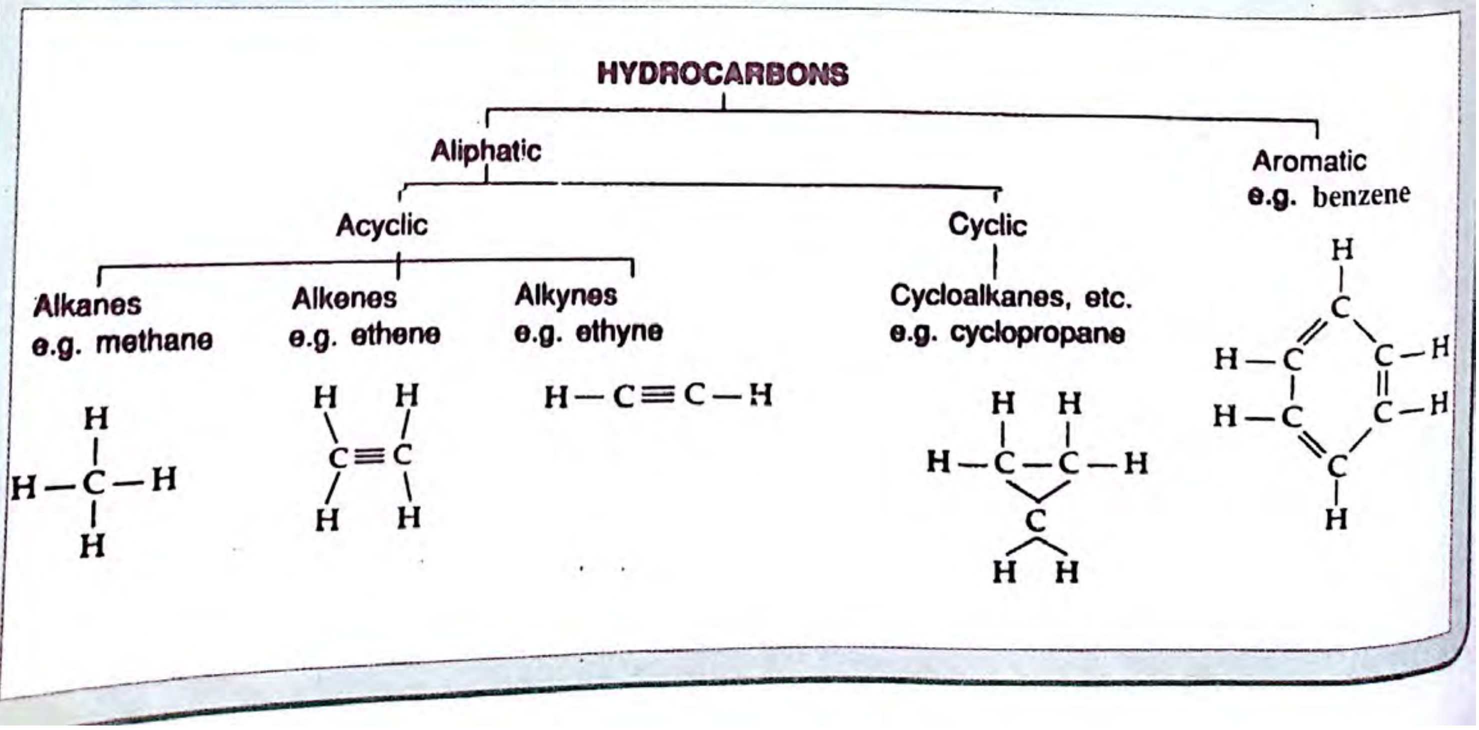
Petroleum is a mixture of gaseous, liquid and solid alkanes, alkenes, cycloalkanes, aromatic hydrocarbons and others. Natural gas consists mainly of methane.

Origin of Crude Oil and Natural Gas

Crude oil and natural gas are formed from the remains of marine algae and animals. When these tiny aquatic organisms died, their remains gradually settled on the seabeds. Over the years, the remains became covered by mud, silt and other sediments. As the sediments piled up, their mass exerted a great pressure on the lower layers, changing them to hard sedimentary rocks. During this process, bacterial activity, heat and pressure probably changed the plant and animal remains into crude oil and natural gas.

The oil and gas so formed slowly moved to other areas through the tiny holes or pores in the porous rocks around them. Since oil and gas are not dense.

Fig. 28.1 Classification of hydrocarbons.



they tend to seep upwards until they meet a non-porous layer of rocks and are trapped under it, thus forming an *oil trap*.

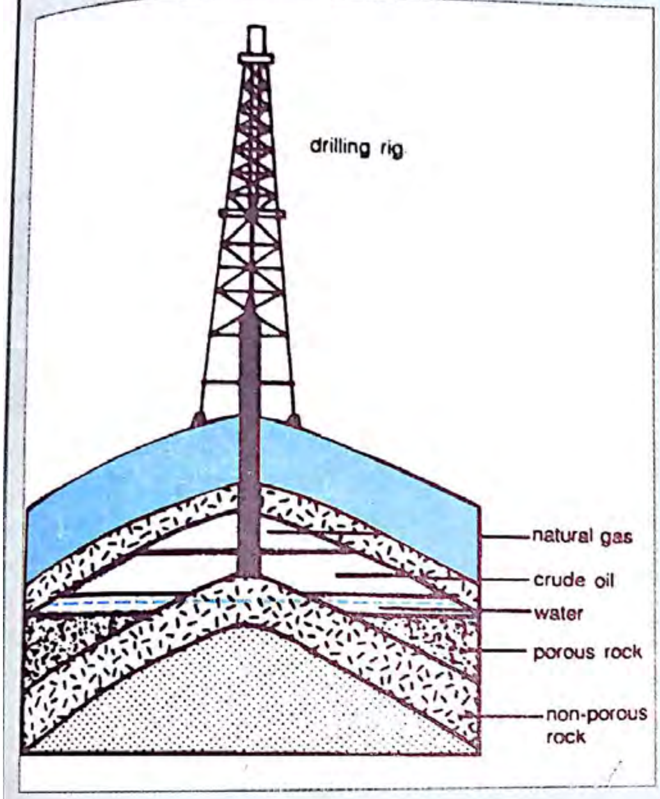


Fig. 28.2 Formation of crude oil and natural gas.

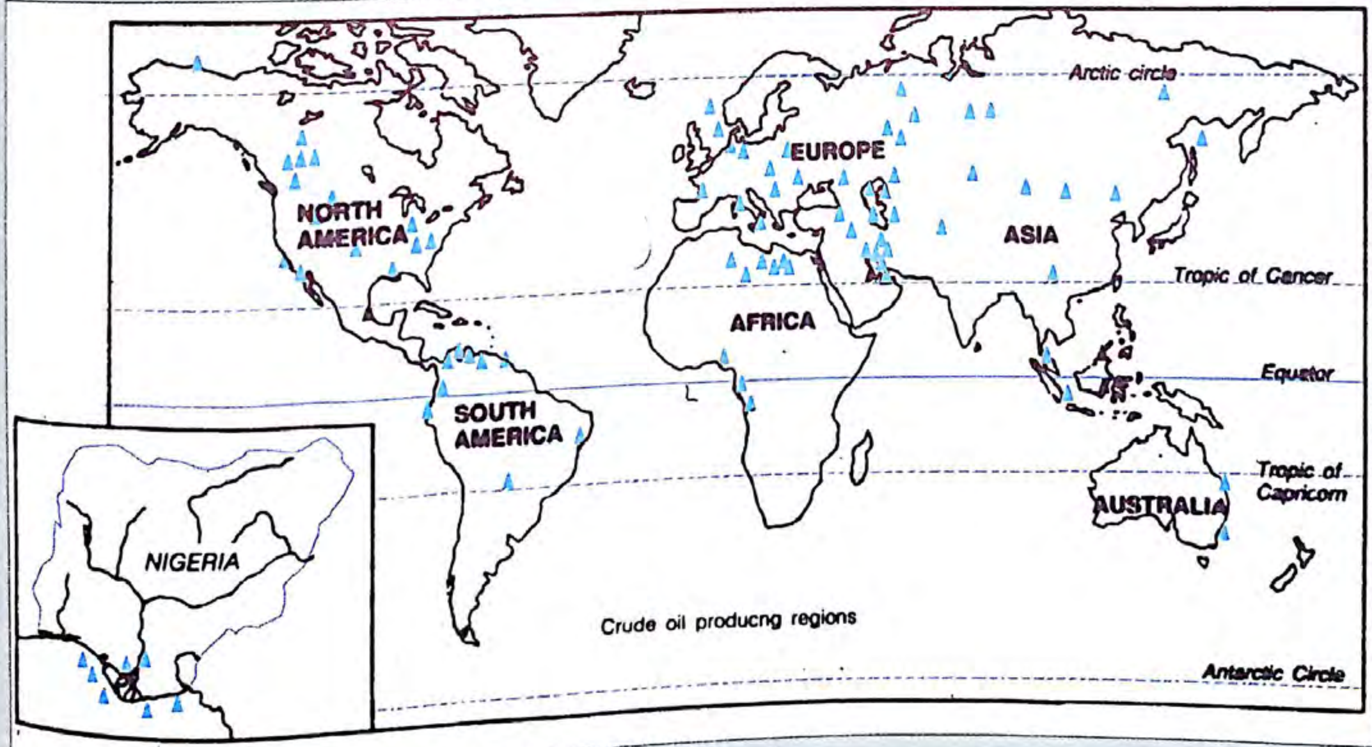
World Crude Oil Reserves

About three-fifths of the world's oil reserves are in Asia, with most of it concentrated in the Middle East. Other Asian countries rich in oil are China and Indonesia. Russia has the next largest oil reserves. The remaining important oil reserves are found in northern and western Africa, United States, Canada, Venezuela and Australia.

Nigerian crude oil reserves

Since it was first discovered at Oloibiri in 1956, crude oil has brought in much money to Nigeria. On land, large deposits of oil have been found in the Niger delta — Afam, Abata, Bomu, Owaza, Egbema and the Ughelli–Kokori–Oleh zone. Offshore, oil occurs at Calabar and in the Burutu–Forcados–Escravas zone of Delta State. From fields all over Nigeria, oil is pumped through pipelines to the oil terminals at Bonny or Forcados for export or to the refineries at Port Harcourt, Warri and Kaduna. Oil production has been increasing steadily over the years. Today, Nigeria ranks among the top ten oil producers of the world.

Fig. 28.3 Crude oil producing regions of the world.



Crude Oil Exploration and Drilling

Likely oil-bearing rock layers are located by

- aerial photography,
- examining the surface rocks,
- core drilling, and
- mapping the earth's rock layers.

Mapping is done by exploding dynamite in deep holes in the earth's crust and recording the reflections of the shock waves from the rock layers. From the recordings, a geologist can map the rock layers and detect possible oil-bearing areas.

Crude oil is extracted by drilling deep holes or wells into the ground. The drilling is done by a rotary rig which is supported by a derrick. When a well reaches an oil-bearing layer, crude oil and gas may shoot up into the air under high pressure. Usually the crude oil has to be pumped out. It is then stored in large steel tanks until it is sent to oil refineries by pipelines or tankers.

Off-shore oil rig.

Oil storage tanks at the waterfront.

Fractional Distillation of Crude Oil

Crude oil is not a single compound but a complex mixture of hydrocarbons. It is so valuable that people call it 'black gold', yet, as obtained from the ground, crude oil is just about useless. To justify its true worth, crude oil must undergo fractional distillation first.

In this process, it is separated into different portions called *fractions* (see experiment 28.1). Each fraction contains several compounds, all of which fall within a certain boiling point range. We can differentiate these fractions from one another by their different volatility, odour, colour, texture and their relative ease of ignition and burning.

Oil Refineries

Industrially, the fractionation is done on a far larger scale than that described in experiment 28.1. Crude oil is treated in oil refineries, i.e. in huge industrial complexes that separate, break down and sometimes also recombine crude oil into different fractions, each meeting a particular end use. An oil refinery processes a few million tonnes of crude oil yearly and may occupy an area as large as a town.

Industrial fractionation

The distillation process is carried out in huge fractionating columns or towers, each standing some 40 to 50 metres high and 7 metres across. The crude oil is preheated to about 400 °C in an electric furnace where about 75% of the crude oil is vaporized. The mixture of hot vapour and liquid flows through pipes to the fractionating column.

The fractionating column is divided into several compartments by perforated plates called trays, each of which is maintained within a specific range of temperature. Each tray is a little cooler than the one below, so that towards the bottom of the column, the temperature is around 400 °C, while the temperature at the top part of the column is only 40 °C.

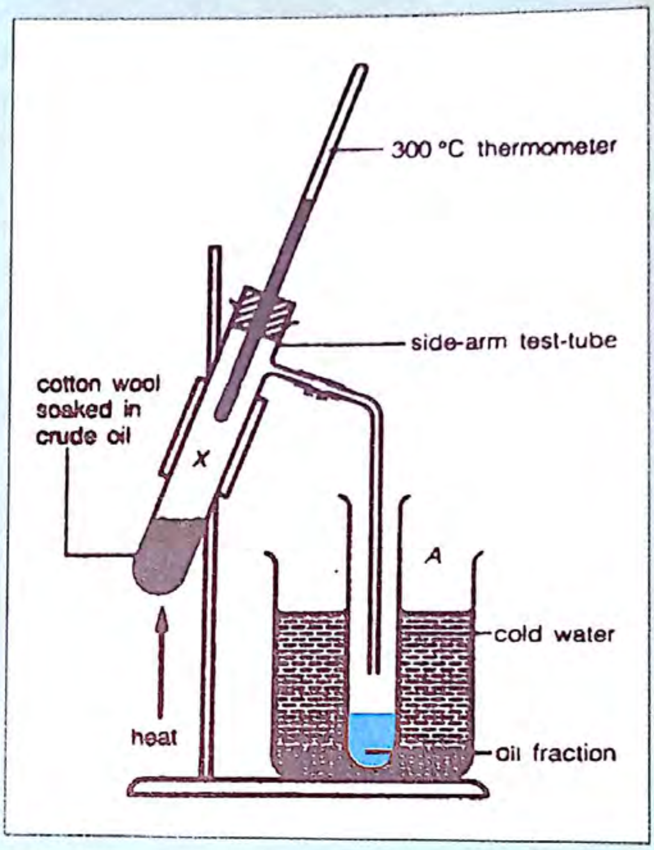
As the vapour containing a mixture of substances ascends the column, it cools, condenses and separates out into several fractions according to the volatility of the substances in the mixture. This means that substances with higher boiling points separate out in the trays on the lower part of the column, while those with lower boiling points separate out on the trays in the upper part of the column.

The different fractions are drawn off at different heights on the column, redistilled to improve purity and then further treated to obtain different liquid fuels and petrochemicals.

xperiment 28.1 To fractionally distil crude oil and then test the properties of each fraction.

Method Fill a test-tube *X*, which has a side-arm, to a depth of 3 cm with cotton wool. Pour about 3 cm^3 of crude oil to soak the cotton wool. Set up the apparatus as shown.

Fig. 28.4 The fractionation of crude oil in the laboratory.



Heat the test-tube near the top end of the cotton wool with a low Bunsen flame. Collect the distillate that comes off between room temperature and 100 °C in test-tube *A* that is partially immersed in a beaker of cold water. This distillate is the first fraction. Remove the test-tube *A*, and the beaker of cold water. Stopper test-tube *A*.

Heat test-tube *X* with a stronger flame and collect the second fraction with boiling points that range from 100 °C to 200 °C in test-tube *B*. Similarly, collect a third fraction with boiling points that range from 200 °C to 250 °C in test-tube *C*.

Remove the black sticky residue in test-tube *X* with a steel spatula. Note the colour and viscosity of each fraction and the residue. Test each of them for:

(a) its flammability (by slowly bringing a lighted match to a few drops of the fraction on a watch-glass and noting how easily it ignites);

(b) the nature of the flame produced (i.e. sootiness and colour); and

(c) its volatility (i.e. the temperature at which it evaporates).

Result Tabulate your results in the table below.

PROPERTIES FRACTIONS	Flammability and nature of flame	Volatility	Colour	Viscosity
First fraction				
Second fraction				
Third fraction				
Residue				

Conclusion All oil fractions and residue burn easily and evaporate readily, but the ease of burning and evaporation decreases progressively from the lower to the higher boiling-point fractions. The lowest boiling-point fraction burns completely producing a non-sooty flame, while the higher boiling-point fractions burn less completely producing sooty flames. The higher boiling-point fractions are also more viscous, and have a darker colour.

Fractions of crude oil

The following are the principal fractions obtained by the fractional distillation of crude oil.

Petroleum gases These gases are liberated at the top of the column at temperatures below 40 °C. They are mainly hydrocarbons consisting of one to four carbon atoms per molecule, e.g. methane, ethane, propane, butane and ethene. They are used mainly as fuels for homes and industries, and for the manufacture of products like hydrogen, carbon(IV) sulphide, tetrachloromethane and ethyne.

Petroleum ethers and ligroin This mixture of very volatile liquids consists of hydrocarbons with five or seven carbon atoms per molecule. The petroleum ether or light petroleum distils over between 2 °C to 60 °C, while the ligroin or light naphtha distils over between 60 °C to 100 °C. Both the products are used as organic solvents.

Petrol Petrol or gasoline is a mixture of hydrocarbons consisting of four to twelve carbon atoms per molecule. It is a volatile liquid which distils over in the temperature range of 40 °C to 200 °C. Petrol is used as a fuel for aeroplanes and motor-vehicles. It is also a good solvent for paints and grease.

Kerosene Kerosene contains hydrocarbons with twelve to eighteen carbon atoms per molecule. It distils over in the temperature range of 200 °C to 250 °C. It is a fairly volatile liquid and is used as a fuel for lighting and heating, and for driving tractors and some modern jet engines. It is also a good solvent for grease and paints.

Gas oil and diesel oil These are mixtures of hydrocarbons with twelve to twenty-five carbon atoms per molecule. They distil over in the temperature range of 250 °C to 350 °C. They are used mainly as fuels for heating and diesel engines and as raw materials for the cracking process.

Lubricating oils These are heavy oils. They consist

An oil refinery is a huge complex which may occupy an area as large as a town. A few million tonnes of crude oil are usually processed annually in such a refinery.

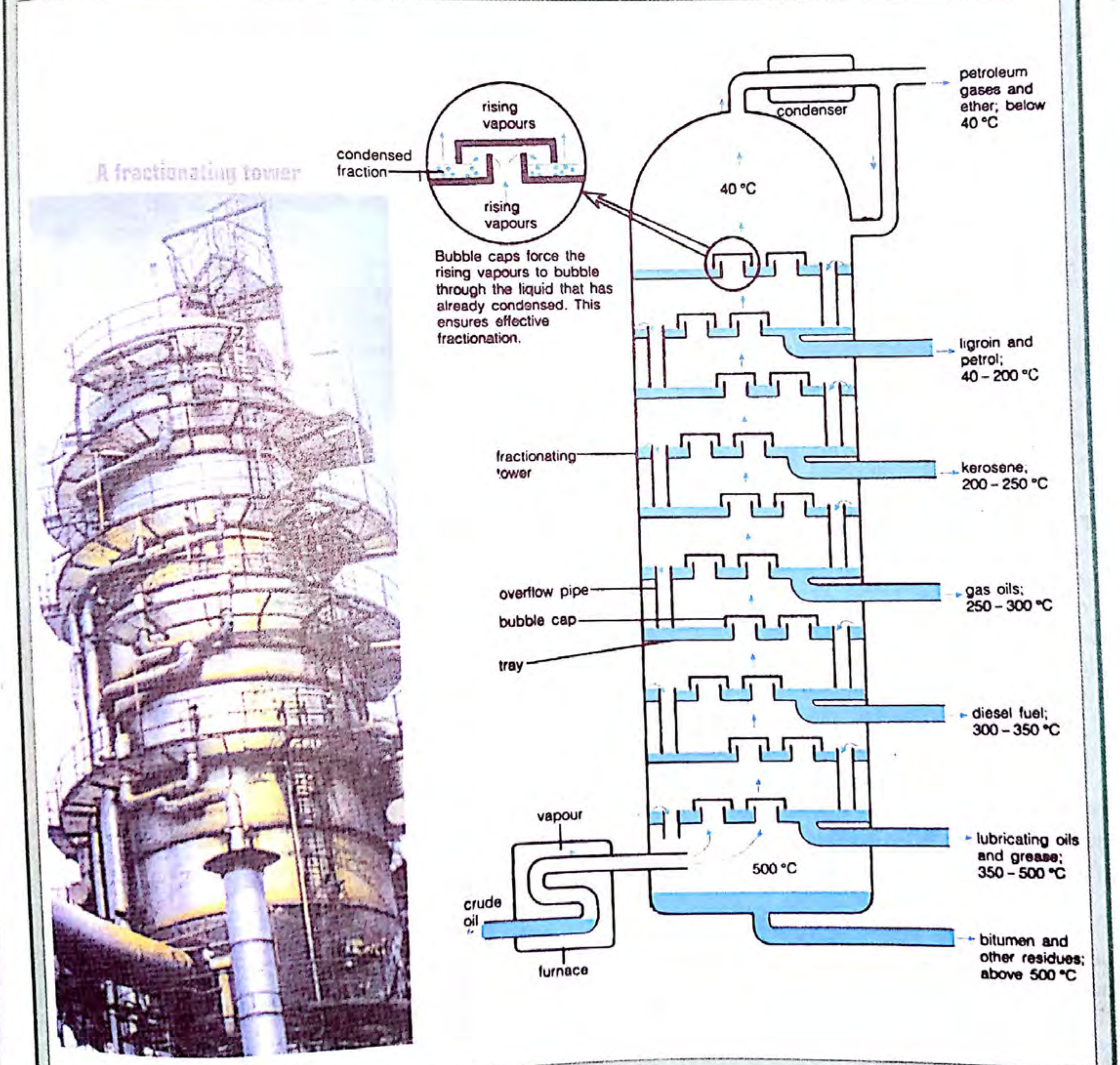
of hydrocarbons with more than twenty carbon atoms per molecule, which distil over in the temperature range of 350 °C to 500 °C. They are viscous liquids used for lubricating moving parts of engines and machines. Grease, which is semi-solid, also belongs to this group. Vaseline and paraffin wax are solid, long-chain hydrocarbons which are obtained on redistillation of these heavy oils. Vaseline is used in hair-care products while paraffin wax is used in making candles, waterproof materials, polish, ointments and creams.

Bitumen and other residues These are solid residues left behind at temperatures above 500 °C. Bitumen or pitch is used for surfacing roads and airfields while other residues may be used as fuel, in protective paints, as well as in pipecoating and waterproofing roofs.

Further treatment of crude oil fractions

The hydrocarbons obtained from the fractional distillation of crude oil range from those with one

Fig. 28.5 Fractional distillation of crude oil.



carbon atom like methane to those with more than sixty carbon atoms. It is only the low molecular mass and low boiling fractions (which make up 49% of the fractions) that are useful as fuels and raw materials in the chemical industry. It is economical to convert some of the higher boiling hydrocarbon fractions to lower boiling ones. This can be achieved by the process of *cracking*, i.e. the breaking of bigger hydrocarbons into smaller hydrocarbons. The main methods used are *thermal cracking* and *catalytic cracking*.

Fuel for Petrol Engines

Petrol engines A motor-car engine has a number of cylinders (usually four) fitted with pistons. When the engine is working, the pistons move up and down inside the cylinders. Each upward or downward movement of a piston is known as a stroke. The motor-car engine works on a four-stroke energy cycle. This means that the fuel-air mixture is ignited at each cycle to provide energy. For efficient working of the motor-car engine, the fuel-air mixture

- must ignite at the correct stage in each cycle,
- must be completely burnt.

The fuel should possess the correct volatility and temperature of ignition for it to be burnt at the right time of the cycle. If the fuel is too volatile and has too low an ignition point, it would be burnt prematurely. When this happens, a condition called *knocking*, or *pinking*, results. This is a characteristic metallic sound caused by vibrating pistons. This knocking reduces the efficiency of the motor-car engine and shortens its life. On the other hand, a fuel which is not volatile enough and has too high an ignition temperature may not be burnt completely. Excessive black smoke and unburnt hydrocarbons are expelled from the car exhaust, causing air pollution.

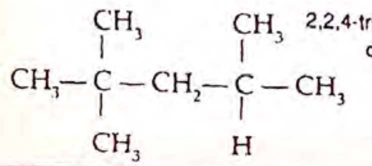
Petrol is the only fuel that meets all the requirements necessary to power a motor-car engine. Thus, motor-car engines are known as petrol engines. Nowadays, more efficient petrol engines have been designed. These have a tendency to 'knock' if low-quality petrol is used.

Octane number system The grade or quality of petrol is measured according to a scale called the octane-number system.

Petrol containing a higher percentage of straight-chain hydrocarbons causes more knocking than that containing a higher percentage of branched-chain ones. A straight-chain alkane like heptane is assigned an octane number of 0, while 2,2,4-trimethylpentane, a highly branched octane is assigned an octane number of 100. Therefore, the quality of any petrol is rated according to its octane number, i.e. the percentage of heptane to 2,2,4-trimethylpentane in a mixture.

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$$

heptane octane number = 0



$$CH_3—C(CH_3)_2—CH_2—CH(CH_3)—CH_3$$

2,2,4-trimethylpentane (iso-octane) octane number = 100

To determine the octane number of petrol, the amount of knocking caused by the petrol, when tested in a calibrated standard engine, is compared with a standard of different mixtures of heptane and 2,2,4-trimethylpentane. For example, a fuel with an octane number of 50 has a performance equivalent to a 50–50 mixture of heptane and 2,2,4-trimethylpentane. Petrol which is graded as Premium, Super or Extra has an octane number closer to 100 than petrol that is graded as Regular or Ordinary.

NOTE The octane number of straight-chain hydrocarbons is related to their molecular mass, i.e. the lower the molecular mass of the hydrocarbon, the higher the octane number. Some fuels which are superior to 2,2,4-trimethylpentane have an octane number greater than 100.

Table 28.1 Octane number of some hydrocarbons.

Straight-chain hydrocarbon	Relative molecular mass	Octane number
Propane	44	100
Butane	58	92
Pentane	72	61
Hexane	86	25
Heptane	100	0
Octane	114	–27
Nonane	128	–45

Natural Gas

Natural gas, usually found together with crude oil, consists of gaseous hydrocarbons, mainly methane. Formerly, natural gas was burnt off as waste at the oil

A variety of useful plasric household items are in common use in Nigeria.

wells. Now, most of it is piped for industrial and domestic use. Components like butane and propane which liquefy readily under pressure, are sold as bottled gas.

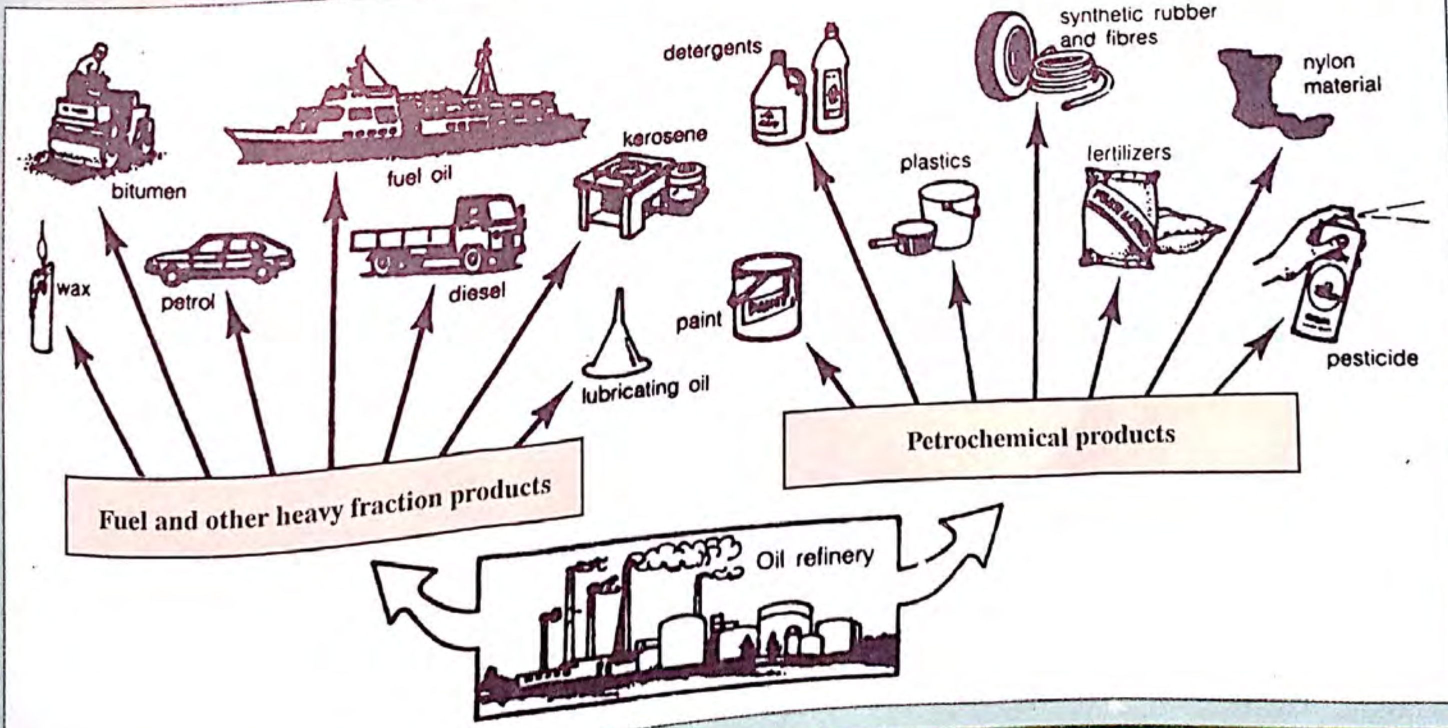
In Nigeria, natural gas is used as fuel for heavy-duty vehicles and engines. The gas power stations at Ughelli and Sapele use natural gas to generate electricity. Nigeria also proposes to set up a Liquefied Natural Gas Plant. This will enable Nigeria not only to increase its natural gas consumption at home, but also to export the gas.

Petrochemicals

Petroleum and natural gas are now used in increasing amounts to produce many organic compounds. Examples include ethanol, ethene, propane 1,2,3-triol, benzene and toluene. They used to be obtained from other sources. These small-molecule organic compounds are in turn used to make large-molecule organic compounds like plastics, synthetic rubber, insecticides, detergents and synthetic fibres like nylon and dacron. Substances manufactured from the by-products of petroleum are called petrochemicals. In recent years, the manufacture of such compounds has become an important industry.

Natural gas is an important domestic fuel in Nigeria.

Fig. 28.6 The products of oil.



SUMMARY

- Hydrocarbons are very simple organic compounds composed only of the elements, hydrogen and carbon. They can be grouped into aliphatic and aromatic hydrocarbons.
- The main source of hydrocarbons is crude oil or petroleum.
- Crude oil is a dark viscous liquid found in underground deposits. It is formed from marine algal and animal remains as a result of bacterial activity, heat and pressure.
- Nigeria has huge deposits of crude oil, especially in the Niger delta area.
- Crude oil is extracted by drilling deep wells into the ground. It is then transported to oil refineries where it undergoes fractional distillation.
- During fractional distillation, crude oil is separated into the following main fractions.

Name of fraction	Boiling point range in °C	Carbon atoms in molecules	Uses
Petroleum gas	Below 40	1–4	Fuel and manufacture of other organic compounds.
Petrol	40–200	4–12	Fuel in aeroplanes and motor-vehicles.
Kerosene	200–250	12–18	Fuel for lighting, heating and jet engines.
Gas oil and diesel oil	250–350	12–25	Fuel for heating and diesel engines. Raw materials for cracking process.
Lubricating oils	350–500	More than 20	Lubricating moving parts of machines. Making candles, creams and hair-care products.
Bitumen	Above 500	More than 35	Surfacing roads.

- Cracking is used to obtain petrol from the heavier, or less volatile, fractions of crude oil. The grade of petrol is measured on an octane number scale. High-grade petrols have octane numbers nearer 100, while low grade petrols have octane numbers nearer 0. Low-grade petrols cause knocking in the motor-car engine. This reduces the efficiency of the engine and shortens its life.
- Natural gas occurs together with crude oil. It consists of gaseous hydrocarbons — mainly methane. It is used as a domestic and industrial fuel.
- Petrochemicals are substances that are manufactured from the by-products of petroleum. These include plastics, synthetic rubber and fibres.

EXERCISES

1. Oil deposits in Nigeria are
   A on land and offshore.
   B only offshore.
   C mainly imported.
   D downstream.

2. Fractional distillation involves the following processes.
   A Boiling.
   B Boiling and condensation.
   C Boiling, evaporation and condensation.
   D Condensation and collection.

3. Which is the odd-man?
   A Petroleum ether, petroleum gases, kerosene.
   B Gas oil and diesel lubricating oil.
   C Petroleum ether and bitumen.
   D Haemitite and ashphalt.

4. Which of the petrol samples are likely to cause knocking?
   A Octane
   B 2, 2, 3, 3 – tetra methyl butane
   C 2, 2, 3 – drimethyl pentane
   D 2, 2, 3 trimethyl pentane

5. Nigeria earns money from
   A petroleum gas and liquids only.
   B petroleum liquids and solids only.
   C petroleum liquids like petrol and kerosene oil.
   D petroleum gases, liquids and solids.

6. Describe how you would show that crude oil is not a single compound.

7. What are hydrocarbons? Give three example and their main sources in nature.

8. With the help of a diagram, briefly describe the industrial fractionation of petroleum.

9. Write short notes on (a) cracking, (b) octane number and (c) petrochemicals.

29

ORGANIC CHEMISTRY (1)

WHAT IS ORGANIC CHEMISTRY?

Originally, the term organic chemistry applied only to the study of substances of plant or animal origin, i.e. substances formed only by living organisms. Nowadays, most of these substances can be synthesized from inorganic materials in the laboratory. Many other similar compounds which do not have any connection with living organisrns are also known. We now define organic chemistry as *the chemistry of carbon compounds*. Apart from a few compounds such as the oxides, the trioxocarbonates(IV) and the metallic carbides, which are conventionally regarded as inorganic, all other carbon compounds are grouped together in this separate branch of chemistry. This grouping is justified because of

- their large number;
- their many common features; and
- the great medical, biochemical and economic importance of many of them.

VARIETY OF ORGANIC COMPOUNDS

Organic compounds are made up of

- the main element, carbon;
- hydrogen and oxygen which are usually present; and
- elements such as nitrogen, the halogens, phosphorus, sulphur and some metals which are sometimes present.

The presence of numerous organic compounds is due to the following properties of carbon.

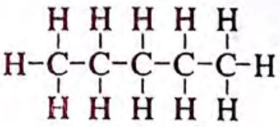
1 The exceptional ability of carbon atoms to *catenate*, i.e. to combine with one another to form straight chains, branched chains or ring compounds containing many carbon atoms.

2 The ease with which carbon combines with hydrogen, oxygen, nitrogen and the halogens.

3 The ability of carbon atoms to form single, double or triple covalent bonds.

We can illustrate the ability of carbon to form a variety of compounds by showing how five carbon atoms can join together to form some compounds.

pentane



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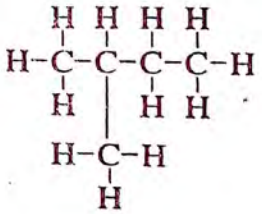
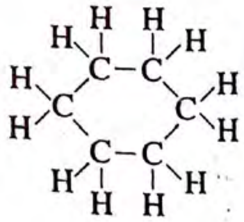
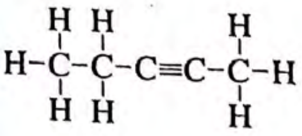


2-methyl butane

cyclohexane





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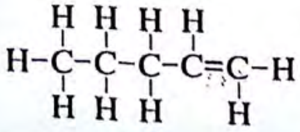
pent-2-yne



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & & & \\ & & | & & | & & | & & | & & & & \\ H & - & C & - & C & - & C & - & C & = & C & - & H \\ & & | & & | & & | & & & & | & & \\ & & H & & H & & H & & & & H & & \end{array}$$

pent-1-ene

We have only shown five of the possible compounds that can be formed by using five carbon atoms. Many more compounds can be formed using various combinations of straight chains, branch chains, rings, multiple bonds and other atoms such as oxygen and the halogens. This is why there are so many organic compounds.

CHARACTERISTIC FEATURES OF ORGANIC COMPOUNDS

Covalent nature Carbon atoms form stable covalent bonds with one another. A carbon-carbon single covalent bond has an energy of 346 kJ mol^{-1}. This high energy indicates a strong bond. Most organic compounds are stable because of the strong carbon-carbon bonds. Since they have a covalent nature, they do not ionize in solution and are non-conductors of electricity.

Polarity and solubility Carbon-hydrogen bonds are, non-polar, like the carbon-carbon bonds. This is because of the almost equal electronegativities of the two elements. Most organic compounds are non-polar unless the compounds consist of very electronegative elements like chlorine or groups like the hydroxyl group.

Since most organic compounds are non-polar, they cannot form bonds with water molecules. So most organic compounds are insoluble in water. For example, petrol, kerosene and paraffin oil do not dissolve in water. If an organic compound contains polar groups, hydrogen bonds can form between the polar groups in the molecules of the organic compound and the water molecules. This enables the compound to dissolve in water. For example, an ethanol molecule contains a hydroxyl group which is polar, so it is soluble in water.

Non-polar substances are held together only by weak intermolecular forces such as the van der Waals forces, and so they can intermingle easily. This is why most organic compounds dissolve only in non-polar solvents like benzene or ether.

Low melting and boiling points Organic compounds generally have lower melting and boiling points than inorganic compounds. This is because these compounds possess relatively weak intermolecular bonds which can be easily broken by heat energy. Many of them (mainly those with low relative molecular masses) tend to be volatile and boil at temperatures below 300 °C.

Thermal instability Many organic compounds are thermally unstable, decomposing into simpler molecules when heated to temperatures above 500 °C. However, this property is sometimes of commercial importance as in the cracking of petroleum.

Flammability Most organic compounds are flammable and burn exothermically in a plentiful supply of air to yield carbon(IV) oxide and water. Thus, most fuels such as wood, coal, oil, petrol and natural gas are organic and their combustion provides our main source of heat energy.

Reactivity Reactions involving organic compounds tend to be much slower than the ionic reactions commonly encountered in inorganic chemistry. They usually require heating, thorough mixing and catalyst to speed up the reactions.

TERMS IN ORGANIC CHEMISTRY

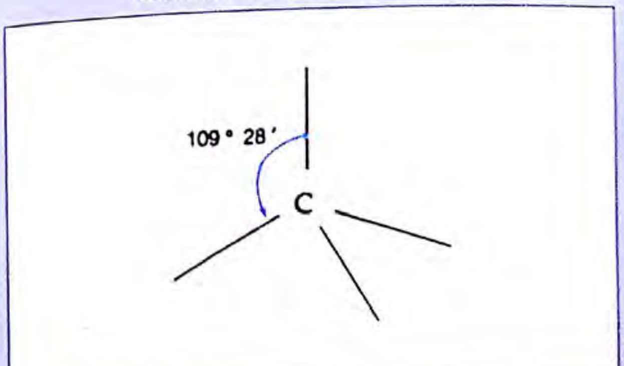
In the study of organic chemistry, several terms are used frequently. Some of these important terms are introduced and explained here to facilitate better understanding in the subsequent sections.

Electronic configuration of the carbon atom

The carbon atom has an electronic configuration of $1S^2\ 2S^1\ 2Px^1\ 2Py^1\ 2Pz^1$, or K^2L^4, i.e. it has four, unpaired valence electrons in its outermost (L) shell. This enables the carbon atom to form four single covalent bonds by sharing electrons with neighbouring atoms (which may be carbon atoms or atoms of other elements) so that the outermost shell of its atom is completely filled.

The four covalent bonds of carbon are directed symmetrically in space at an angle of 109° 28′ to one another, i.e. they are arranged tetrahedrally, so that they point towards the corners of a regular tetrahedron when the carbon atom is placed in its centre.

Fig. 29.1 Tetrahedral arrangement of the four covalent bonds of a carbon atom.



Homologous series

The numerous organic compounds can be grouped into a comparatively small number of *series* or *families of compounds* known as *homologous series.* The simplest series of compounds in organic chemistry is the *alkanes.* We shall study this series to illustrate what a homologous series means.

The alkanes are a series of hydrocarbons with a general molecular formula of C_nH_{2n+2}, where n is a whole number with a value of one or more.

From table 29.1, we see that each individual member of the alkane series differs from the preceding or the following member by one carbon atom and two hydrogen atoms, i.e. $-CH_2-$ group. Such a family of compounds is known as a homologous series and each individual member is referred to as a homologue.

> *A homologous series is a family of organic compounds which follows a regular structural pattern, in which each successive member differs in its molecular formula by a* $-CH_2-$ *group.*

Other homologous series include the alkenes, C_nH_{2n}, the alkanols, $C_nH_{2n+1}OH$, and the carboxylic acids, $C_nH_{2n+1}COOH$. Homologous series have the following common characteristics.

General molecular formula All members share a general molecular formula, i.e. C_nH_{2n+2} for the alkanes, C_nH_{2n} for the alkenes, and so on.

Difference between successive homologues Each successive member in such a series differs in its molecular formula by the addition of a $-CH_2-$ group, and in its relative molecular mass by an increase of 14.

Physical properties The physical properties of the members change gradually as the number of carbon atoms per molecule increases. For example, the boiling points of the alkanes increase down the series, so that the first four members are gases at room temperature and standard pressure; members with five to seventeen carbon atoms per molecule are volatile liquids; while the higher members are wax-like solids. Similarly, the melting points and densities of the alkanes also increase, while their solubility in water decreases down the series.

Chemical properties The members show similar chemical properties. For example, the alkanes are fairly unreactive under ordinary conditions. They burn in air, forming carbon(IV) oxide and water, and undergo substitution reactions with other substances such as halogens.

General methods of preparation All members can usually be prepared by using the same general methods, e.g. alkanes can be prepared by the action of hot soda lime on the appropriate sodium salt of an acid.

Table 29.1 Properties of the first ten members of the alkane series.

Name of alkane	Molecular formula (C_nH_{2n+2})	Relative molecular mass	Physical state*	Boiling point (℃)	Melting point (℃)
Methane	CH_4	16	Gases	−162	−183
Ethane	C_2H_6	30		−89	−172
Propane	C_3H_8	44		−42	−187
Butane	C_4H_{10}	58		−1	−138
Pentane	C_5H_{12}	72	Liquids	36	−130
Hexane	C_6H_{14}	86		69	−94
Heptane	C_7H_{16}	100		98	−91
Octane	C_8H_{18}	114		125	−57
Nonane	C_9H_{20}	128		151	−54
Decane	$C_{10}H_{22}$	142		174	−30

*At room temperature and standard pressure

Alkyl Groups

Alkyl groups Many homologous series can be regarded as being derived from the alkanes by the substitution of one or more of the hydrogen atoms by other elements or groups. The univalent group which is formed from an alkane by the loss of a hydrogen atom is known as the *alkyl* group. Thus, the compound that is formed by substitution can be considered as being made up of the alkyl group and the substituent group. For example, chloromethane, CH_3Cl, is composed of the methyl group, CH_3-, (obtained from methane, CH_4, by the loss of a hydrogen atom) linked to the substituent chlorine atom. –Cl.

> *The general term alkyl group includes all groups derived from the alkanes by the loss of a hydrogen atom.*

Alkyl groups have a general formula of C_nH_{2n+1}. They are named after the parent alkanes by replacing the ending *-ane* by *-yl*.

Alkyl groups are given the general symbol, *R*. Sometimes, *R* may stand for more complex groups than just simple alkyl groups.

Table 29.2 The alkyl groups derived from the first six members of the parent alkane series.

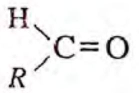
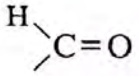
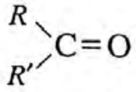
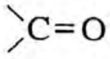
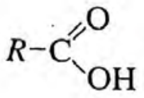
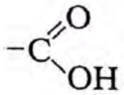
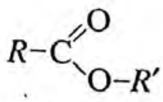
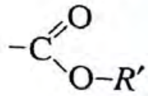
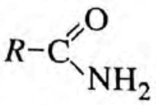
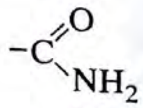
Parent alkane	Alkyl group	Formula
Methane	Methyl	CH_3-
Ethane	Ethyl	C_2H_5-
Propane	Propyl	C_3H_7-
Butane	Butyl	C_4H_9-
Pentane	Pentyl	$C_5H_{11}-$
Hexane	Hexyl	$C_6H_{13}-$

Functional groups The alkyl group of a compound is fairly inert chemically because of the stability of the carbon-hydrogen bonds. The chemical reactivity of an alkyl compound is determined mainly by the substituent group. These groups are referred to as the functional groups, e.g. the hydroxyl group, –OH, the amino group, $-NH_2$, the carboxyl group, –COOH, and the double covalently bonded carbon atoms, C=C. Each functional group has its own characteristic properties. When two or more functional groups occur in one molecule, the properties of one are often modified or influenced by the presence of the others. Thus, the presence of the functional group or groups determines the chemical properties of a homologous series.

> *A functional group is an atom, a radical (group of atoms) or a bond common to a hamologous series, and which determines the main chemical properties of the series.*

Table 29.3 gives the general formulae and specifies the functional groups present in many of the homologous series which are derived from the alkanes.

Table 29.3 The homologous series derived from alkanes.

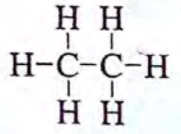
Homologous series	General formula	Functional group
Alkanes	*R*—H	—
Haloalkanes	*R*—*X* (where *X* = F, Cl, Br or I)	—*X*
Alkanols	R—OH	—OH
Ethers	R—O—R′	—O—R′
Alkanals	 $R-CHO$	 $-CHO$
Alkanones	 $R-CO-R'$	 $>C=O$
Carboxylic acids	 $R-COOH$	 $-COOH$
Esters	 $R-COO-R'$	 $-COO-R'$
Primary amines	R—NH_2	—NH_2
Amides	 $R-CONH_2$	 $-CONH_2$
Nitriles	R—C≡N	—C≡N

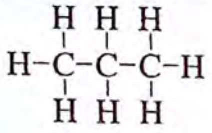
NOTE *R* and *R'* may be the same or different alkyl groups or they may represent a more complex group than an alkyl group

Effect of the alkyl and functional groups The functional group determines the basic chemistry of a compound, while the alkyl group affects the physical properties of a compound. For example, the polar hydroxyl group in the alkanols promotes solubility in water but the non-polar alkyl group opposes it. For all alkyl groups larger than C_4H_9-, this opposing effect is sufficient to greatly limit the solubility of the compound in water.

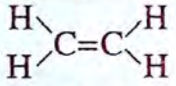
Saturated and unsaturated compounds

If an organic compound contains atoms joined only by single covalent bonds, the compound is said to be *saturated*. The alkanes are said to be saturated hydrocarbons. For example,


ethane


propane

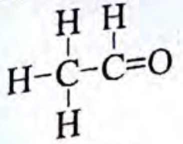
If an organic compound contains carbon atoms joined by double or triple covalent bonds, the compound is said to be *unsaturated*. For example,

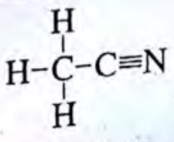

ethene

$H-C\equiv C-H$
ethyne

Hydrocarbons possessing a set of carbon-carbon double covalent bonds, $>C=C<$, in their carbon chains form the homologous series called alkenes while those possessing a set of carbon-carbon triple covalent bonds, $-C\equiv C-$, in their carbon chains form the alkyne series. Ethene and ethyne are the first members of the alkenes and alkynes respectively. Both these series can be considered as being derived from the saturated alkanes by the removal of hydrogen atoms and the subsequent introduction of double and triple bonds respectively in their carbon chains. The carbon-carbon double and triple covalent bonds represent the functional groups in these series because the availability of electrons in these multiple bonds makes the unsaturated compounds chemically more reactive.

Compounds containing double or triple bonds between a carbon atom and an atom of another element can also be said to be unsaturated. For example,


thanal

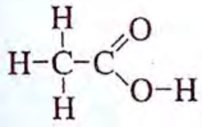

ethanonitrile

Formulae of organic compounds

Empirical formula The simplest formula of a compound is called its empirical formula. It indicates the relative numbers of each kind of atom in a molecule of a substance. It is found by determining the percentage composition of the substance by quantitative analysis.

Molecular formula A more useful formula than the empirical formula is the molecular formula of a substance. It indicates the actual numbers of each kind of atoms in a molecule of a substance. The molecular formula is deduced from the relative molecular mass of the substance and its empirical formula.

Structural formula In inorganic chemistry, a molecular formula is informative enough to distinguish one substance from another. This is not the case in organic chemistry where the molecular formula may represent more than one substance. A more informative formula called the structural formula is often used to represent a particular organic substance. Such a formula indicates how the atoms are arranged within the molecule of a substance. The structural formula of ethanoic acid can be represented as follows:


ethanoic acid

– single covalent bond
= double covalent bon
≡ triple covalent bond

The formula shows which atoms are linked together and how they are linked by using conventional symbols.

The structural formula can also be written in a condensed form where the alkyl and functional groups present in the molecule are shown and arranged in the correct order. Ethanoic acid can be represented as follows:

CH_3COOH

This condensed structural formula is usually preferred because it indicates clearly the functional groups present in the substance. The structural formula can be determined through various spectroscopic methods.

The structural formula is usually shown as planar for convenience and does not imply a flat molecule. A true molecular representation of an alkane, for example, should show the actual arrangement of the atoms in space and the angles between the bonds. Thus, the methane molecule, CH_4, should show a central carbon atom joined to each hydrogen atom by covalent bonds which are distributed tetrahedrally around the carbon atom, i.e. the bonds are at an angle of 109° 28′ to one another. This is known as the *spatial or three dimensional representation* of the methane molecule. Fig. 29.2 shows the spatial representations of the molecules of several common organic compounds. Methane, ethane and propane show tetrahedral structures while ethene is planar and ethyne linear.

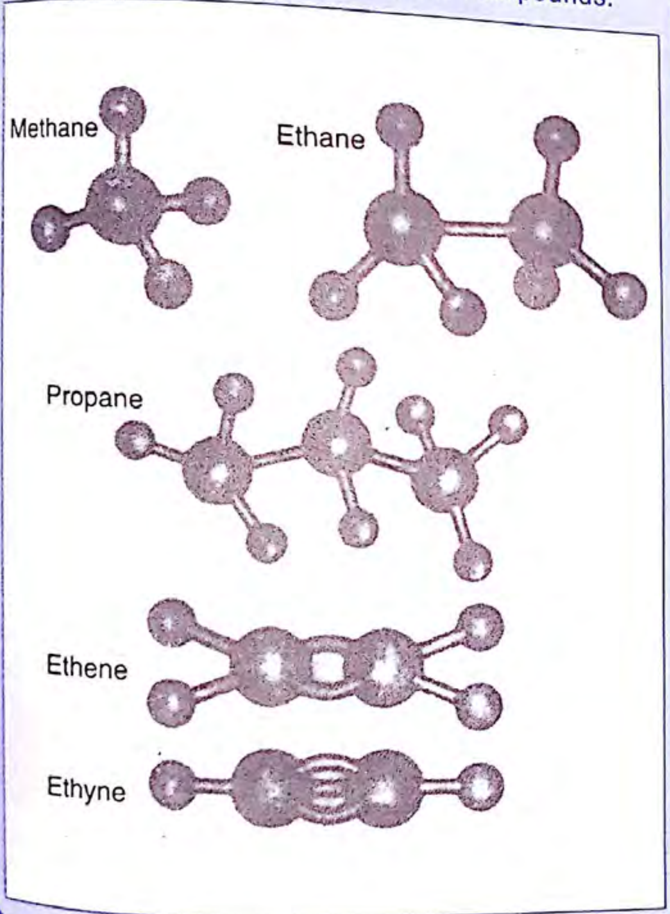


Fig. 29.2 Spatial representation of the molecular structure of some organic compounds.

THE IUPAC NOMENCLATURE FOR ALIPHATIC COMPOUNDS

The International Union of Pure and Applied Chemistry (IUPAC) has put forward a system of nomenclature which relates the name of the compound to its molecular structure. In this system, every name consists of a *root*, a *suffix* and as many *prefixes* as necessary.

Root

The root is generally an aliphatic hydrocarbon. All aliphatic compounds are regarded as being derived from this root hydrocarbon by

- the replacement of hydrogen atoms by alkyl or functional groups;
- the introduction of multiple bonds (i.e. double and triple covalent bonds).

The systematic name of a compound is formed from the root hydrocarbon by adding a suffix and prefixes to denote the substitution of the hydrogen atoms.

Table 29.4 gives the common functional groups which usually replace the hydrogen atoms in the root

Table 29.4 Names of functional groups when they are used as suffixes or prefixes.

Functional group	Name as suffix	Name as prefix
$-COOH$	-carboxylic acid	carboxy-
$-{}^{*}C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown OH}$	-oic acid	—
$-COOR$	alkyl...–carboxylate	alkoxy carbonyl-
$-{}^{*}C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown OR}$	alkyl...oate	—
$-{}^{*}C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown NH_2}$	-amide	—
$-{}^{*}C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown H}$	-al	oxo-
$-{}^{*}C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown}$	-one	oxo-
$-CN$	-carbonitrile	cyano-
$-OH$	-ol	hydroxy-
$-NH_2$	-amine	amino-
$-Cl$	—	chloro-
$-Br$	—	bromo-
$-I$	—	iodo-

Note Only the carbon atoms marked with asterisks, *C, are counted as part of the carbon chain which forms the root hydrocarbon.

hydrocarbon, together with their names when they are used as suffixes or prefixes.

Suffixes

A suffix is added to the root to indicate the presence of the principal substituent, which is usually also the principal functional group in the molecule. Compounds having the same functional groups, such as those belonging to the same homologous series, would carry a common suffix at the end of their names. The following are some examples.

Alkanes The names of alkanes end with *-ane,* e.g. methane, CH_4, ethane, C_2H_6 and propane, C_3H_8.

Alkenes The members of the alkene series are formed from the alkanes by the removal of two hydrogen atoms and the introduction of a double bond in the carbon chain. They are named after the corresponding alkanes by changing the *-ane* ending to *-ene,* e.g. C_2H_4 is ethene, C_3H_6 is propene and C_4H_8 is butene.

Alkynes Each member of this series is formed by the removal of four hydrogen atoms and the introduction of a triple bond in the appropriate alkane molecule. They are named by replacing the *-ane* ending by *-yne,* e.g. C_2H_2 is ethyne and C_3H_4 is propyne.

Alkanols The members of this series, ROH, are named after the corresponding alkanes by replacing the *-e* ending with *-ol,* e.g. CH_3OH is methanol and C_3H_7OH is propanol.

Alkanoic acids Also known as carboxylic and organic acids, RCOOH, the members of this series are named by replacing the *-e* ending in the corresponding alkanes by *-oic acid,* e.g. CH_3COOH is ethanoic acid, C_2H_5COOH is propanoic icid and C_3H_7COOH is butanoic acid.

Esters Esters, *RCOOR',* are formed when a carboxylic acid reacts with an alkanol. They have a general formula of *RCOOR',* where *RCO-* is the group derived from the acid and *-OR'* is the group derived from the alkanol. In naming an ester, the alkyl group, *R',* is named first, followed by the name of the acid group with a *-oate* ending as the suffix. For example, $HCOOCH_3$ is methyl methanoate, CH_3COOCH_3 is methyl ethanoate and $CH_3(CH_2)_2COOC_2H_5$ is ethyl butanoate.

Amides Members of this series, *R*$CONH_2$, have an *-amide* ending in their names, instead of the *-e* in the corresponding alkanes. For example, CH_3CONH_2 is ethanamide and $C_2H_5CH_2CONH_2$ is butanamide.

Alkanals or (aldehydes) The members of this series, *R*CHO, are named by replacing the *-e* ending in the corresponding alkanes by *-al.* For example, HCHO is methanal, CH_3CHO is ethanal and C_4H_9CHO is pentanal.

Alkanones or (ketones) The members of this series, *RCOR',* have an *-one* ending in their names, instead of the *-e* in the corresponding alkanes, e.g. CH_3COCH_3 is propan-2-one and $CH_3COC_2H_5$ is butan-2-one.

Amines The members of this series, *R*NH_2, are named by adding the *-amine* ending to the alkyl group, e.g. CH_3NH_2 is methylamine and $C_2H_5NH_2$ is ethylamine.

Prefixes

Cyclic compounds can be indicated by adding the prefix *cyclo-* to the names of the corresponding aliphatic compounds, e.g. cyclohexane and cyclopentene. Prefixes are also used to indicate the presence of substituted alkyl or functional groups other than the principal group, as well as the positions of these substituents in the carbon chain.

Alkoxy prefix In the case of ethers, which have the general formula of *R–O–R',* where *R* and *R'* may be the same or different alkyl radicals, the prefix *alkoxy-* is used. This prefix, *–OR',* is composed of the name of the simpler alkyl group in the molecule with the *-yl* ending replaced by *-oxy.* The alkoxy prefix is then followed by the name of the corresponding alkane of the other alkyl group in the molecule. For example, $CH_3OC_2H_5$ is methoxyethane and $C_2H_5OC_2H_5$ is ethyloxyethane.

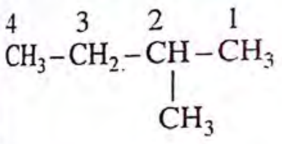
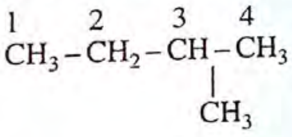
Rules for naming more than one prefix When more than one of the same substituent group is present, the multiplying prefixes, such as *di-* for two, *tri-* for three and *tetra-* for four are used. If more than one prefix is needed, they are placed in alphabetical order. Multiplying prefixes do not affect this order. For example, $ClCH_2CHBr_2$ is bromochloroethane and $ClCH_2CHBr_2$ is 1,1,dibromo-2-chloroethane.

Numbering of the carbon atoms

The positions of the substituent groups and the multiple bonds in the carbon chain of a compound are indicated by the number of the carbon atom or atoms to which they are attached. The IUPAC convention is to number all the carbon atoms in the longest chain starting from the end which is the closest to the branch chain or other modifications of the simple alkane structure. This is done so as to give

- the lowest possible number to the group cited by the suffix, and then
- the lowest possible individual numbers to the groups cited as prefixes.

For example,

Correct numbering	**Incorrect numbering**
 $\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{\underset{\displaystyle CH_3}{\underset{\vert}{CH}}}-\overset{1}{CH_3}$	 $\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}-\overset{4}{\underset{\displaystyle CH_3}{\underset{\vert}{CH_3}}}$
2-methylbutane	3-methylbutane
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}\equiv\overset{1}{CH}$	$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}\equiv\overset{4}{CH}$
but-1-yne	but-3-yne
$\overset{3}{ClCH_2}-\overset{2}{CH2}-\overset{1}{CH_2OH}$	$\overset{1}{ClCH_2}-\overset{2}{CH2}-\overset{3}{CH_2OH}$
3-chloropropan-1-ol	1-chloropropan-3-ol

Numbers (especially 1) are often omitted when the structure can be deduced without them, e.g. butanone can only be $CH_3CH_2COCH_3$.

Basic rules for naming organic compounds

Aliphatic organic compounds can be named by following these basic rules.

1 Take the longest continuous carbon chain as the root hydrocarbon and name it according to the number of carbon atoms it contains, adding the appropriate suffix to indicate the principal substituent group.

2 Number the carbon atoms in the root hydrocarbon from the end which will give the lowest number to the suffix, and then the prefix(es).

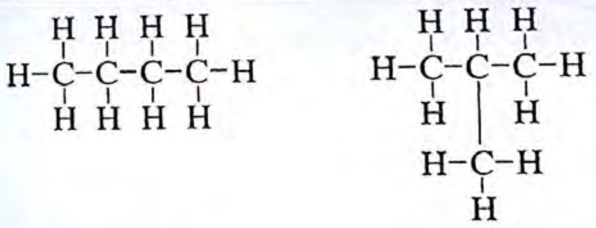
3 Indicate the other substituents by prefixes preceded by numbers to show their positions on the carbon chain.

STEREOCHEMISTRY

Stereochemistry is the study of structure in three dimensions. Here we are interested in the phenomena of isomerism.

Isomerism

If we study the structural formula of butane or other higher hydrocarbons of the alkane series, we will observe that it is possible to arrange the atoms in the molecule in more than one way. This means that it is possible to have two or more different structural arrangements for the same molecular formula. For example, the four carbon atoms and ten hydrogen atoms in the butane molecule can be linked in two different ways which will satisfy the valencies of carbon and hydrogen.



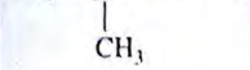
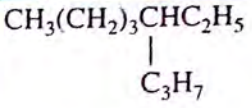
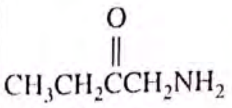
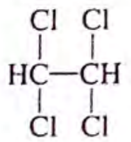
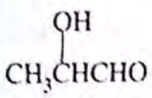
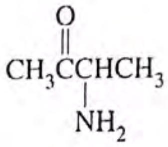
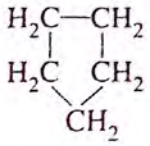
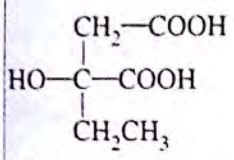
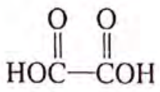
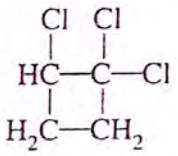
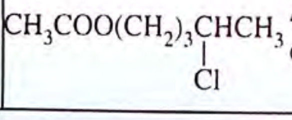
$CH_3(CH_2)_2CH_3$ butane

$CH_3CH(CH_3)CH_3$ 2-methylpropane (isobutane)

This would mean that there are two compounds (shown above) with the molecular formula C_4H_{10}. This has been supported by experimental evidence which shows that there are two compounds with different physical properties (e.g the boiling point of one is 0.6 °C, while that of the other is 12 °C) but with the same molecular formula of C_4H_{10}. Such a phenomenon is known as *isomerism*.

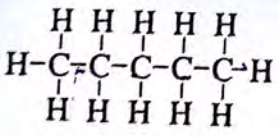
NOTE The branched compound 2-methylpropane (isobutane) has the lower boiling point than normal butane due to the presence of weaker van der Waals forces between the molecules.

Table 29.5 Naming compounds according to the IUPAC system of nomenclature.

Strutural formula	IUPAC name	Structural formula	IUPAC name	Strutural formula	IUPAC name
 $CH_3CH_2CH(CH_3)CH=CH_2$	3-Methyl-pentene	$CH_2=CHCH=CH_2$	Buta-1,3-diene	 $CH_3(CH_2)_3CH(C_3H_7)C_2H_5$	4-Ethyloctane
$CNCH_2C\equiv CCH_3$	4-Cyano-but-2-yne	 $CH_3CH_2C(=O)CH_2NH_2$	2-Oxo-butylamine		1,1,2,2-Tetra-chloroethane
 $CH_3CH(OH)CHO$	2-Hydroxy-propanal	 $CH_3C(=O)CH(NH_2)CH_3$	3-Amino-butan-2-one		Cyclopentane
	3-Carboxy-3-hydroxy-pentanoic acid		Ethanedioic acid		1,1,2-Trichloro-cyclobutane
$HCOOC_8H_{17}$	Octyl methanoate	 $CH_3COO(CH_2)_3CH(Cl)CH_3$	4-Chloropentyl-ethanoate		

> *Isomerism is the existence of two or more compounds (known as isomers) with the same molecular formula but different molecular structures.*

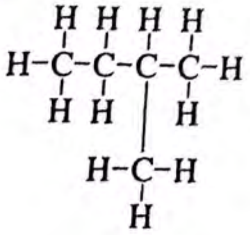
Isomerism is a very common feature in organic chemistry. As the number of carbon atoms in a molecule increases, the number of isomers also increases. For example, pentane has the following three possible isomers.



n-Pentane

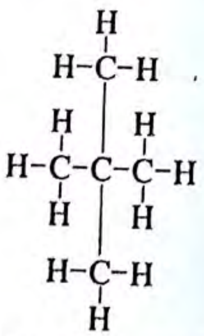
$CH_3(CH_2)_3CH_3$

C_5H



2-methyl butane

$CH_3CH_2CH(CH_3)CH_3$

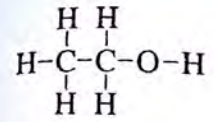


2 ,2-dimethyl propane

$C(CH_3)_4$

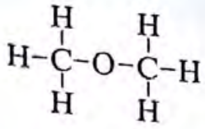
Hexane, C_6H_{14}, has five possible isomers, whi calculations show that there are 75 isomers for decane, $C_{10}H_{22}$ and up to 366319 isomers for eicosane; $C_{20}H_{42}$.

Generally, isomers with the same molecular formula and belonging to the same homologous series tend to have similar chemical properties (as they have the same functional group), but slightly different physical properties as a result of their structural differences. However, it is also possible to have isomers with the same molecular formula but belonging to different homologous series. For example, both ethanol and methoxymethane (dimethyl ether) have the same molecular formula of C_2H_6O, but belong to the alkanol and ether series respectively. Such isomers usually have different physical as well as chemical properties because of their different structural formulae and functional groups respectively. Thus, ethanol is a liquid at room temperature and it reacts readily with phosphorus(V) chloride due to the presence of the hydroxyl group, –OH. Methoxymethane, which has a lower boiling point, exists as a vapour at room temperature and does not react with phosphorus(V) chloride due to the absence of the hydroxyl group.



CH_3CH_2OH

ethanol

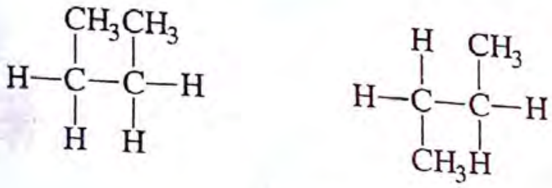


CH_3OCH_3

methoxymethane

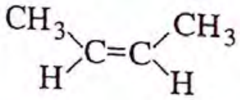
Geometric Isomerism

We can write the structural formula of butane in two ways; since each carbon atom joined by the single covalent bond has two different atoms/groups attached to it. However, only one form of butane exists because there is free rotation about the C–C single bond.



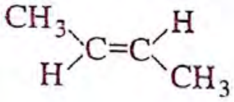
butane

The situation differs if double bonds are present instead of single bonds. Thus at any given moment, a compound like but-2-ene may exist in two forms as represented by the following structural formulae.



cis-but-2-ene

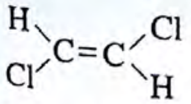
and



trans-but-2-ene

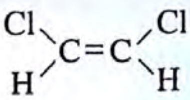
In but-2-ene, the presence of the double bond between the carbon atoms hinders free rotation. So the two forms, *cis*- and *trans*- are locked in shape, giving rise to geometric isomerism.

Geometric isomers have similar chemical properties, but their physical properties are different, e.g. the trans-form of 1,2-dichloroethene boils at 48 °C while the cis-form boils at 60 °C.



trans-1,2-dichloroethene

and



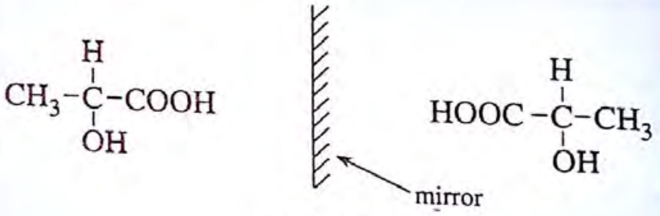
cis-1,2-dichloroethene

Geometric isomerism is common among alkenes. An alkene where each carbon atom joined by a double bond is attached to two different atoms or groups can exist in the cis- and trans-forms.

Note When two heavy or large groups (groups with large molecular masses) are on the same side of the double bond, the molecule is said to have a cis configuration. When two such groups lie on the opposite side of the double bond, the molecule is said to possess a trans configuration.

Optical Isomerism

Optical isomerism is the existence of two or more compounds with the same molecular formula but with different configurations, and because of molecular asymetry they rotate plane polarised light. Consider white light. This vibrates in many directions (planes), but when passed through a Nicolprism, the light vibrates in one plane only and is said to be plane polarised. A compound that rotates plane polarised light is said to be optically active. For a compound to be optically active, it must have a carbon atom which is substituted by four different groups e.g. Lactic acid.



Lactic Acid

The compound and its mirror images must not be superimposable on each other. When the compound rotates the plane polarised light to the right, it is said to be dextro-rotatory and is represented by d– or (+). When the light is rotated to the left, the compound is Laevo-rotatory and is designated L– or (–).

CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds can be classified into aliphatic and aromatic compounds according to their molecular structures, i.e. the arrangement of atoms in the molecules.

Aliphatic Compounds

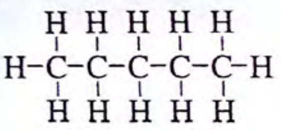
Compounds whose molecules are composed of chains of carbon atoms are known as *aliphatic compounds.*

There is no limit to the number of carbon atoms in a given chain. Often, a given carbon chain may even have one or more branches. Some examples of aliphatic compounds are

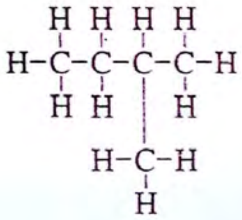
- pentane (a straight chain compound), and
- 2-methylbutane (a branched chain compound).

Such straight and branched chain aliphatic compounds are called *acyclic compounds.*

In the actual molecular structures, the carbon chains are not in truly straight lines as is conveniently represented on paper. Instead, the chains are in zig-zag lines because of the tetrahedral nature of the carbon bonds (fig. 29.3).

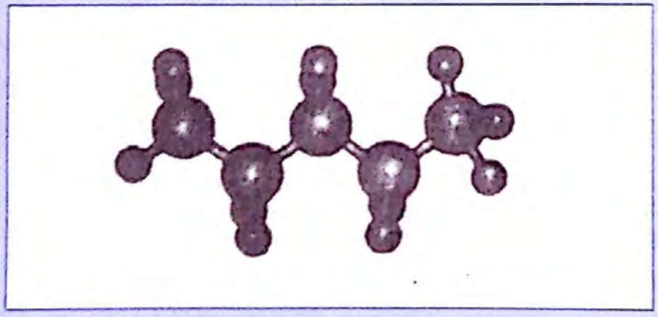


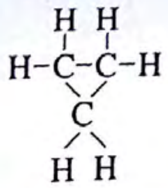
pentane



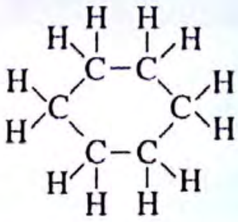
2-methylbutane

Fig. 29.3 Spatial representation of the molecular structure of pentane.





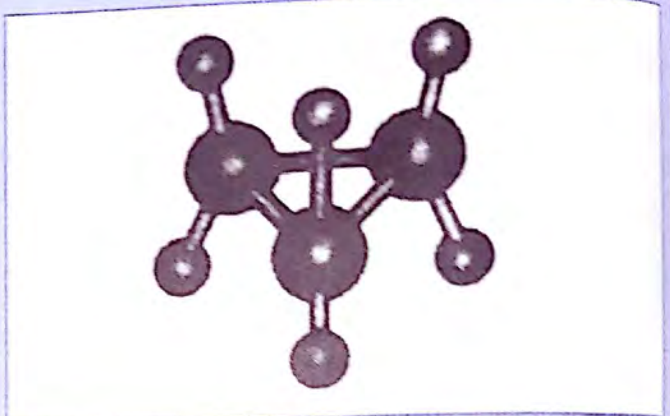
cyclopropane



cyclohexane

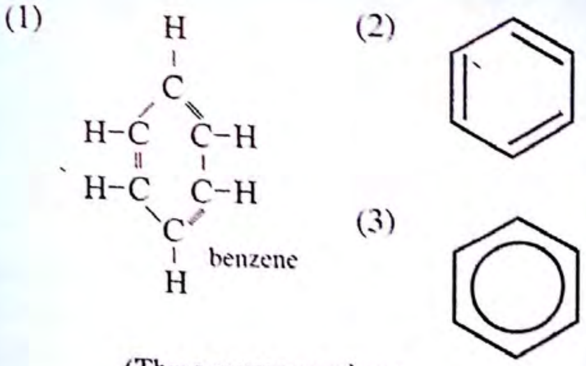
Sometimes, the end carbon atoms of an open aliphatic chain can also join together to form a closed system or ring as in cyclopropane and cyclohexane. Such compounds are known as *cyclic compounds.*

Fig. 29.4 Spatial representation of the molecular structure of cyclopropane.

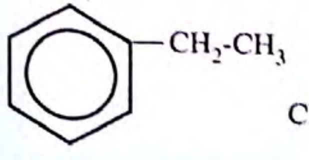


Aromatic Compounds

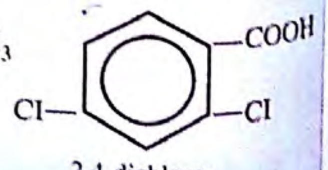
Aromatic compounds are a special class of cyclic compounds based on benzene, C_6H_6, a 6-carbon ring compound. All other aromatic compounds are derivatives of benzene, e.g. phenylamine (aniline) and phenol. Some derivatives may also contain straight carbon chains as side chains. The following are some examples of aromatic compounds.



(Three representations of the benzene structure.)

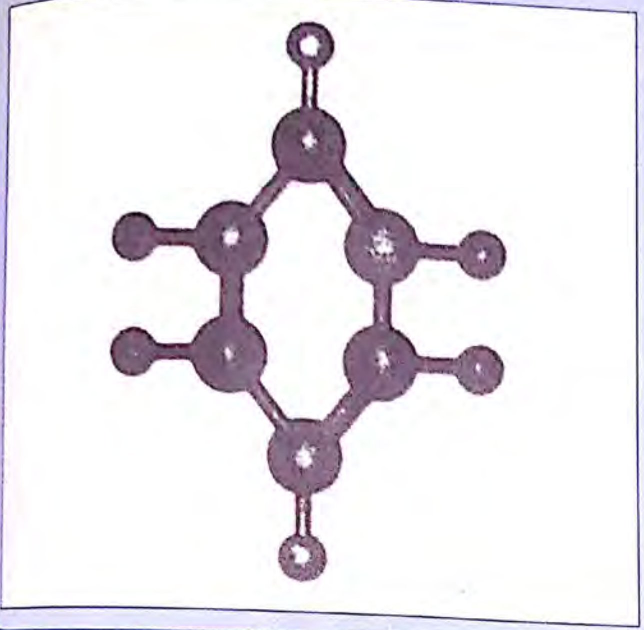


ethylbenzene



2,4-dichloro-benzoic acid

Fig. 29.5 Spatial representation of the molecular structure of benzene.



HYDROCARBONS

Hydrocarbons are among the simplest organic compounds because they are composed only of two elements, namely carbon and hydrogen. All hydrocarbons have the molecular formula of C_xH_y, where x and y are positive whole numbers. Some examples are methane, CH_4, propane, C_3H_8, and benzene, C_6H_6.

Hydrocarbons are classified into two main groups– the aliphatic hydrocarbons and the aromatic hydrocarbons, according to their structure.

Sources of Hydrocarbons

The natural sources of hydrocarbons are coal, natural gas and petroleum. These are often known as fossil fuels because they are

- the remains of plants and animals that died millions of years ago, and
- used mainly as fuels, that is burnt to release heat or other forms of energy.

Coal is a solid fuel, petroleum is a dark viscous liquid fuel and natural gas is a gaseous fuel.

Petroleum

Crude oil or petroleum is the most important source of fuel nowadays. Petroleum is first fractionally distilled. Then the less volatile fractions are subjected to further treatment called *cracking*.

Cracking of petroleum

In the early days, the petroleum fractions in highest demands were the lubricating oils and paraffin wax. Since the invention of the motor car, the demand for the petrol fraction has been increasing.

Generally, for most crude oils, the petrol fraction makes up only 20 to 40% of the distillates, and out of these, only a small portion is suitable for use as a fuel in the engines of motor cars. Due to the high demand for petrol, other less useful fractions such as kerosene and gas oil are converted into petrol by a process called the *cracking* of petroleum. Cracking means breaking down or decomposition of a compound by the action of heat alone. This process involves splitting larger molecules into smaller molecules by subjecting them to high temperatures and pressures, usually in the presence of a catalyst.

In thermal cracking of petroleum, the less volatile crude oil fractions are simply passed through a chamber heated to a very high temperature (above 1000 °C). Long chain alkanes are converted into smaller chain alkanes, alkenes and hydrogen, with ethene, C_2H_4, being the predominant alkene present. Depending on the reaction conditions, cracking can take place at any point along the main carbon skeleton of the alkane to give shorter chain alkanes or alkenes. The cracking of decane is shown.

NOTE The products given are only some of the many possible products formed during the cracking of decane.

Thermal cracking is not particularly efficient because there is poor control over the cracking pattern to yield alkanes of desirable chain length. This is due to the fact that the carbon-to-carbon bonds of the alkanes in the heavy oil fractions are about the same strength.

Nowadays, *catalytic* cracking is the method used for the cracking of petroleum in the presence of a catalyst. Higher boiling-point fractions, particularly gas oil, are brought into contact with a finely divided silica-alumina catalyst at a temperature of 450 °C to 550 °C and under a slight pressure. Catalytic cracking is better because firstly, the process is more controllable, i.e. the conditions can be adjusted such

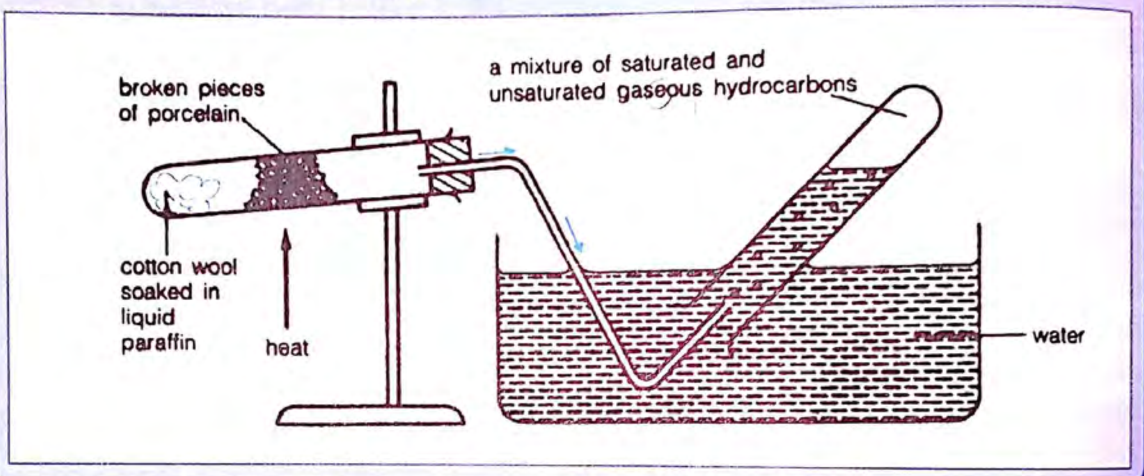
Experiment 29.1 To crack medicinal paraffin.

Theory Medicinal paraffins are obtained from the re-distillation of the heavy oil fraction. They are long-chain hydrocarbons which on cracking yield simpler liquid and gaseous unsaturated hydrocarbons.

Method Soak a wad of cotton wool in some liquid medicinal paraffin in a test-tube and clamp the tube horizontally on a retort stand. Pack some small pieces of porcelain in the middle section of the test-tube as shown. Heat the porcelain strongly with a Bunsen flame. Allow the expanded air to escape, then place an inverted test-tube filled with water over the mouth of the delivery tube. Still keeping the porcelain pieces as hot as possible, occasionally shift the flame to heat the liquid paraffin.

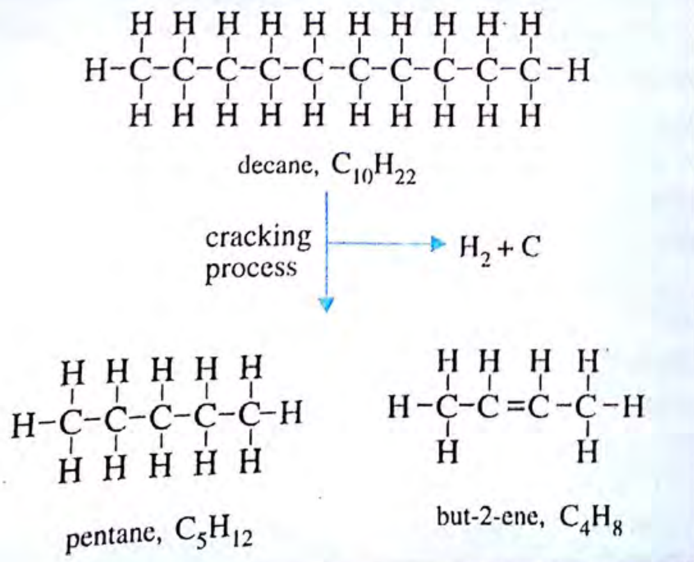
Collect any gas evolved and test it with a lighted wooden splinter. Look for drops of oily sticking to the inside of the delivery tube or floating on the surface of the water in the trough. Collect about 2 cm^3 of these liquid drops. Add a few drops of bromine dissolved in tetrachloromethane to this liquid and shake. (This is a test for unsaturation.) Observe any change in the colour of the bromine solution.

Fig. 29.6 Cracking of medicinal paraffin.



Result On cracking the medicinal paraffin, the gas evolved gives a pop sound with the lighted splinter and the oily liquid decolorizes the bromine solution.

Conclusion The results indicate the presence of hydrogen gas and unsaturated compounds. Thus, it can be inferred that the cracking of a long-chain hydrocarbon compound like medicinal paraffin yields unsaturated compounds, most probably alkenes, and hydrogen.



that desirable products of certain chain lengths are obtained. This process thus yields a source of alkenes which serve as raw materials for a great variety of organic chemicals. Secondly, the process not only yields more petrol but also gives petrol of high quality. In fact, this petrol is a higher grade petrol than the one obtained directly from the petrol fraction during the distillation of crude oil.

Petrochemicals

Petrochemicals are processed products from petroleum. These petrochemicals are often known as *value-added products* because after processing, the market value of the petrochemicals can go up to thirteen times that of the original crude petroleum.

Common petrochemicals include synthesis gas, alkenes and aromatic compounds.

Synthesis gas This is a mixture of gases like hydrogen, carbon(IV) oxide, carbon(II) oxide and impurities like dihydrogen sulphide. It can be used as a source of carbon(IV) oxide, hydrogen, sulphur and tetraoxosulphate(VI) acid. From synthesis gas, we can obtain ammonia, methanol, gasoline, fertilizers, refrigerants, explosives, urea, polymers and petrol additives.

Alkenes These are obtained from the cracking of crude oils. Alkenes such as ethene and propene can be made into poly(ethene), poly(chloroethene), poly(phenylethene), nylon, ethanol, propanone and alkanes. Products like cosmetics, dynamite, synthetic rubber can be made from these petrochemicals.

Aromatic compound From petroleum, we get aromatic compounds like benzene, toluene and xylene. The processed products are synthetic fibres such as nylon, plastic, insecticides, detergents and solvents.

Petroleum and Its Effect on the Nigerian Economy and Environment

Hydrocarbons are very useful substances in our present-day world. They are very important sources of fuels and starting material for many synthetic products like plastics and nylon.

The most important source of hydrocarbons is petroleum, which is much sought after by the developed industrialized countries. If these countries do not have their own source of petroleum, they have to import it.

Nigeria has huge deposits of petroleum. Petroleum was first exported from Nigeria in 1958, when it brought in about eight million naira in foreign exchange. By 1975, petroleum alone accounted for 90% of all export earnings. Till today, petroleum is still the major source of foreign exchange earnings.

With money from petroleum exports, Nigeria built many roads, buildings and set up many public utilities services. The revenue from petroleum is also used for development projects in agriculture and industry.

The extraction, transport and refining of petroleum itself has provided employment for the Nigerians. Once Nigeria sets up a petrochemical industry, it will increase its wealth as well as provide further employment opportunities.

Since fuel is easily available, the number of motor vehicles on the roads of Nigerian cities and towns have increased tremendously. Petroleum products like plastics and synthetic fibres have become part of our daily life. Thus, we see that the petroleum industry has helped to improve our standard of living.

The distribution of the population too has changed with the discovery of petroleum. People have moved from rural areas to areas where employment opportunities, created as a result of petroleum mining and in industries set up using the revenue from petroleum, abound.

Petroleum did not only bring benefits to our society, it also brought along some serious environmental pollution problems. The burning of petrol and diesel oil by motor vehicles, power plants and factories releases a lot of pollutants into the air. For example, for every 1 000 dm^3 of petrol burnt, an average car releases about

- 0.15 kg carbon(II) oxide,
- 0.01 kg nitrogen oxides,
- 0.008 kg unburnt hydrocarbons,
- 0.0005 kg solid particles, and
- 0.0005 kg sulphur(IV) oxide

to the atmosphere. A stationary car that has its engines still running adds much more pollutants than what is given above. Often, lead compounds such as tetraethyl lead are added to petrol to prevent knocking. Burning such petrol releases lead compounds into the atmosphere.

All air pollutants affect the health of people seriously. They cause dizziness, fatigue and lethargy. The solid particles clog and damage the lung tissues. Lead compounds have been shown to cause brain damage in young children. Animals and plants are also adversely affected by air pollutants.

The problem of air pollution is serious in big cities and industrial areas where coal, gas and petroleum are used as energy sources.

Besides air pollution, there is also the problem of oil spills. These occur when there are accidents or blow-up of offshore oil rigs, or when tankers transporting oil leak it into the sea. When oil spills occur, the surrounding coasts are coated with oil. As a result, sea-birds, fish and other marine life may be killed in large numbers. It is very difficult and expensive to clean up oil spills.

Conservation of Petroleum

Petroleum is the most popular fuel at present. More important, it also provides the raw materials for the manufacture of petrochemicals. However, our petroleum reserves are limited. Therefore, we have to conserve our existing petroleum reserves.

We can conserve petroleum by

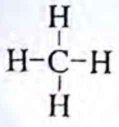
- eliminating wastage at the oil-fields and using it more economically;
- finding other sources of fuel.

Wastage at oil-fields can be got rid of by improving draining methods. The oil fractions should be used as sources of petrochemicals rather than as sources of fuels.

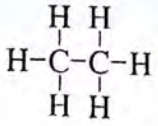
Solar energy and nuclear energy are alternatives to the use of petroleum as fuel. Both can be used to produce electricity and so can replace petroleum in electrical power plants. However, many problems have to be solved and advances in technology have to be made before solar energy and nuclear energy can be used.

ALKANES

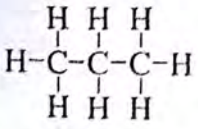
The alkanes are aliphatic hydrocarbons. They form a homologous series of saturated hydrocarbons, which can be represented by the general molecular formula, C_nH_{2n+2}. In each alkane member, all the carbon atoms are tetrahedrally bonded to the hydrogen and other carbon atoms. The structural formulae of the first five members of this series are given.



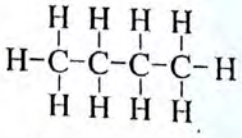
methane, CH_4



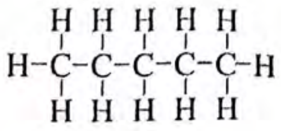
ethane, C_2H_6



propane, C_3H_8

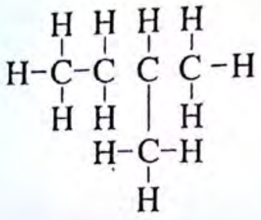


butane, C_4H_{10}



pentane, C_5H_{12}

The general molecular formula, C_nH_{2n+2}, remains unchanged for branched alkanes. For example, pentane, a straight-chained 5-carbon alkane, and 2-methyl butane, a branched 5-carbon alkane, have the same molecular formula, C_5H_{12}.



2-methylbutane
C_5H_{12}

Since all the four valence electrons of each carbon atom in an alkane molecule are used up, the alkanes are very stable compounds.

METHANE

Methane is the simplest compound in the alkane series with the molecular formula of CH_4. Besides being a component of petroleum gas, it is the major constituent of *natural gas* which issues from the ground in great quantities in certain parts of the world. Methane is produced during the decomposition of plant matter in the absence of air. It is given off from swamps and is often known as *marsh gas*. It is also found in poorly ventilated coal mines as the dreaded *fire damp*, which is the main cause of explosions in these mines.

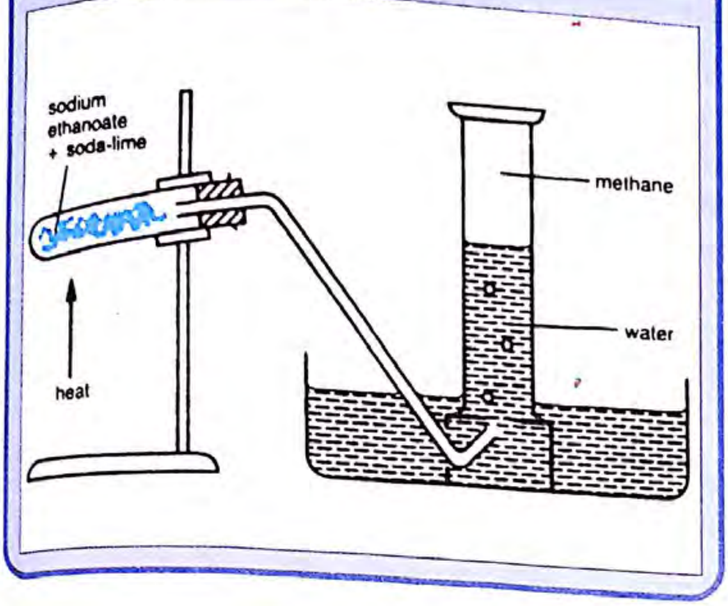
Laboratory Preparation

Methane is usually prepared by heating anhydrous sodium ethanoate with an alkali, usually soda-lime. Soda-lime is quicklime slaked with a concentrated solution of sodium hydroxide. It is used in preference to caustic soda because it is not deliquescent and does not attack glass so readily.

Anhydrous sodium ethanoate is ground with an equal mass of soda-lime and then heated in a hard glass test-tube. Methane is given off and can be collected over water.

CAUTION The delivery tube must be withdrawn from the water immediately after heating is stopped. This is to prevent the sucking back of water into the hot flask.

Fig. 29.7 Preparation of methane.



$$CH_3COONa(s) + \underset{\text{from soda-lime}}{NaOH(s)} \rightarrow Na_2CO_3(s) + CH_4(g)$$

The other alkanes in the series can be similarly prepared by heating an appropriate sodium salt with soda-lime.

Physical Properties

1 Methane is a colourless and odourless gas.
2 It is only slightly soluble in water.
3 It is less dense than air.
4 It has no action on litmus.

Chemical Properties

Combustion

The general equation for combustion of alkanes can be represented as follows:

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \rightarrow \frac{y}{2}\ H_2O(g) + xCO_2(g)$$

Methane, for example, burns in air or oxygen with a pale non-luminous flame to produce steam, carbon(IV) oxide and a lot of heat.

$$CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$$

A mixture of methane and air or oxygen may explode violently when ignited. This is the main cause of explosions in coal-mines.

Chlorination

Methane reacts with chlorine in the presence of ultraviolet light (which acts as a catalyst) to yield a mixture of products. These products are formed by the successive replacement or displacement of the hydrogen atoms in the methane molecule by the chlorine atoms. The hydrogen is not released as free hydrogen but in combination with chlorine as hydrogen chloride.

$$CH_4(g) + Cl_2(g) \rightarrow HCl(g) + \underset{\text{chloromethane}}{CH_3Cl(g)}$$

$$CH_3Cl(g) + Cl_2(g) \rightarrow HCl(g) + \underset{\text{dichloromethane}}{CH_2Cl_2(g)}$$

$$CH_2Cl_2(g) + Cl_2(g) \rightarrow HCl(g) + \underset{\text{trichloromethane}}{CHCl_3(l)}$$

$$CHCl_3(l) + Cl_2(g) \rightarrow HCl(g) + \underset{\text{tetrachloromethane}}{CCl_4(l)}$$

Similar substitution products are formed between methane and gaseous bromine, but the reactions are much slower. Such substitution reactions are characteristic of all saturated compounds.

A substitution reaction involves the direct displacement of an atom or group by another atom or group.

Although methane undergoes substitution reaction rather spontaneously in the presence of light, it is a very inert gas. It does not react at ordinary temperatures and pressures with acids, alkalis or oxidizing agents. Similarly, the other alkanes are also very inert and do not undergo any reactions other than combustion and substitution reactions.

Uses

1 Methane is mainly used as a fuel, either by itself or mixed with other gases.
2 It is used for making hydrogen, carbon black,

carbon(IV) sulphide alkynes, hydrocyanic acid, trichloromethane (chloroform), an anaesthetic used in surgical operations, and tetrachloromethane (carbon tetrachloride), an important organic solvent.

ALKENES

The alkenes are a homologous series of hydrocarbons with a general molecular formula of C_nH_{2n}, where n is a positive whole number which is equal to or greater than 2 (CH_2 does not exist). They contain two hydrogen atoms less than the alkanes. This is because, unlike the alkanes which are saturated compounds, the alkenes are unsaturated compounds which contain a carbon-carbon double bond in their molecular structures.

Ethene, propene, but-1-ene and but-2-ene are colourless gases at ordinary temperatures and pressures, the next thirteen members of the series (i.e. C_5H_{10} to $C_{17}H_{34}$) are liquids, while the higher members are solids.

Alkenes tend to burn with a more luminous and smoky flame than the corresponding alkanes, since they contain a greater percentage of carbon. The availability of electrons in the double bonds also makes them chemically more reactive than the alkanes.

Table 29.6 The IUPAC and common names of some alkenes.

Molecular and structural formulae		IUPAC name	Common name
C_2H_4	$CH_2{=}CH_2$	Ethene	Ethylene
C_3H_6	$CH_2{=}CHCH_3$	Propene	Propylene
C_4H_8	$CH_2{=}CHCH_2CH_3$	But-1-ene	1-Butylene
C_4H_8	$CH_3CH{=}CHCH_3$	But-2-ene	2-Butylene
C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	Pent-1-ene	Pentylene

ETHENE

Ethene is the most important alkene. It is one of the main products obtained during the cracking of the gas oil fraction of petroleum.

$$C_{17}H_{36}(l) \rightarrow C_8H_{18}(g) + 3C_2H_4(g) + C_3H_6(g)$$

Laboratory Preparation

Ethene is prepared by heating ethanol with excess concentrated tetraoxosulphate(VI) acid at 170 °C. The reaction occurs in two stages. On mixing the ethanol and the acid in a volume ratio of 1:2 respectively, the ester, ethyl hydrogentetraoxosulphate(VI), is formed.

$$C_2H_5OH(aq) + H_2SO_4(aq) \rightarrow C_2H_5HSO_4(aq) + H_2O(l)$$

On heating, the ethyl hydrogentetraoxosulphate(VI) decomposes in the presence of excess tetraoxosulphate(VI) acid to produce ethene.

$$C_2H_5HSO_4(aq) \rightarrow C_2H_4(g) + H_2SO_4(aq)$$

The overall reaction can be regarded as a dehydration of ethanol by hot concentrated tetraoxosulphate(VI) acid because the overall change is the removal of one molecule of water from ethanol.

$$C_2H_5OH(aq) \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} C_2H_4(g)$$

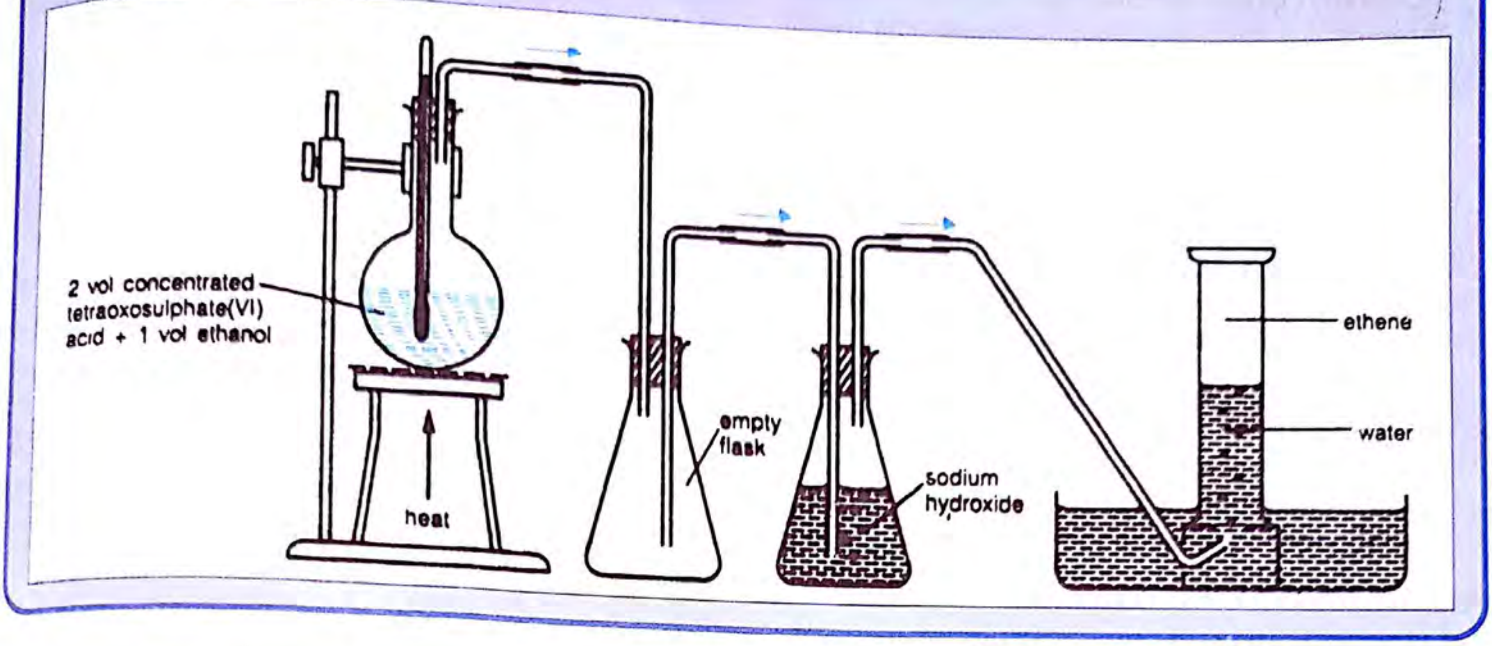
To prepare ethene, add two volumes of concentrated tetraoxosulphate(VI) acid slowly to one volume of ethanol in a flat-bottomed flask and shake gently to mix. Set up the apparatus as shown, heat the mixture gently for a while and then strongly to about 170 °C. Pass the gas evolved through concentrated sodium hydroxide to remove any gaseous impurities, which are mainly carbon(IV) oxide and sulphur(IV) oxide (formed from a certain amount of oxidation by the hot acid) and acid fumes. The almost pure ethene gas is collected over water.

CAUTION To prevent the sodium hydroxide from sucking back into the reaction mixture, insert an empty conical flask between them.

Physical Properties

1 Ethene is a colourless gas with a faint sweetish smell.
2 It is only sparingly soluble in water.
3 It is slightly less dense than air.
4 It has no action on litmus.

Fig. 29.8 Preparation of ethene.



Chemical Properties

Combustion

Ethene burns readily in air or oxygen with a smoky and luminous flame because of its high proportion by mass (about 86%) of carbon. In the process, it oxidizes completely to form water and carbon(IV) oxide.

$$C_2H_4(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g)$$

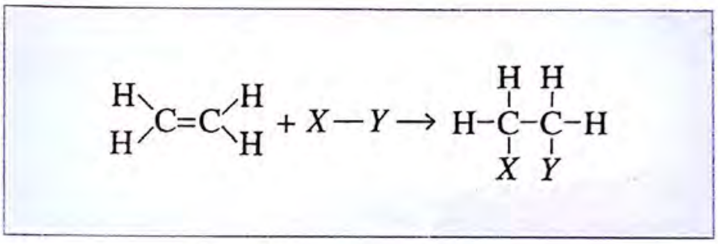
Ethene forms explosive mixtures when mixed with air or oxygen.

Addition reactions

Ethene undergoes addition reactions with hydrogen, halogens, hydrogen halides and many other compounds. Addition reactions are characteristic of all unsaturated compounds. During an addition reaction, two substances,

- an unsaturated compound, and
- an attacking reagent,

combine to form a single new substance without forming any other products. When ethene undergoes addition with a compound *XY*, for example, where both *X* and *Y* are monovalent, the reaction is essentially:



$$\mathrm{H_2C{=}CH_2} + X{-}Y \rightarrow \mathrm{H}-\underset{X}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{Y}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$$

In the process, the double bond in ethene is converted into a single covalent bond due to the addition of two monovalent atoms or radicals.

> *An addition reaction involves the direct addition of an attacking reagent across the double or triple bond of an unsaturated compound to yield a saturated product or at least one in which the degree of saturation is increased.*

With hydrogen If a mixture of hydrogen and ethene is passed over a finely divided nickel, platinum or palladium catalyst, ethane is formed as an addition compound.

$$CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3 \text{ or } C_2H_6(g)$$

This reaction, which is also known as *hydrogenation*, is very important in the hardening of oils.

With the halogens Chlorine and bromine add on to ethene readily at room temperature to form the halogenated products 1,2-dichloroethane and 1,2-dibromoethane respectively.

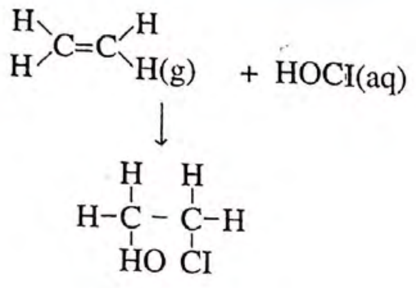
$$CH_2{=}CH_2(g) + Cl_2(g) \rightarrow CH_2ClCH_2Cl \text{ or } C_2H_4Cl_2(l)$$
$$CH_2{=}CH_2(g) + Br_2(l) \rightarrow CH_2BrCH_2Br \text{ or } C_2H_4Br_2(l)$$

Similarly, with iodine solution (iodine dissolved in ethanol), 1,2-diiodoethane is formed at room temperature.

With the hydrogen halides Ethene combines readily with hydrogen iodide vapour at room temperature to form iodoethane. Hydrogen chloride and hydrogen bromide react in a similar manner but more slowly.

$$CH_2{=}CH_2(g) + HI(g) \rightarrow CH_3CH_2I \text{ or } C_2H_5I(l)$$

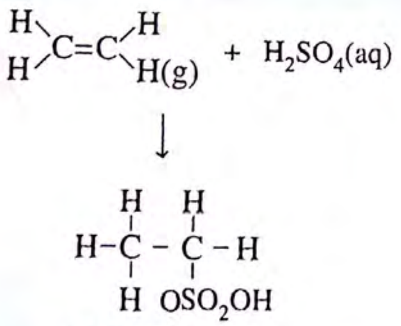
With chlorine and bromine water Chlorine water, which contains oxochlorate(I) acid, HOCl, combines with ethene to give 2-chloroethanol.



or $CH_2OHCH_2Cl(aq)$

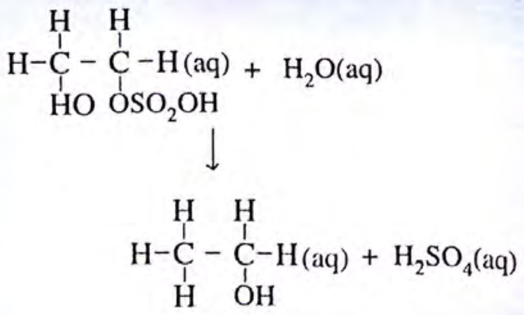
Similarly, bromine water, which contains oxobromate(I) acid, HOBr, reacts with ethene to form 2-bromoethanol.

With tetraoxosulphate(VI) acid The concentrated acid readily absorbs ethene at room temperature to form ethyl hydrogentetraoxosulphate(VI).



or $C_2H_5HSO_4(aq)$

This reaction is important because the product undergoes hydrolysis when boiled with water and yields ethanol. Tetraoxosulphate(VI) acid is also regenerated.



ethanol

With tetraoxomanganate(VII) When bubbled through a dilute solution of potassium tetraoxomanganate(VII), ethene is oxidized rapidly to ethane-1,2-diol (ethylene glycol).

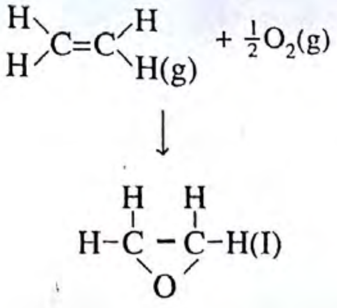
$$CH_2{=}CH_2(g) + \underbrace{H_2O(l) + [O]}_{\text{from tetraoxo-manganate(VII)}} \rightarrow CH_2OHCH_2OH(aq)$$

In the process, the purple potassium tetraoxomanganate(VII) solution is reduced to

- a green solution of potassium tetraoxomanganate(VI) if the solution is alkaline, or
- a colourless solution of a manganese(II) salt if the solution is acidic.

The addition product, ethane-1,2-diol, is an important compound used in anti-freeze mixtures for car radiators and for the making of *Terylene*, an important polyester.

With air or oxygen When ethene is mixed with air or oxygen and passed over a silver catalyst at about 250 °C, epoxyethane (ethylene oxide) is formed.



epoxyethane

Epoxyethane is used in making ethane-1,2-diol and some liquid detergents.

Polymerization

Polymerization is a process whereby two or more simple molecules are linked to form a much larger molecule. Ethene and its derivatives undergo polymerization to form important compounds such as poly(ethene) and poly(chloroethene).

Uses

1 Ethene is the main source of many important organic compounds such as ethane, ethanol, ethanoic acid, epoxyethane, ethane-1,2-diol, tetraethyl lead(IV), and so on.

2 Ethene is the raw material used for making many important plastics such as
   - poly(ethene);
   - poly(chloroethene), also known as *polyvinyl chloride* (PVC), formed by the polymerization of chloroethene or vinyl chloride;
   - poly(phenylethene), also known as *polystyrene,* formed by the polymerization of phenylethene or styrene.

3 Ethene is also used to produce synthetic rubber such as
   - styrene-butadiene rubber (SBR), formed by the polymerization of phenylethene;
   - thiokol, formed by first converting ethene to 1,2-dichloroethane, and then heating it carefully with sodium polysulphide.

4 A derivative of ethene, 1,2-dibromoethene is used as a petrol additive.

5 In agriculture, low concentrations of ethene are used to hasten the ripening of fruits.

ALKYNES

Alkynes are the homologous series of unsaturated hydrocarbons with a general molecular formula of C_nH_{2n-2}, where n is a positive whole number which is equal to or greater than 2. Each alkyne molecule contains four hydrogen atoms less than the corresponding alkane, and two hydrogen atoms less than the corresponding alkene. This is because each alkyne molecule contains a carbon-carbon triple bond ($-C\equiv C-$), where two carbon atoms are bonded to each other by the sharing of three pairs of electrons. Thus, the alkynes show a higher degree of unsaturation than the alkenes; hence, they are chemically more reactive than the corresponding alkanes or alkenes. Their electron-rich triple bonds make the alkynes very prone to addition reactions. The names of all the alkynes end with *-yne.*

Table 29.7 The IUPAC and common names of some alkynes.

Molecular and structural formulae		IUPAC name	Common name
C_2H_2	$CH\equiv CH$	Ethyne	Acetylene
C_3H_4	$CH\equiv CCH_3$	Propyne	Methyl-acetylene
C_4H_6	$CH\equiv CCH_2CH_3$	But-1-yne	Ethyl-acetylene
C_4H_6	$CH_3C\equiv CCH_3$	But-2-yne	Dimethyl-acetylene
C_5H_8	$CH\equiv C(CH_2)_2CH_3$	Pent-1-yne	Propyl-acetylene

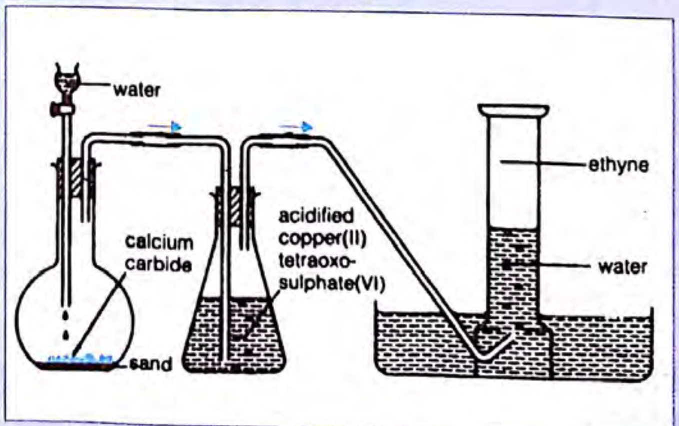
ETHYNE

Ethyne is the first member of the alkyne series. It has a molecular formula, C_2H_2, and a structural formula, $CH\equiv CH$.

Preparation

Ethyne is usually prepared in the laboratory by the action of cold water on calcium carbide. The gas evolved is first passed through an acidified copper(II) tetraoxosulphate(VI) solution to remove any phosphine, PH_3, present as an impurity, and then

Fig. 29.9 Preparation of ethyne



collected over water. The process is accompanied by the release of a large amount of heat. The reaction is performed on a heap of sand inside the flask to prevent the latter from cracking.

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$$

Physical Properties

1 Ethyne is a colourless gas with a characteristic sweet smell when pure.
2 It is only sparingly soluble in water.
3 It is slightly less dense than air.
4 It is unstable and may explode on compression to a liquid. For storage purposes, it is usually dissolved in propanone (acetone) and kept in steel cylinders at about 12 atmospheres pressure.

Chemical Properties

Combustion

Ethyne burns in air to give a very smoky and luminous flame, owing to its high carbon content (about 92% by mass). A mixture of ethyne with air or oxygen may explode violently on ignition. In pure oxygen, ethyne undergoes complete combustion and burns with a non-luminous, very hot flame of about 3 000 °C. This flame is made use of in the oxy-ethyne (oxyacetylene) torch which is used in welding and cutting metal scraps.

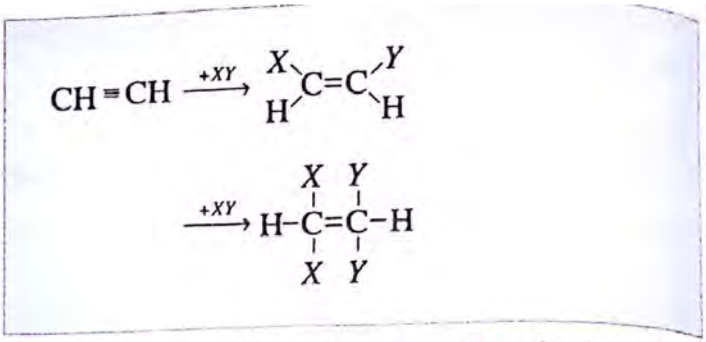
$$2C_2H_2(g) + 5O_2(g) \rightarrow 2H_2O(g) + 4CO_2(g)$$

Additional reactions

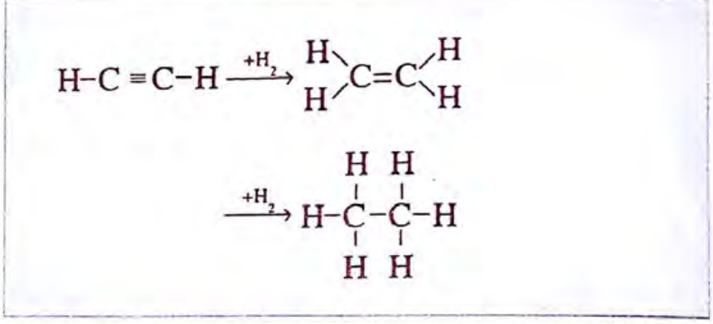
Ethyne is highly unsaturated, containing a carbon-carbon triple bond in its structure. It can readily form addition products, combining with a maximum of four univalent atoms or radicals per molecule. These reactions take place in two stages:

- the first stage yields a product with a carbon-carbon double bond;
- the second stage converts this into a fully saturated compound with only carbon-carbon single bonds.

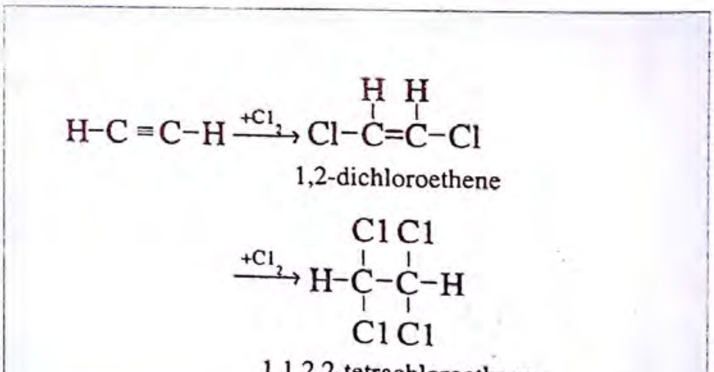
NOTE X and Y are univalent atoms or groups. Both the X atoms or groups are usually attached to the same carbon atom, as are the two Y atoms or groups.



With hydrogen Ethyne reacts with twice its volume of hydrogen in the presence of a nickel catalyst at about 200 °C to form first ethene, and then ethane by successive additions of hydrogen atoms across the carbon-carbon triple bond.



With the halogens Ethyne reacts with chlorine and bromine in the presence of a metallic halide catalyst at room temperature to yield halogenated compounds.



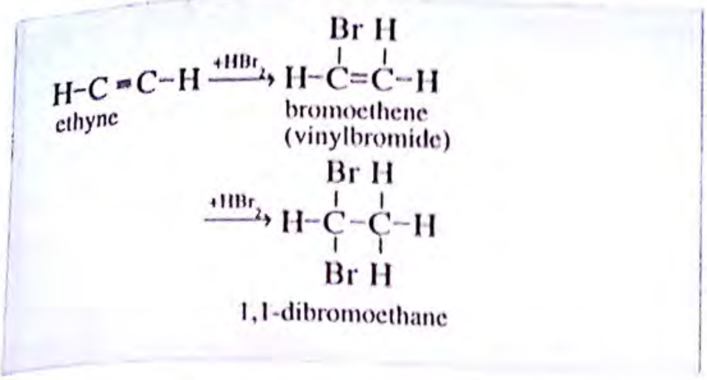
1,2-dichloroethene

1,1,2,2-tetrachloroethane

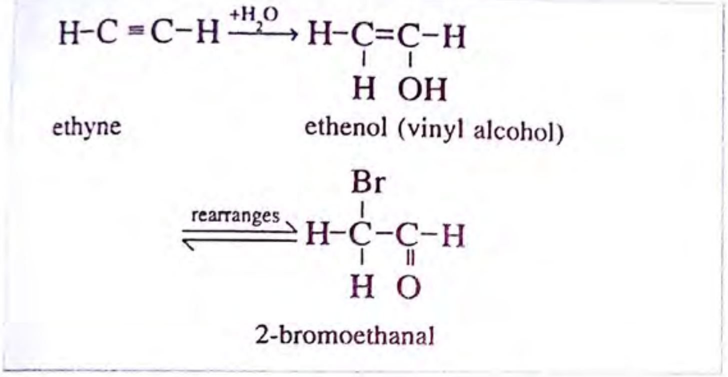
In the case of chlorine, the reaction is very different if pure ethyne and chlorine are used in the absence of a catalyst. Instead of an addition compound, carbon and hydrogen chloride will be formed with a violent explosion.

$$C_2H_2(g) + Cl_2(g) \rightarrow 2C(s) + 2HCl(g)$$

With hydrogen halides Ethyne combines readily with hydrogen iodide at room temperature, and with hydrogen bromide at 100 °C. The reaction with hydrogen chloride, however, is very slow.



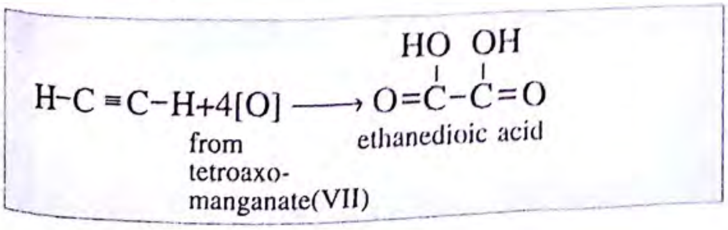
With water If ethyne is passed through dilute tetraoxosulphate(VI) acid, at about 60 °C, with mercury(II) tetraoxosulphate(VI) as a catalyst, addition of water takes place as shown forming ethanal.



Ethenol and ethanal are isomers. Ethenol is too unstable to be isolated, but exists in dynamic equilibrium with ethanal, with the equilibrium very much towards the formation of ethanal.

This reaction is of considerable industrial importance because it is the first stage in the formation of ethanoic acid.

With tetraoxomanganate(VII) Like ethene, ethyne rapidly decolorizes an acidified potassium tetraoxomanganate(VII) solution while it turns an alkaline solution green at room temperature. In the process, ethyne is converted into ethanedioic acid (oxalic acid).



Substitution reactions

If ethyne is passed through ammoniacal solutions of copper(I) chloride and silver trioxonitrate(V) at room temperature, precipitates of *copper(I) dicarbide* (reddish-brown) and *silver dicarbide* (*whitish-yellow*) will be formed respectively.

$$C_2H_2(g) + 2CuCl(aq) \rightarrow Cu_2C_2(s) + 2HCl(aq)$$
$$C_2H_2(g) + 2AgNO_3(aq) \rightarrow Ag_2C_2(s) + 2HNO_3(aq)$$

Both the dicarbides are explosive when dry and both give ethyne if warmed with a dilute acid. These reactions are important because they distinguish ethyne from ethene, which does not form these metallic derivatives. All alkynes with a triple bond at the end of their carbon chain (RH≡CH) undergo similar substitution reactions.

$$Cu_2C_2(s) + H_2SO_4(aq) \rightarrow Cu_2SO_4(aq) + C_2H_2(g)$$

Polymerization

Ethyne polymerizes to form the aromatic hydrocarbon, benzene, when it is passed through a hot tube containing a complex organo-nickel catalyst.

$$3C_2H_2(g) \rightarrow C_6H_6(l)$$

Test for unsaturation

Unsaturated compounds are best recognized by their addition reactions. The most convenient test is the reaction with bromine or bromine water (reddish-brown) since these reagents become colourless on reacting with unsaturated compounds. A purple solution of potassium tetraoxomanganate(VII) also becomes colourless when added to unsaturated compounds, but this is not by itself a distinctive test since reducing agents too bring about the same result.

Uses

1 Ethyne is sometimes used as fuel in lamps such as miners' lamps. The ethyne lamp can be very bright if there is a sufficient supply of air.
2 Ethyne is mixed with oxygen to produce a very hot and easily controllable flame, known as the oxy-ethyne flame, which is used for cutting and welding metals.
3 Ethyne is a source of ethanal and the solvents, 1,1,2-trichloroethene and 1,1,2,2-tetrachloroethene, which are extensively used in industry and in dry cleaning for dissolving grease.
4 Polymerization of ethyne and its derivatives leads

Table 29.8 Comparison of alkanes, alkenes and alkynes.

Feature	Alkane	Alkene	Alkyne
General formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
Degree of saturation	Saturated	Unsaturated	Highly unsaturated
Carbon to hydrogen ratio	Low	Intermediate	High
Combustion, using lighted splint for gas and strong heating for solids or liquids	Blue flame (least smoky)	Yellow luminous flame(smoky)	Smocky flame due to high carbon: hydrogen ratio
Common reactions	Substitution reactions	Addition reactions	Addition reactions (more reactive than alkenes
Reaction with bromine solution in the dark	None (alkanes do not undergo substitution reaction in the dark)	Decolorizes bromine solution	Decolorizes bromine solution
Reaction with cold, acidified potassium tetraoxomanganate(VII)	No reaction	Decolorizes the solution	Decolorizes the solution
Reaction with silver trioxonitrate(V)	No reaction	No reaction	Terminal alkynes form a white precipitate

NOTE The reaction with silver trioxonitrate(V) dissolved in alcohol my be used to distinguish alkenes from alkynes. Only a terminal alkyne gives a precipitate with silver trioxonitrate(V).

to the synthesis of products such as

- poly(chloroethene), a plastic,
- poly (propenonitrile), a synthetic fibre, and
- neoprene, an artificial rubber

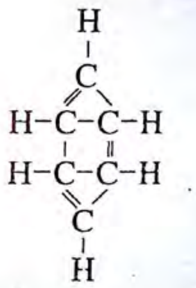
AROMATIC HYDROCARBONS - BENZENE

Aromatic compounds are benzene and compounds that resemble benzene in chemical behaviour. Thus, it is important to understand the structure, the properties and the uses of benzene.

Benzene is obtained from the destructive distillation of coal. It is also produced from naphtha which is obtained from one of the light petroleum fractions.

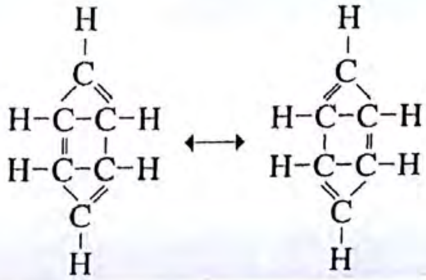
Structure

The compound benzene has been known since 1825. Its structure remained a mystery until 1865 when August Kekulé proposed his structure for benzene. He suggested that since the molecular formula of benzene obtained from quantitative analysis and relative molecular mass determination was found to be C_6H_6, the most logical structure would be for the six carbon atoms to form a ring as represented below.



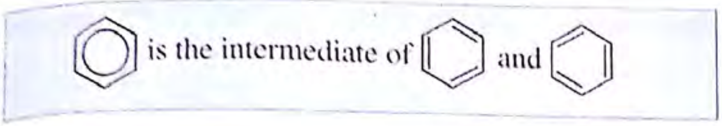
Formula for benzene, proposed by Kekulé.

According to Kekulé there should be three alternate carbon-carbon double bonds in the ring. However, from bond length studies, all the carbon-carbon bonds in benzene are found to be equal and intermediate in length, between those of single and double bonds, i.e. the carbon-carbon bonds in benzene are not really single or double bonds.



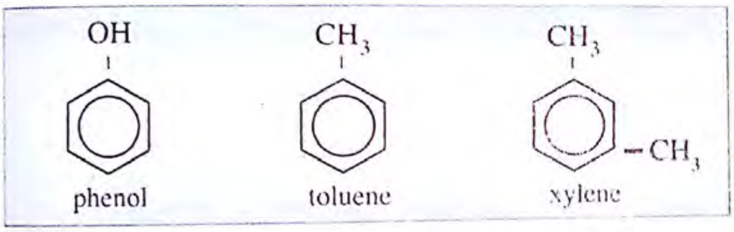
In 1945, the concept of resonance was used to explain the structure of benzene. Resonance occurs when two equivalent forms of a compound are in equilibrium.

The real structure of benzene is represented as a hexagon with a ring in it, indicating that the double bonds are shifting at all times. The ring also shows that the six electrons involved in the double bonds are moving around the six carbon atoms in benzene.



NOTE It is conventional to represent the six carbon atoms in benzene by the six corners of a hexagon and the six hydrogen atoms are implied.

Benzene-type compounds Some common aromatic compounds are phenol, toluene and xylene. These compounds are obtained by substituting the hydrogen atoms in the benzene ring with the appropriate atom(s) or group(s).



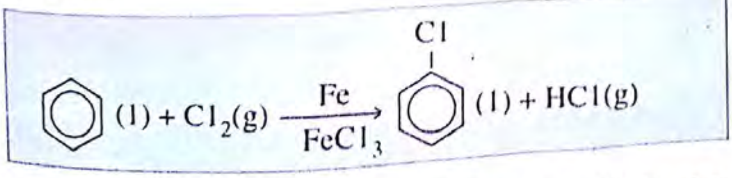
phenol toluene xylene

Physical Properties

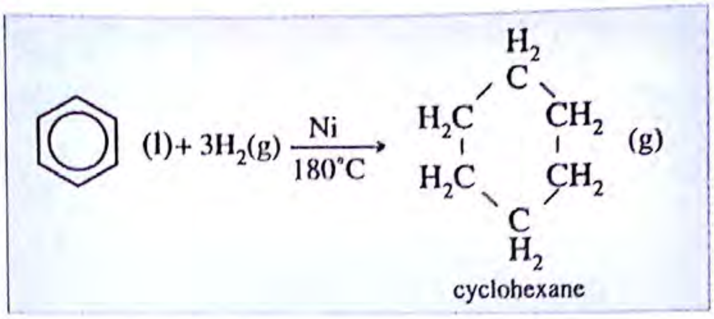
1. Benzene is a colourless liquid with a sweet smell.
2. It is insoluble in water.
3. It has a boiling point of 80 °C.

Chemical Properties

Benzene undergoes substitution reactions, e.g. chlorobenzene is formed when benzene reacts with chlorine.



Benzene also undergoes addition reactions, e.g. cyclohexane is formed when a mixture of benzene vapour and hydrogen are passed over a nickel catalyst at 180 °C.



cyclohexane

Uses

Benzene can be converted to styrene which is used in the manufacture of synthetic fibres like nylon.

Benzene is an important source of phenols, aniline and chemicals which are used as pesticides and detergents.

Many derivatives of benzene are useful. Toluene is used in making explosives. Phenol is used as a disinfectant and as a raw material for making plastics. Aniline and aniline-type compounds are used for making dyes and drugs.

ALKANOLS

Aliphatic alkanols are compounds in which hydroxyl groups are linked to alkyl groups. They can be considered as being derived from the corresponding alkanes by replacing the hydrogen atoms with hydroxyl groups. The hydroxyl group is the functional group of the alkanols as it is responsible for their characteristic chemical properties.

Most common aliphatic alkanols contain only one hydroxyl group in each molecule. They are referred to as *monohydric alkanols.* The monohydric alkanols form a homologous series with the general molecular formula $C_nH_{2n+1}OH$ (or $CnH_{2n+2}O$). Since the group C_nH_{2n+1} is the alkyl group and can be represented generally by R, the general formula of the monohydric alkanols can also be written as ROH. The name of each homologue is derived by dropping the end -e of the corresponding alkane and replacing it with *-ol.*

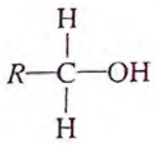
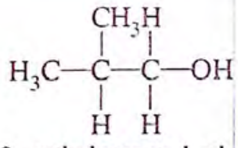
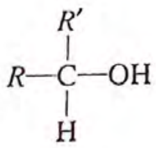
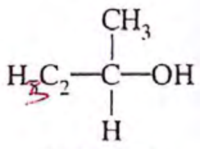
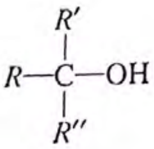
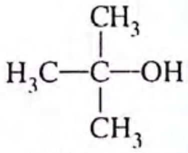
The simplest member of the series is methanol, CH_3OH, sometimes known as *wood spirit,* because it was produced by the destructive distillation of wood in the early days. It is poisonous and can cause blindness if it is consumed. Ethanol, C_2H_5OH, is the second member of the series and by far the most important. In fact it is often referred to simply as alcohol.

Table 29.9 *The IUPAC and common names of the first few members of the alkanol series.*

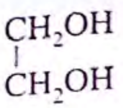
Molecular formula	Structural formula	IUPAC name	Common name
CH_4O	CH_3OH	Methanol	Methyl alcohol
C_2H_6O	CH_3CH_2OH	Ethanol	Ethyl alcohol
C_3H_8O	$CH_3(CH_2)_2OH$	Propan-1-ol	*n*-Propyl alcohol
C_3H_8O	$CH_3CHOHCH_3$	Propan-2-ol	*iso*-Propyl alcohol
$C_4H_{10}O$	$CH_3(CH_2)_3OH$	Butan-1-ol	*n*-Butyl alcohol

There are three types of alkanols--*primary, secondary* and *tertiary.* A primary alkanol has only one alkyl group attached to the carbon atom that carries the hydroxyl group, a secondary alkanol has two and a tertiary alkanol has three.

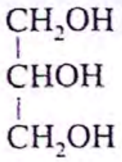
Table 29.10 *Primary, secondary and tertiary alkanols.*

General name	General structure	Example
Primary alkanol		 2-methylpropan-1-ol
Secondary alkanol		 butan-2-ol
Tertiary alkanol		 2-methylpropan-2-ol

Some alkanols contain more than one hydroxyl group per molecule. They are known as *polyhydric alkanols.* Two important examples are ethane-1,2-diol (ethylene glycol) which is a *dihydric alkanol,* and propane-1,2,3-triol (glycerol) which is a *trihydric alkanol.*



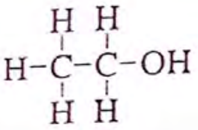
ethane-1,2-diol



propane-1,2,3-triol

ETHANOL

Ethanol has the molecular formula C_2H_5OH and the following structure.



It is a very important compound because it has more uses than almost any other organic compound. It is the essential ingredient in alcoholic drinks and is well-known for its intoxicating effect on consumers.

Preparation

Ethanol can be prepared in the laboratory by several methods, e.g.

- hydrolyzing iodoethane with an alkali;
- hydrolyzing ethyl esters with a hot alkali;
- reducing ethanal with nascent hydrogen.

Commercially, ethanol is usually prepared

- from ethene; and
- by fermentation.

Preparation from ethene

Ethene is obtained in large quantities by the cracking of petroleum. It is first absorbed in 95% tetraoxosulphate(VI) acid at 80 °C and 30 atm to form ethyl hydrogentetraoxosulphate(VI). This is then hydrolyzed by boiling with water.

$$C_2H_4(g) + H_2SO_4(aq) \rightarrow C_2H_5HSO_4(aq)$$

$$C_2H_5HSO_4(aq) + H_2O(l) \rightarrow C_2H_5OH(aq) + H_2SO_4(aq)$$

The ethanol formed is distilled off, leaving the acid which can be concentrated and used again.

In a more recent process, ethene is hydrated directly by passing a mixture of ethene and steam over tetraoxophosphate(V) acid, the catalyst, at 500 to 600 °C and 80 to 100 atm. Most of the ethanol required for industrial use is prepared from ethene by this process.

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$$

Preparation by fermentation

Ethanol has been prepared for thousands of years, by fermentation from raw materials that contain starch and sugar.

> *Fermentation is the slow decomposition by micro-organisms of large organic molecules (such as starch) into smaller molecules (such as ethanol).*

A common micro-organism that is used in fermentation is yeast. It contains a variety of enzymes that bring about the decomposition of starches and sugars to ethanol.

From starchy foodstuff Starchy foodstuff like potatoes and cereals (e.g. rice, maize, guinea corn, millet and barley) are the main source of ethanol in many countries. The starch granules are first extracted by crushing and pressure-cooking the material. They are then treated with malt at 50 to 60 °C for an hour. Malt is partially germinated barley, which contains the enzyme *diastase*. The starch is converted by this enzyme into maltose.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_n(s)} + nH_2O(l) \xrightarrow{\text{diastase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}(aq)}$$

Yeast is then added at room temperature. Yeast contains two enzymes, namely maltase which converts the maltose to glucose, and zymase which then decomposes the glucose into ethanol and carbon(IV) oxide.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2C_6H_{12}O_6(aq)}$$

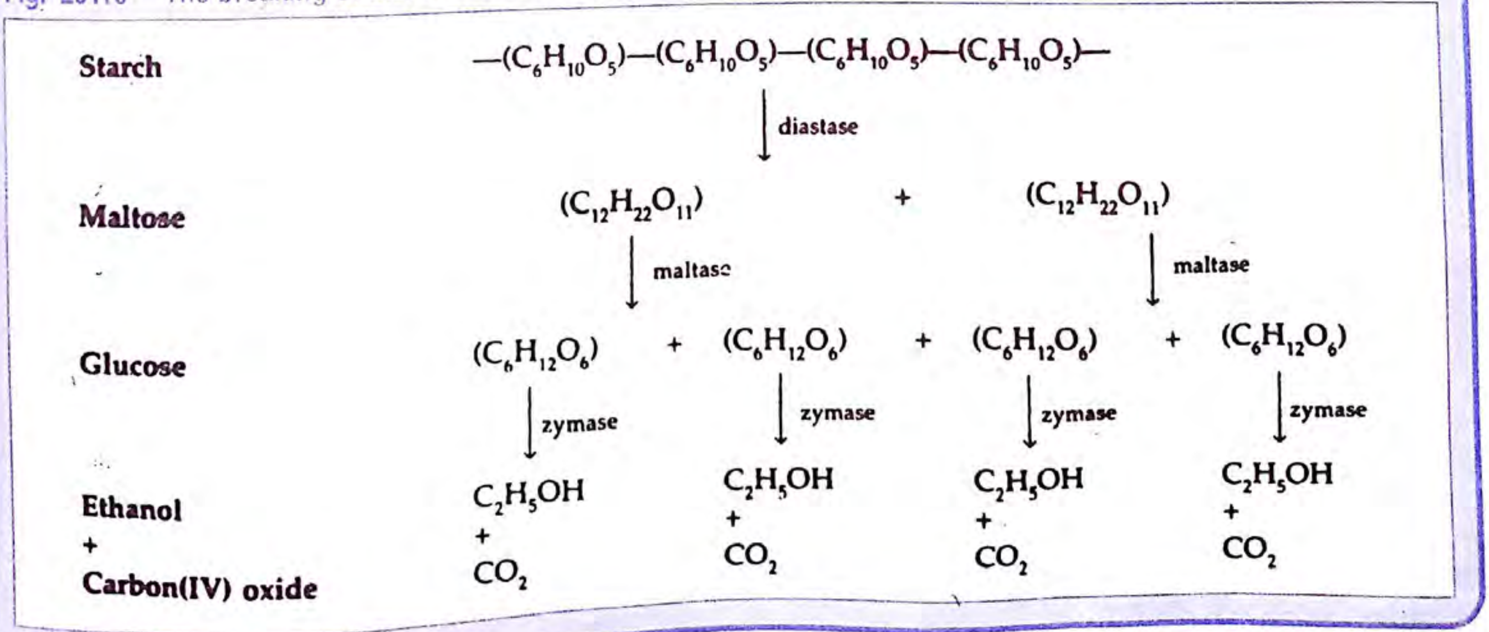
$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

From molasses In countries like the United States and the United Kingdom, the main raw material used is molasses, a syrupy liquid that remains after the crystallization of sugar. It contains sucrose, a type of sugar. The enzyme invertase in yeast acts upon sucrose and converts it to two simple isomeric sugars, glucose and fructose, which are both fermented into ethanol by zymase.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$$

From other sources Other sources of ethanol are fruits (especially grapes, plantains, pineapples and

Fig. 29.10 The breaking of starch molecules into ethanol and carbon(IV) oxide.



apples), sugar cane and honey. In some parts of Africa, the local gin is obtained by fermenting fresh palm wine which is reasonably rich in sugar.

Concentration of ethanol

The ethanol obtained from fermencation only has a maximum concentration of 18% as yeast cells die above this concentration. Further concentration and purification is done by fractional distillation.

The various alcoholic drinks contain different concentrations of ethanol. Their flavour too varies according to the raw material used.

The ethanol which is generally sold contains 95% ethanol. It is called *rectified spirit*. Further purification of rectified spirit by distilling over quicklime results in *absolute ethanol* which contains 99.5% ethanol. It is very hygroscopic and must be kept away from atmospheric moisture if it is to remain anhydrous.

Physical Properties

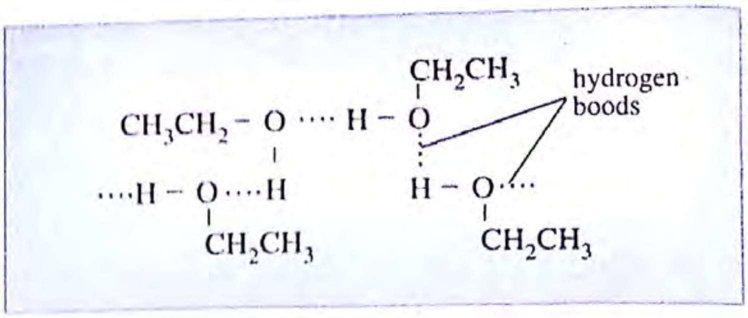
1 Ethanol is a colourless, volatile liquid with a characteristic taste and smell.
2 It is readily soluble in water in all proportions (due to the presence of the hydroxyl group).
3 It has a boiling point of 78 °C.
4 It has no action on litmus.

Table 29.11 Types of alcoholic drinks.

Raw material	Alcoholic drink	Ethanol (% by volume)	Method of preparation
Barley	Beer	3–8	Fermentation alone
Grapes/ Rice	Wines	8–18	
Barley	Whisky	30–60	Fermentation and distillation
Grapes	Brandy		

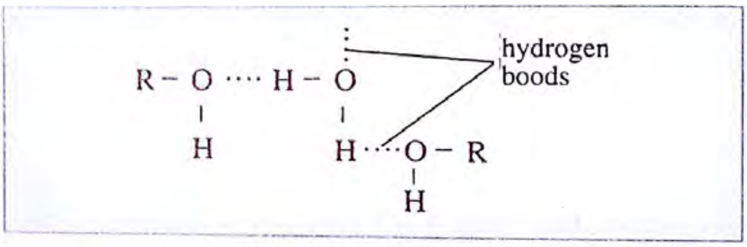
Note Methanol is very similar to ethanol in physical properties although it has a lower boiling point of 67 °C.

The physical properties, especially the boiling point and solubility, of alkanols are affected by the presence of hydrogen bonding in alkanols. The hydroxyl group is capable of bonding to other alkanol molecules. The hydrogen bonding between molecules of ethanol is shown below.



On comparing the boiling point of n-pentane (36 °C) with that of butan-1-ol (118 °C), we see that the boiling point of the alkanol is much higher even though the two compounds are of similar relative molecular mass. This is due to the presence of hydrogen bonds in butanol. Although hydrogen bonds are not strong, much energy is still required to break them before the butan-l-ol molecules can escape as vapour.

Generally, hydrocarbons are not soluble in water, but alkanols are soluble because the hydroxyl groups in their molecules can form hydrogen bondings with the water molecules.



Solubility decreases as the number of carbon atoms increases in alkanols. Primary alkanols with more than five carbon atoms are insoluble in water.

Chemical Properties

Combustion

Ethanol readily burns in air or oxygen with a pale-blue flame, yielding water and carbon(IV) oxide.

$$C_2H_5OH(aq) + 3O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$$

Reaction with sodium and potassium

If a small piece of metallic sodium is added to some ethanol at room temperature, hydrogen will be liberated. (Compare this with the action of sodium on cold water.)

$$\underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2Na(s) \rightarrow \underset{\text{sodium ethoxide}}{2C_2H_5ONa(aq)} + H_2(g)$$

$$\underset{\text{cold water}}{2H_2O(l)} + 2Na(s) \rightarrow \underset{\text{sodium hydroxide}}{2NaOH(aq)} + H_2(g)$$

On evaporating the solution, a white deliquescent solid, known as sodium ethoxide, is left behind. Sodium ethoxide is rapidly hydrolyzed by cold water, giving an alkaline solution.

$$C_2H_5ONa(s) + H_2O(l) \rightarrow C_2H_5OH(aq) + NaOH(aq)$$

Metallic potassium also reacts with ethanol in the same way as sodium. These reactions are characteristic of the hydroxyl group. Other alkanols in the series also show corresponding reactions.

Reactions with the chlorides of phosphorus

Ethanol reacts vigorously with phosphorus(V) chloride in the cold, liberating steamy fumes of hydrogen chloride and chloroethane vapour.

$$C_2H_5OH(aq) + PCl_5(l) \rightleftharpoons C_2H_5Cl(g) + POCl_3(l) + HCl(g)$$

Phosphorus(III) chloride gives a similar but less vigorous reaction.

$$3C_2H_5OH(aq) + PCl_3(l) \rightarrow 3C_2H_5Cl(g) + H_3PO_3(aq)$$

Oxidation

Ethanol is readily oxidized to ethanal by warming with potassium heptaoxodichromate(VI) solution which has been acidified with dilute tetraoxosulphate(VI) acid. Ethanal is given off as a pungent vapour, leaving behind a green liquid.

$$C_2H_5OH(aq) \xrightarrow[\text{from potassium heptaoxodichromate(VI)}]{[O]} CH_3CHO(g) + H_2O(l)$$

On further oxidation in the presence of excess tetraoxosulphate(VI) acid, the ethanal is converted to ethanoic acid.

$$CH_3CHO(g) \xrightarrow[\text{from potassium heptaoxodichromate(VI)}]{[O]} CH_3COOH(aq)$$

These oxidations can also be brought about catalytically by passing the ethanol vapour over finely divided copper at 300 °C, and the ethanal vapour over manganese(II) ethanoate respectively.

NOTE Wine sometimes becomes sour on prolonged exposure to air because of the bacterial oxidation of ethanol to ethanoic acid.

Generally, primary alkanols are oxidized to alkanals and carboxylic acids, and secondary alkanols to alkanones, while tertiary alkanols are not oxidized.

Esterification

Ethanol reacts reversibly with acids forming ethyl esters. This process is known as *esterification.*

$$\text{alkanol} + \text{acid} \rightleftharpoons \text{ester} + \text{water}$$

For example, ethanol and ethanoic acid react to give ethyl ethanoate.

$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} + C_2H_5OH(aq) \rightleftharpoons \underset{\text{ethyl ethanoate}}{CH_3COOC_2H_5(l)} + H_2O(l)$$

Dehydration

In the presence of excess concentrated tetraoxosulphate(VI) acid at a temperature above 170 °C, ethanol reacts to form ethyl hydrogentetraoxosulphate(VI), $C_2H_5HSO_4$, which then decomposes to yield ethene.

(1) $C_2H_5OH(aq) + H_2SO_4(aq) \rightarrow C_2H_5HSO_4(aq) + H_2O(l)$

(2) $C_2H_5HSO_4(aq) \rightarrow \underset{\text{ethene}}{C_2H_4(g)} + H_2SO_4(aq)$

On the other hand, if the alkanol is in excess, and the temperature is lower, it will react with the acid to yield ethoxyethane (diethyl ether).

(1) $C_2H_5OH(aq) + H_2SO_4(aq) \rightarrow C_2H_5HSO_4(aq) + H_2O(l)$

(2) $C_2H_5HSO_4(aq) + C_2H_5OH(aq) \rightarrow \underset{\text{ethoxyethane}}{C_2H_5OC_2H_5(g)} + H_2SO_4(aq)$

The formation of ethene and ethoxyethane from ethanol can be considered as dehydration reactions because the overall reactions are the loss of one molecule of water from one molecule and two molecules of ethanol respectively.

$$C_2H_5OH \xrightarrow{-H_2O} C_2H_4$$

$$2C_2H_5OH \xrightarrow{-H_2O} C_2H_5OC_2H_5$$

Uses

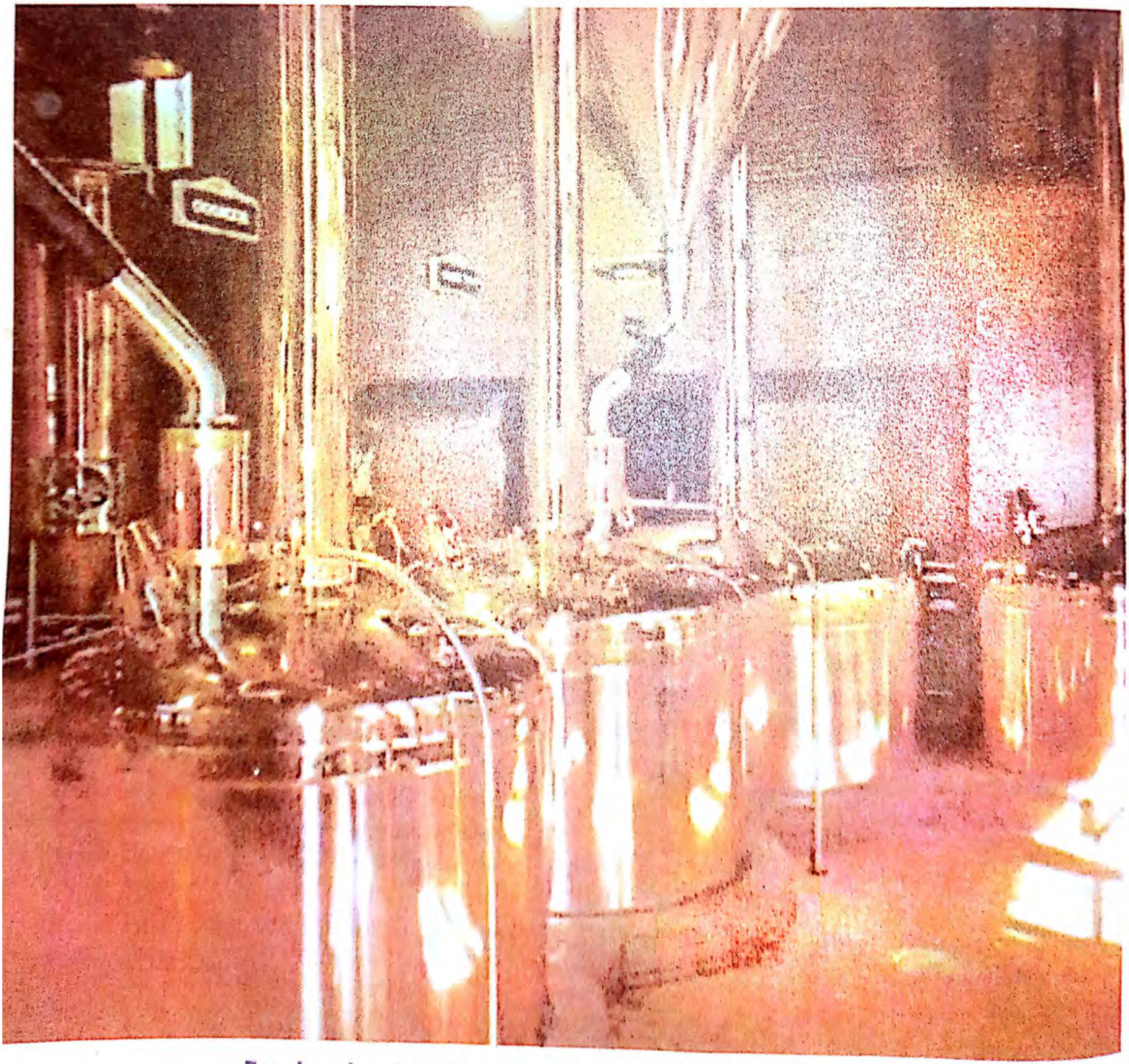
1 Ethanol is an important solvent used to dissolve resins, varnishes, lacquer, soaps, perfumes, dyes, drugs and flavouring extracts.

2 It is the raw material used in the manufacture of many important compounds, e.g. ethanal, ethyl ester, halides, ethoxyethane and trichloroethanal (chloral).

3 It is used as a fuel, either by itself or mixed with petrol, in racing cars and in rockets.

4 Because of its low freezing point (−117 °C), ethanol is sometimes used as an anti-freeze in automobile radiators.

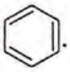
5 Ethanol is present in many alcoholic beverages such as beers, wines and spirits (e.g. whisky, gin, brandy, rum, etc.).



Beer brewing plant-ethanol is an important ingredient in beer.

SUMMARY

- Organic chemistry is the chemistry of carbon compounds. Other than the main element, carbon, organic compounds may contain hydrogen, oxygen and sometimes nitrogen, halogens, phosphorus and sulphur. Organic compounds are covalent in nature.
- A homologous series is a family of organic compounds with a regular structural pattern, in which each successive member differs in its molecular formula by a $-CH_2-$ group.
- A functional group is an atom, a radical or a bond common to a homologous series. This functional group determines the main chemical properties of the series.
- Isomerism is the existence of two or more compounds with the same molecular formula but different molecular structures. Isomers could arise from
  - (a) branching,
  - (b) existence as members of different homologous series, and
  - (c) positioning of carbon-carbon multiple bonds.
- Organic compounds can be classed into aliphatic acyclic compounds, aliphatic cyclic compounds and aromatic compounds.
- The natural sources of hydrocarbons are coal, natural gas and petroleum. Hydrocarbons are used as fuels and starting materials for many synthetic petrochemicals. However, the use of hydrocarbons causes serious environmental pollution problems.
- Alkanes are saturated hydrocarbons with the molecular formula (C_nH_{2n+2}). Alkanes with one to four carbon atoms are gases while the others are liquids and soft solids. Alkanes are only slightly soluble in water and are neutral. They undergo combustion and substitution reactions.
- Alkenes are unsaturated hydrocarbons with the molecular formula C_nH_{2n}. Combustion of alkenes give a more smoky flame compared to combustion of alkanes. This is due to the higher carbon-to hydrogen ratios of alkenes. Due to the existence of double bonds, alkenes can undergo addition reactions.
- Alkynes are unsaturated hydrocarbons with the molecular formula C_nH_{2n-2}. They have a higher degree of unsaturation than alkenes. The triple bonds in their structure allow for addition reactions.
- The most well-known aromatic compound is benzene, C_6H_6. The structure of benzene is best represented as

   which is an intermediate of  and .

- (a) Alkanols are represented by the molecular formula $C_nH_{2n+1}OH$. The three classes of alkanols are the primary, secondary and tertiary alkanols.
  (b) Ethanol, the most important alkanol, can be prepared from ethene and by fermentation.
  (c) The physical and chemical properties of alkanols are governed by the existence of the –OH functional group. Alkanols have higher boiling and melting points due to hydrogen bondings. Alkanols can undergo oxidation, esterification and dehydration.

EXERCISES

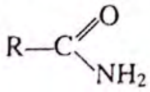
1. Exceptional large number of carbon compounds is essentially due to the ability of
- A carbon to catenate liberally.
- B various groups to catenate.
- C nitrogen, hydrogen, phosphorus and the halogens to catenate with themselves.
- D hydrocarbons to dominate other groups.

2. The name of $C(CH_3)_4$ is
- A butane.
- B tetramethyl butane.
- C methyl propane.
- D 2-methyl propane.

3. The following are general characteristics of carbon except
- A covalent nature and non-polar.
- B low melting and low boiling points.
- C low reactivity with other elements except oxygen and the halogens.
- D hydrogen bond in petrol.

4. Functional groups in organic compounds
- A determine the chemical properties of the homologous series
- B does not modify the other when they are more than one in a molecule.
- C have a general formula which may include the functional group.
- D are responsible for the physical properties.

5. Homologous series with the general formula



is

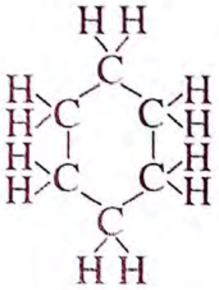
- A an amine.
- B amino acids.
- C oxy-amines.
- D amides.

6. The name of $CH_3(CH_2)_2CONH_2$ is
- A methyl amine.
- B butyl amine.
- C butyl amide.
- D urea.

7. The name of $ClCH_2–CH_2–CH_2OH$ is
- A 1 chloropropan-3-ol
- B 3 chloropropan-1-ol
- C 1-chloropropanol
- D 3 chloropropanol

8. Two or more other compounds obtained from C_2H_6O by making adjustments in their molecule is
- A allotropy.
- B tantamerism.
- C mirror isomerism.
- D structural isomerism.

9. The name of



is

- A benzene.
- B hexane.
- C cyclo hexane.
- D hydro benzene.

10. The main natural sources of hydrocarbons are from fossil fuels and these include except one
- A natural gas.
- B coke.
- C coal.
- D petroleum.

11. Petroleum provides usefully
- A fuels only.
- B fuels and money.
- C fuels and pollutants.
- D fuels and petrochemical raw materials.

12. Funtional group for the alkanols is
- A CnH_{2n} + 1.OH
- B $CnH_{2n} - 2$
- C carboxylic group.
- D hydroxyl group.

13. Alkenes and alkynes react the same except with
- A ammonical $AgNO_3$ solution.
- B oxygen.
- C bromine water.
- D acidified $KMnO_4$ solution.

14. Primary alkanols are oxidized to carboxylic acids, secondary alkanols are oxidized to alkanones while tertiary alkanols are

A oxidized to alkanals.
B oxidized to mixture of alkanones.
C oxidized to alkoxides.
D not oxidized.

15. Which of these compounds exhibits resonance?

A Ethanol
B Ethane
C Benzene
D Butyne
E Propylene

16. The solubility of alkanols in water is due to

A their covalent nature.
B hydrogen bonding.
C their low boiling points.
D their low freezing points.
E their ionic character.

17. Which of these is an aromatic hydrocarbon?

A Cyclopentane
B Toluene
C Pentanal
D Ethene
E Methylamine

18. (a) Write briefly on the following:
(i) Cracking
(ii) Isomerism
(iii) Homologous series
(iv) Esterification
(v) Polymerization
(vi) Addition reaction
(vii) Fermentation
(viii) Substitution reaction
(ix) Functional group

(b) What are alkanes? Give two examples of liquid alkanes together with their formulae.

(c) Write the structural formulae for 2,3-dimethyl pentane.

19. (a) How would you prepare a few jars of ethene? Give a diagram of the apparatus used and the equation of the reaction.

(b) How does ethene react with the following substances? Give the equations and the conditions of the reactions.
(i) Hydrogen
(ii) Tetraoxosulphate(VI) acid
(iii) Chlorine

20. (a) Explain,using a diagram, how you would prepare methane in the laboratory. Write the equation of the reaction.

(b) Give the various substituted products formed when methane reacts with chlorine.

21. (a) Write the general formula for the alkynes. How would you prepare ethyne in the laboratory?

(b) How would you obtain ethanal from ethyne? Give the equation of the reaction.

(c) How would you distinguish ethyne from ethane?

22. (a) What is the general formula of alkanols?

(b) Give the names and structural formulae for all the alkanols represented by the formula C_3H_8O.

(c) Give the formula of propanol and indicate the alkyl group.

(d) Outline how cane sugar (sucrose) can be fermented to yield ethanol. Give the equations of the reactions that take place.

(e) Explain what happens when ethanol is refluxed with acidified sodium heptaoxodichromate(VI) solution for a long time. Give the equations of the reactions.

(f) Explain why wine turns sour on exposure to air.

(g) Give three industrial uses of alkanols.

23. Give the IUPAC names of the following organic compounds.

(a) CH_3Cl
(b) C_3H_7OH
(c) $CH_2(OH)CH_2(OH)$
(d) CH_3CHO
(e) $CH_3CH(OH)CH_3$
(f) $CH_2(OH)CH(OH)CH_2(OH)$
(g) $C_2H_4Cl_2$
(h) CCl_4
(i) C_3H_7I
(j) $CH_3COOC_2H_5$

24. Write the formulae of the following organic compounds.

(a) 2-methyl-2-hydroxypropane
(b) 2-methylpropan-2-ol
(c) Propanoic acid
(d) Methyl ethanoate
(e) Methyl propanoate
(f) 3-methylpentene
(g) 2-hydroxypropanoic acid

30 ORGANIC CHEMISTRY (

ALKANOIC ACIDS

Alkanoic acids, also known as *organic* or *carboxylic acids*, contain the carboxyl group, –COOH, as their functional group.

The most common of these are the *aliphatic monocarboxylic acids* which contain one carboxyl group per molecule. They form a homologous series with the general molecular formula of $C_nH_{2n+1}COOH$ where $n \geq 0$. They are sometimes called fatty acids because some of them are found in natural fats and oils. The IUPAC name of each homologue is obtained by changing the *-e* ending of the corresponding alkane to *-oic acid.*

Dicarboxylic acids have two carboxyl groups per molecule, e.g.

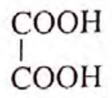
- ethanedioic acid (oxalic acid),
- cis-butenedioic acid (maleic acid), and
- 2,3-dibydroxybutanedioic acid (tartaric acid),

while *tricarboxylic acids* have three carboxyl groups per molecule, e.g.

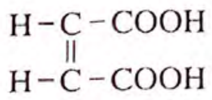
- 2-hydroxypropane-1,2,3-tricarboxylic acid (citric acid).

Two important aromatic carboxylic acids are

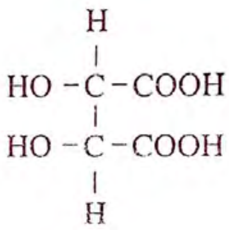
- benzoic acid and
- 2-hydroxybenzoic acid (salicylic acid).



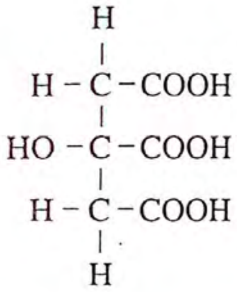
ethanedioic acid



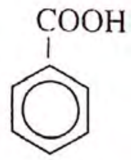
cis-butenedioic acid



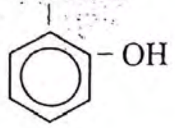
2,3-dihydroxy-butanedioic acid



2-hydroxypropane-1,2,3-tricarboxylic acid



benzoic acid



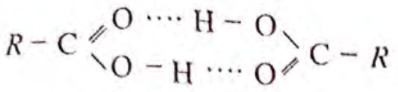
2-hydroxybenzoic acid

Table 30.1 The first few members of the alkanoic acid series.

Molecular formula	Structural formula	IUPAC name	Common name
CH_2O_2	HCOOH	Methanoic acid	Formic acid
$C_2H_4O_2$	CH_3COOH	Ethanoic acid	Acetic acid
$C_3H_6O_2$	CH_3CH_2COOH	Propanoic acid	Propanoic acid
$C_4H_8O_2$	$CH_3(CH_2)_2COOH$	Butanoic acid	n-Butyric acid
$C_4H_8O_2$	$(CH_3)_2CHCOOH$	2-Methyl propanoic acid	iso-Butyric acid

General properties

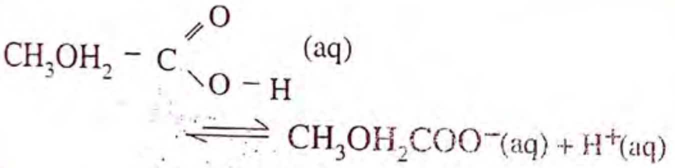
The lower members of the alkanoic acids are colourless liquids at room temperature. Their boiling points are much higher than expected when compared with their molecular sizes. This is due to the hydrogen bonds that bind the molecules.



Alkanoic acids dissociate in aqueous solutions to produce hydrogen ions.

$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

This type of dissociation occurs less readily for propanoic acid than for ethanoic acid because the ethyl group, $CH_3CH_2–$, donates more electrons to the carboxyl group and makes the oxygen-hydrogen bond stronger. Therefore, propanoic acid is less acidic than ethanoic acid.

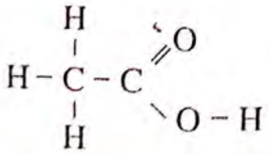


$$CH_3OH_2 - C\begin{matrix}{}^{\nearrow O}\\ {}_{\searrow O-H}\end{matrix}(aq) \rightleftharpoons CH_3OH_2COO^-(aq) + H^+(aq)$$

As the number of carbon atoms in the alkyl group increases, the acidic nature as well as the solubility of the alkanoic acids in water decreases.

ETHANOIC ACID

Ethanoic acid is the acid present in vinegar. It has the following structure.



Laboratory Preparation

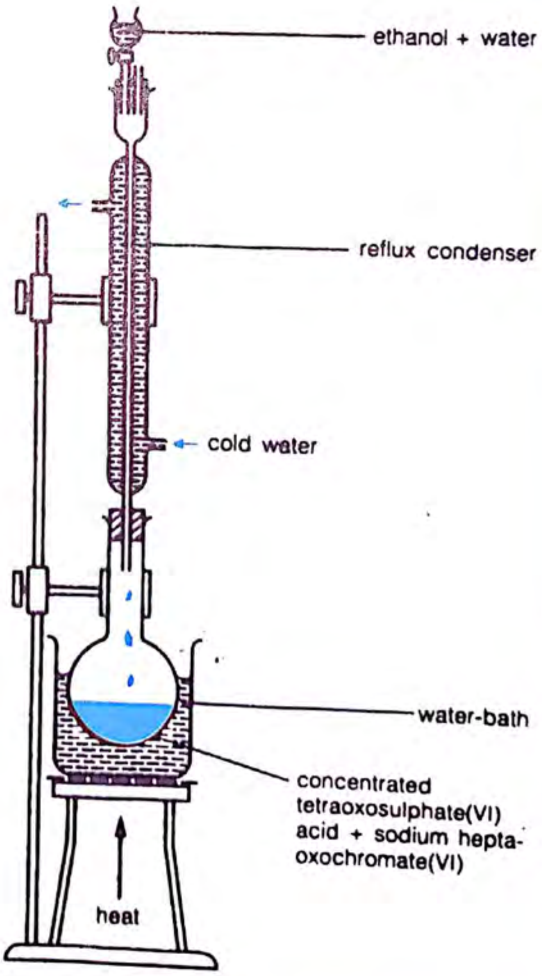
Ethanoic acid can be prepared by the complete oxidation of ethanol by acidified sodium heptaoxochromate(VI) solution.

$$CH_3CH_2OH(aq) + 2[O] \rightarrow CH_3COOH(g) + H_2O(g)$$

Ethanol undergoes oxidation first to ethanal and then to ethanoic acid. To ensure its complete oxidation to ethanoic acid, the ethanol is dropped into a large excess of the oxidizing agent and distilled under reflux so that the reactants are brought into very close and prolonged contact.

Add 30 cm^3 of concentrated tetraoxosulphate(VI) acid slowly, with continuous stirring, to 70 cm^3 of water in a round-bottomed flask. Cool the acid solution and dissolve 70 g of sodium heptaoxodichromate(VI) in it. Mix about 40 cm^3 of ethanol with 20 cm^3 of water and place the mixture in a dropping funnel. Set up the apparatus as shown in fig. 30.1. Add the ethanol-water mixture slowly to the acidified heptaoxodichromate(VI) solution and reflux the reaction mixture over a water-bath for an hour. The refluxed mixture which remains in the flask is a dilute solution of ethanoic acid in water.

Fig. 30.1 Preparation of ethanoic acid.



The pure acid, however, cannot be isolated directly from the refluxed mixture as the boiling points of ethanoic acid and water are very close. To obtain the pure acid, first convert it to an ethanoate by adding excess copper(II) trioxocarbonate(IV) to the mixture. Filter the mixture; concentrate and cool the filtrate to obtain copper(II) ethanoate crystals. Heat these crystals gently to drive off the water of crystallization. Then distil the anhydrous ethanoate with concentrated tetraoxosulphate(VI) acid and collect the ethanoic acid as a colourless liquid.

Note In the preparation of ethanoic acid, hydrochloric acid cannot be used because it is too volatile. The apparatus must be all glass because hot ethanoic acid vapour attacks cork and rubber.

Ethanoic acid can also be prepared by

- distilling anhydrous sodium ethanoate, CH_3COONa, with concentrated tetraoxosulphate(VI) acid, or
- boiling methyl cyanide, CH_3CN, with an acid.

$$CH_3COONa(s) + H_2SO_4(aq) \rightarrow CH_3COOH(g) + NaHSO_4(aq)$$

$$CH_3CN(aq) + HCl(aq) + 2H_2O(l) \rightarrow CH_3COOH(g) + NH_4Cl(aq)$$

Physical Properties

1. Ethanoic acid is a colourless liquid with a characteristic sharp and pungent smell.
2. The dilute solution has a sour taste.
3. It is very soluble in water.
4. The pure anhydrous ethanoic acid is called glacial ethanoic acid because it freezes into ice-like crystals at temperatures below 17 °C.
5. It has a boiling point of 118 °C.
6. It turns blue litmus red.

Chemical Properties

Ethanoic acid is a fairly stable compound which is not easily decomposed by heat. It is also unaffected by all ordinary reducing agents, oxidizing agents and dehydrating agents.

Acidic properties

As a weak monobasic acid, ethanoic acid shows all the usual acidic properties. Thus, it

- liberates carbon(IV) oxide from trioxocarbonates(IV) and hydrogentrioxocarbonates(IV);
- attacks strongly electropositive metals, e.g. magnesium and calcium; and
- neutralizes bases or alkalis to form salts, known as ethanoates, and water only.

$$2CH_3COOH(aq) + CaCO_3(s) \rightarrow (CH_3COO)_2Ca(aq) + H_2O(l) + CO_2(g)$$

$$2CH_3COOH(aq) + Mg(s) \rightarrow (CH_3COO)_2Mg(aq) + H_2(g)$$

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Note All compounds containing a carboxyl group will exhibit these acidic properties. Dicarboxylic and tricarboxylic acids, which contain two and three carboxyl groups per molecule, will behave like dibasic and tribasic acids respectively.

Ester formation

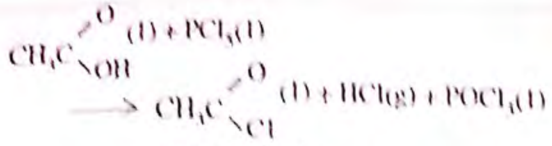
Ethanoic acid reacts reversibly with alkanols to form esters. For example, it reacts with ethanol when heated, to produce ethyl ethanoate, $CH_3COOC_2H_5$. The reaction is catalyzed by tetraoxosulphate(VI) acid.

$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} + \underset{\text{alkanol}}{C_2H_5OH(aq)} \rightleftharpoons \underset{\text{ester (ethylethanoate)}}{CH_3COOC_2H_5(l)} + \underset{\text{water}}{H_2O(l)}$$

Chlorination

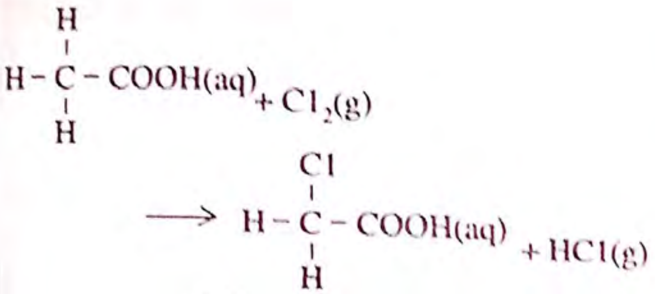
Formation of acyl chloride Glacial or anhydrous ethanoic acid reacts with phosphorus(V) chloride in the cold to form ethanoyl chloride, CH_3COCl, a colourless liquid which fumes in air. The hydroxyl group (–OH) which is part of the carboxyl group (–COOH) in the acid, is substituted by a chlorine atom. Ethanoic acid is chlorinated in a similar way, though more slowly and less vigorously, by phosphorus(III) chloride.

The formation of acyl chlorides is one of the most common reactions of carboxylic acids.


ethanoyl chloride

$3CH_3COOH(l) + PCl_3(l) \rightarrow 3CH_3COCl(l) + H_3PO_3(aq)$

Formation of chloroalkanoic acid If chlorine is passed into boiling ethanoic acid, in the presence of sunlight, iodine or red phosphorus as the catalyst, substitution will take place in the methyl group ($-CH_3$) while the carboxyl group ($-COOH$) remains intact. The product of this reaction is monochloroethanoic acid, $CH_2ClCOOH$.



$$H-\overset{H}{\underset{H}{C}}-COOH(aq) + Cl_2(g) \longrightarrow H-\overset{Cl}{\underset{H}{C}}-COOH(aq) + HCl(g)$$

2-chloro ethanoic acid

If the reaction is prolonged, further chlorination will occur to produce the

- dichloroethanoic acid, $CHCl_2COOH$, and
- trichloroethanoic acid, CCl_3COOH,

successively. Bromine reacts with ethanoic acid in a similar way as chlorine, though less readily.

Decarboxylation reaction

If sodium enthanoate is heated strongly with soda-lime, methane will be produced together with carbon(IV) oxide.

$$CH_3COONa(aq) \xrightarrow{\Delta} CH_4(g) + CO_2(g)$$

Reduction

Alkanoic acids can be reduced to primary alkanols, using lithium tetrahydridoaluminate, $LiAlH_4$, as reducing agent to supply the hydrogen.

$$CH_3COOH(aq) + 4[H] \rightarrow CH_3CH_2OH(l) + H_2O(l)$$

Uses

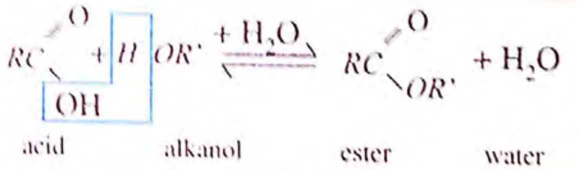
Ethanoic acid is used in making compounds like

- ethenyl ethanoate (vinyl acetate) which is used in vinyl resins;
- ethanoic anhydride which is used in aspirin;
- cellulose ethanoate (cellulose acetate) which is used for packing, in varnishes, in the filter tips of cigarettes, as well as in the manufacture of synthetic fibres like rayon and artificial silk;
- propanone (acetone); and
- various dyes.

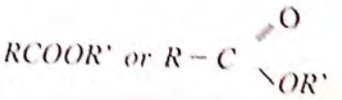
Ethanoic acid is also an important organic solvent. It is used in the food industry as vinegar, for preserving and flavouring food. Sometimes, it is also used for coagulating rubber latex.

ESTERS

When an alkanol reacts with a carboxylic acid, the products are water and an ester, e.g.



Esters of monocarboxylic acids have the following structural formula.



The alkyl groups, *R* and *R'* (of the acid and alkanol respectively), may be the same or different. Two examples of esters are

- methyl ethanoate, CH_3COOCH_3 and
- ethyl (ethanoate), $CH_3COOC_2H_5$.

Esters are the main constituents of many naturally occurring fats and oils. Many of them have pleasant smells and are largely responsible for the fragrance of flowers and the flavours of fruits. For example, pentyl ethanoate, $CH_3COOC_5H_{11}$, has the odour of bananas and is called banana oil, while octyl ethanoate, $CH_3COOC_8H_{17}$, has the smell of oranges.

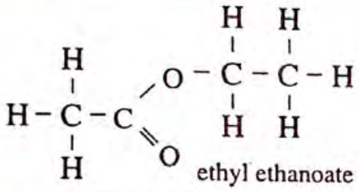
Esterification

The formation of an ester by the reaction between an alkanol and an acid is known as *esterification*. This reaction is extremely slow and reversible at room temperature, and is catalyzed by a high concentration of hydrogen ions.

$$\text{alkanol} + \text{acid} \underset{\text{hydrolysis}}{\overset{\text{esterification}}{\rightleftharpoons}} \text{ester} + \text{water}$$

ETHYL ETHANOATE

All esters are similar chemically, although they may vary in their degree of reactivity. Ethyl ethanoate is one of the simpler esters. Its molecular formula is $CH_3COOC_2H_5$ and it has the following structure.


ethyl ethanoate

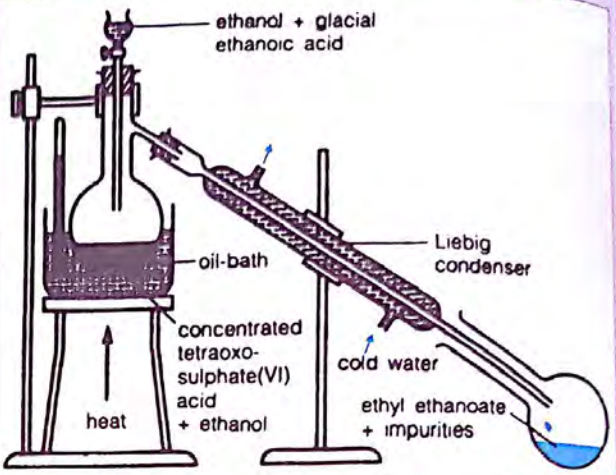
Preparation

Ethyl ethanoate is prepared by the esterification between ethanol and glacial ethanoic acid at 150°C in the presence of concentrated tetraoxosulphate(VI) acid.

$$C_2H_5OH(aq) + CH_3COOH(l) \underset{H^+}{\rightleftharpoons} CH_3COOC_2H_5(l) + H_2O(l)$$

Make a mixture of ethanol and concentrated tetraoxosulphate(VI) acid by adding 25 cm^3 of the acid to 25 cm^3 of ethanol slowly while stirring continuously. Place the mixture in a distillation flask and set up the apparatus as shown in fig. 30.2. Mix equal volumes of ethanol and glacial ethanoic acid and place it in the dropping funnel. When the oil bath is about 150 °C, add the mixture in the dropping funnel into the distillation flask very slowly. The ethyl ethanoate distils over. Continue adding the mixture in the funnel at the same rate as that at which the ethanoate distils over. Besides ethyl ethanoate, the distillate contains impurities like unreacted ethanol, acids, water and ethoxyethane.

Fig. 30.2 Preparation of ethyl ethanoate.



Carry out the following steps to purify the distillate.

- First, shake the distillate in a separating funnel with concentrated sodium trioxocarbonate(IV) solution to remove the acidic impurities.
- Next, discard the lower aqueous layer and shake the upper layer with a concentrated solution of calcium chloride to remove the ethanol.
- Then discard the lower layer again and run the upper layer into a conical flask containing anhydrous calcium chloride and leave it to stand for a day to remove any water present in the mixture.
- Finally, filter the mixture, distil it over a waterbath and collect the fraction which distils over between 74 to 79 °C. This fraction contains pure ethyl ethanoate which is almost free of ethoxyethane.

For small scale preparation of ethyl ethanoate in the laboratory, add about 10 drops of concentrated tetraoxosulphate(VI) acid to about 2 cm^3 of glacial ethanoic acid in a dry test-tube. Mix well, add 4 cm^3 of ethanol and mix again. Warm the mixture in a water-bath (hot but not boiling) for about 25 minutes. Pour the mixture into a beaker partially filled with a sodium or calcium chloride solution. The ethyl ethanoate floats on the mixture as oily globules.

Physical Properties

1 Ethyl ethanoate is a colourless volatile liquid with a pleasant smell.

2 It is only slightly soluble in water but dissolves readily in organic solvents such as ethanol, ethoxyethane and benzene.

3 It has a boiling point of 75°C.

Chemical Properties

Hydrolysis

Ethyl ethanoate can be hydrolyzed by water into its component acid and alkanol again. In practice, this reaction is extremely slow, even on boiling, but it is catalyzed by hydrogen or hydroxide ions i.e. a dilute acid or alkali.

$$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$$

NOTE If an alkali is used as a catalyst, it will immediately react with the carboxylic acid formed to produce the salt of the acid, e.g.

$$CH_3COOC_2H_5(l) + NaOH(aq) \rightleftharpoons CH_3COONa(aq) + C_2H_5OH(aq)$$

Reaction with ammonia

When ammonia is bubbled through an ester like ethyl ethanoate, ethanol and ethanamide, CH_3CONH_2, are produced.

$$CH_3COOC_2H_5(l) + NH_3(g) \rightarrow C_2H_5OH(l) + CH_3CONH_2(s)$$

Reduction

Ethyl ethanoate is reduced to ethanol by hydrogen from strong reducing agents like lithium tetrahydridoaluminate(III).

$$CH_3COOC_2H_5(l) + 4[H] \rightarrow 2C_2H_5OH(l)$$

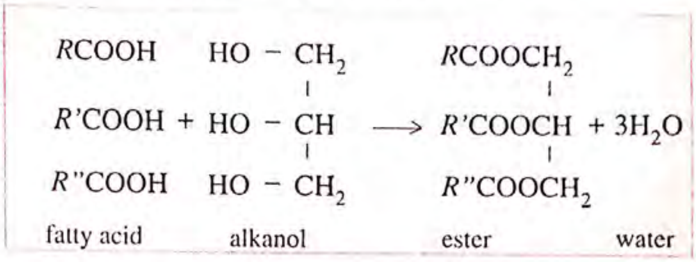
General Uses of Esters

Ethyl ethanoate and other esters are mainly used as solvents for cellulose nitrate and quick-drying substances like paints, nail varnishes, lacquer and adhesives. The commonly known *thinner water* is a mixture of esters, including pentyl ethanoate.

Esters are used in perfumes and cosmetics, and as artificial flavouring for foods.

FATS AND OILS

Fats and oils belong to a general group of compounds known as *lipids*. Fats are solids usually of animal origin while oils are liquids mainly from plants. Both are esters of the trihydric alkanol, propane-1,2,3-triol. Each molecule of propane-1,2,3-triol is esterified with three molecules of fatty acids as follows:



$$\begin{array}{lllll} RCOOH & & HO-CH_2 & & RCOOCH_2 \\ & & \quad\;\; | & & \quad\;\;\; | \\ R'COOH & + & HO-CH & \longrightarrow & R'COOCH + 3H_2O \\ & & \quad\;\; | & & \quad\;\;\; | \\ R''COOH & & HO-CH_2 & & R''COOCH_2 \\ \text{fatty acid} & & \text{alkanol} & & \text{ester} \qquad \text{water} \end{array}$$

where R, R' and R'' can be the same or different.

The fatty acids commonly found in lipids are long chain alkanoic acids of the general formula, $RCOOH$ where R contains about 10 to 18 carbon atoms.

The terminal –COOH group is polar, hence the acid is able to dissolve in water. The carboxylic acid group ionizes in water to a certain degree to form hydrogen ion and the carboxylate ion. Fatty acids are thus weak acids.

$$RCOOH(aq) \rightleftharpoons RCOO^-(aq) + H^+(aq)$$

The long alkyl group is non-polar, and so is not soluble in water. Fatty acids are divided into two groups:

- saturated fatty acids, and
- unsaturated fatty acids.

The saturated fatty acids have no double bonds in their hydrocarbon chain while the unsaturated fatty acids have one or more double bonds in their hydrocarbon chain.

Properties

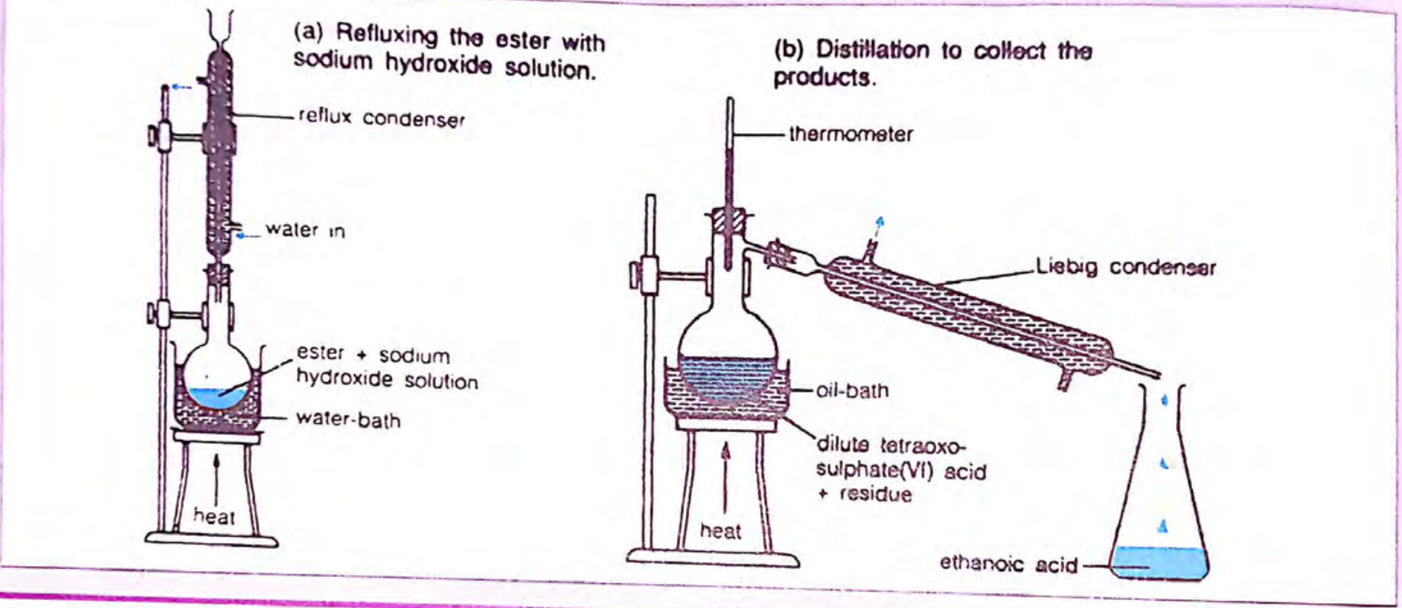
Any particular fat or oil is a complex mixture of propane-1,2,3-triol esters, its properties depending mainly on the proportion of each constituent. Fats have higher melting points because they are composed of a higher proportion of esters of saturated fatty acids.

Experiment 30.1 The hydrolysis of an ester, ethyl ethanoate.

Method Place about 50 cm^3 of a 2 M sodium hydroxide solution in a round-bottomed flask and add to it about 10 cm^3 of ethyl ethanoate. Drop in a few pieces of pumice stone and set up the apparatus as shown in fig. 30.3a. Heat the water-bath. The ester will dissolve as the reaction proceeds. Allow the solutions to reflux for 30 minutes.

Then transfer the mixture to a distillation flask and distil it (fig. 30.3b). Collect the fraction that is given off at 78 °C. This is ethanol, which is one of the products of hydrolysis. When all the ethanol is given off, acidify the sodium ethanoate residue left in the flask with dilute tetraoxosulphate(VI) acid, reflux the mixture and redistil a second time using an oil-bath. When the temperature is above 105 °C, collect the distillate, which is an aqueous solution of ethanoic acid.

Fig. 30.3 Hydrolysis of ethyl ethanoate.



Result Ethyl ethanoate reacts with sodium hydroxide solution to form sodium ethanoate and ethanol. The ethanol is detected by its characteristics alkanoic smell. The salt is obtained as a white residue, which on acidification followed by refluxing liberates the corresponding ethanoic acid.

Conclusion Ethyl ethanoate is hydrolyzed to yield ethanoic acid and ethanol.

Oils have lower melting points because they are composed of a higher proportion of esters of unsaturated fatty acids.

Hydrogenation of oils

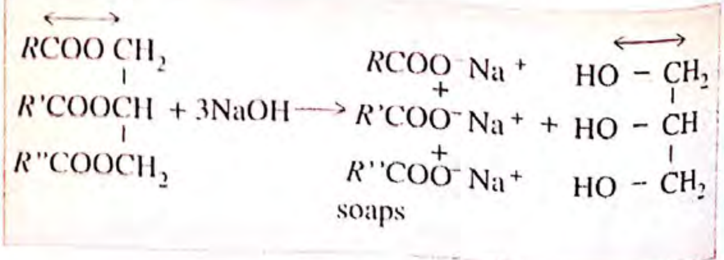
Oil can be changed into fat by hydrogenation. Margarine is made by this process. Oils, usually from plants such as oil palm, groundnut and soyabean oil, are heated to about 180 °C in the presence of finely divided nickel, and hydrogen is bubbled in at about 5 atm. The hydrogen is added across the double bonds in the unsaturated carbon chains in the oils. The hardened oils are then mixed with salt, vitamins, skimmed milk and various fats to form margarine.

Saponification

Hydrolysis of fats and oils with caustic alkali yields propane-1,2,3-triol.and the corresponding sodium and potassium salts of the component fatty acids. These salts are the principal constituents of soap. This process is also known as *saponification*.

fat or oil + caustic alkali

→ soaps + propane-1,2,3-triol



$$\begin{array}{l} RCOO\,CH_2 \\ \quad\quad\;\, | \\ R'COOCH \\ \quad\quad\;\, | \\ R''COOCH_2 \end{array} + 3NaOH \longrightarrow \begin{array}{c} RCOO^-\,Na^+ \\ + \\ R'COO^-\,Na^+ \\ + \\ R''COO^-\,Na^+ \\ \text{soaps} \end{array} + \begin{array}{l} HO - CH_2 \\ \quad\quad\;\, | \\ HO - CH \\ \quad\quad\;\, | \\ HO - CH_2 \end{array}$$

IUPAC name	Old name	Source	Molecular formula
Hexadecanoic acid	Palmitic acid	Palm oil	$CH_3(CH_2)_{14}COOH$
Octadecanoic acid	Stearic acid	Animal fats	$CH_3(CH_2)_{16}COOH$
Octadec-9-enoic acid	Oleic acid	Peanut oil, olive oil	$CH_3(CH_2)_7{=}CH(CH_2)_7COOH$
Octadeca-9,12-dienoic acid	Linoleic acid	Vegetable oils	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

Uses

Most fats are consumed as food. Oils are hardened into fats to make margarine. Tallow (mutton fat) is used for making soaps. Coconut oil and palm oil are used for making soaps and for cooking, while groundnut oil and cotton seed oil are used only for cooking. Linseed oil is used for making paints.

Tests for fats and oils

Paper test A drop of oil or melted fat on a piece of filter paper forms a translucent grease spot.

Sudan III test Shake a few cm^3 of coconut oil with water. Then add 4 to 5 drops of Sudan III stain. The oil is stained red. This is a specific test for fats and oils.

DETERGENTS

Detergent means any substance which has the ability to clean an object. This includes soaps, soap powders and dish washing liquids as well as water.

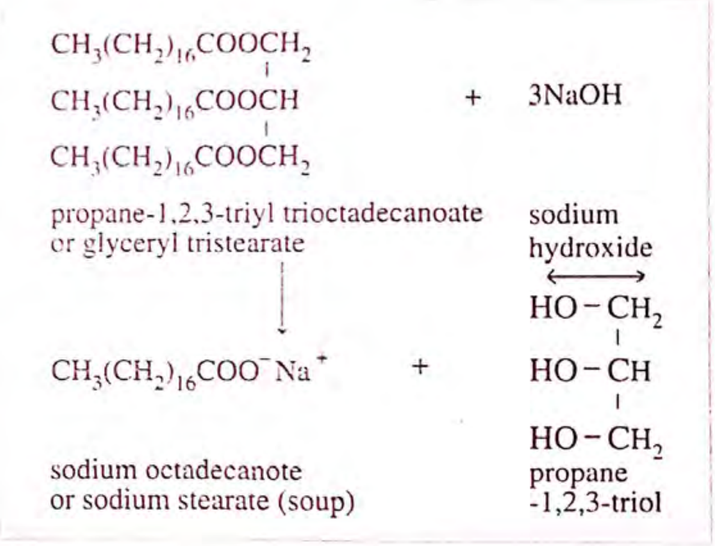
Detergents fall into two main types–soapy detergents and soapless detergents.

Soapy detergents

Soapy detergents or simply soaps are the sodium salts of fatty acids. They are saponification products of fats and oils.

Commercial manufacture of soap Animal fats (e.g. mutton fat) or vegetable oils (e.g. palm oil, coconut oil and olive oil) are steam-heated in large vats with sodium or potassium hydroxide until saponification is completed. A concentrated sodium chloride solution is then added to decrease the solubility of the soap (i.e. the alkaline salts), so that it separates out as a hard cake on the surface on cooling. This is known as *salting out*. The impure soap is purified with steam and water. Dyes, perfumes and disinfectants are added as required before the soap is pressed into bars or tablets.

The properties of the soap produced depend mainly on the alkali and the fat or oil used. Hard soaps used for laundering are chiefly composed of the sodium salts of saturated acids while softer toilet soaps are composed of the potassium salts of unsaturated acids. The soap-making process using octadecanoic or stearic acid, $CH_3(CH_2)_{16}COOH$ can be represented as shown.



Nature of a soap molecule Each molecule of soap possesses a long hydrocarbon chain, *R*, attached to an ionic head which is either COO^-Na^+ or COO^-K^+. The hydrocarbon tail is hydrophobic, so it is insoluble in water but soluble in oil and organic solvents. The ionic head is hydrophilic, so it is soluble in water. Due to this dual nature, at the interphase of an aqueous-oil layer, soap molecules arrange themselves as shown in fig. 30.6.

When soap is dissolved in water, the soap molecules form spherical clusters called *micelles*. Each micelle may contain hundreds of molecules, which are arranged with the hydrocarbon tails pointing inwards and the ionic heads pointing outwards into

Experiment 30.2 To prepare soap from castor oil.

Method To 50 g of castor oil, add 20 cm^3 of 5 M sodium hydroxide solution, a few drops at a time. Heat the mixture to about 90 to 95 °C, stirrig vigorously all the time during the saponification process. Continue stirring with a glass rod until the whole solution has emulsified into one layer. This should take about 15 to 20 minutes. Saponification is complete if the mixture sticks to the glass rod when the rod is withdrawn.

Transfer the contents to a larger beaker and add 10 cm^3 of saturated sodium chloride solution. Continue stirring and boiling for a further three minutes to salt out the soap. Cool the mixture and filter off the solid curds.

Feel the impure soap. Test its lathering properties in water.

Result A soft yellowish paste floats on the surface of the mixture on salting out. This is the impure soap. It feels soapy and when it is shaken vigorously with water, it forms a lather.

Conclusion Saponification of fats and oils followed by the salting out process gives soaps.

Fig. 30.4 To prepara soap from castor oil.

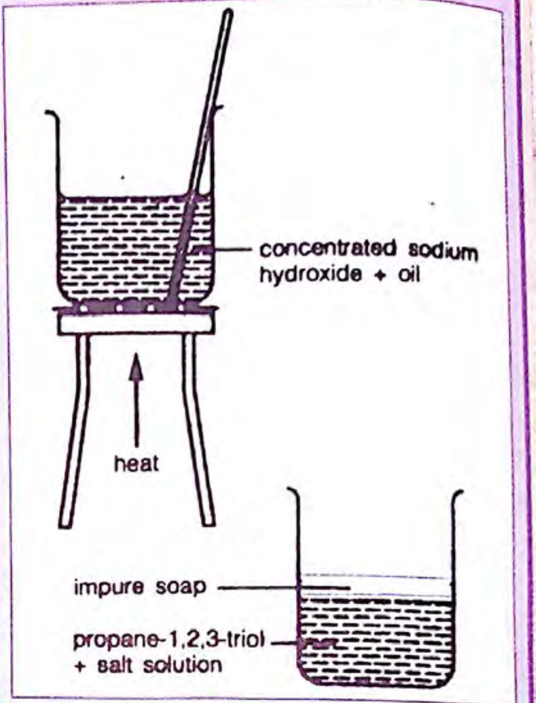


Fig. 30.5 A soap molecule.

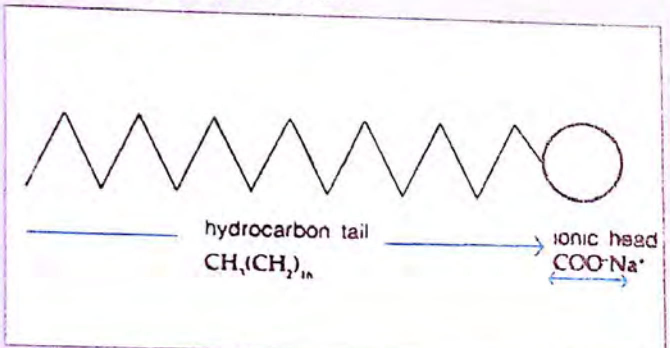
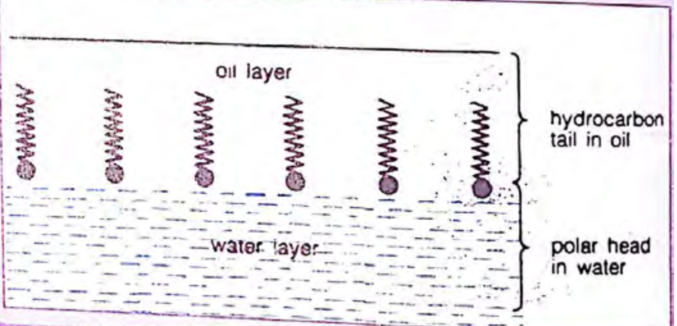


Fig. 30.6 How soap molecules distribute themselves at the oil–water interphase.



the water. Repulsion between the similarly charged ionic heads keeps the micelles apart.

Action of soap as an emulsifying agent If some cooking oil is poured into a beaker of water, the oil will float on the water surface as a separate layer. If the oil-water mixture is shaken vigorously, the oil will be suspended as tiny droplets in the aqueous layer. This is called an oil-water emulsion. The emulsion formed in this case is an unstable one. On standing, the droplets will coalesce to form the oil layer again. If some soap solution is added to the oil-water emulsion, the soap molecules crowd around each oil droplet. The hydrocarbon chains dissolve in the oil,

Fig. 30.7 Micelles in soap solution.

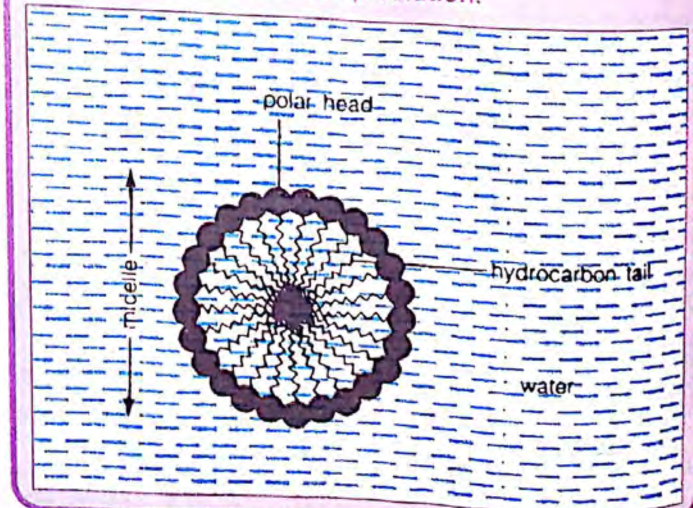
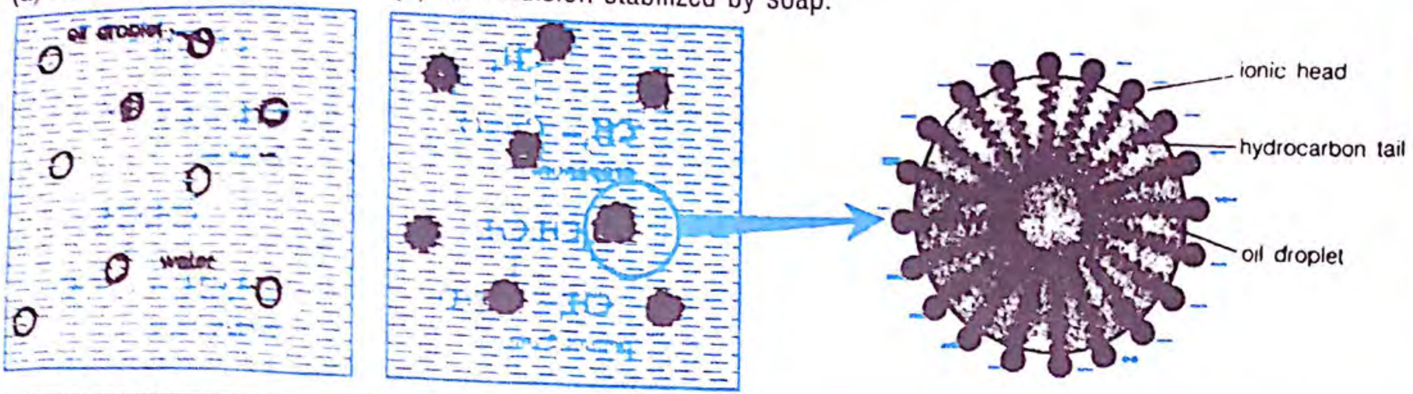


Fig. 30.8 Oil–water emulsion.



(a) An unstable emulsion.

(b) An emulsion stabilized by soap.

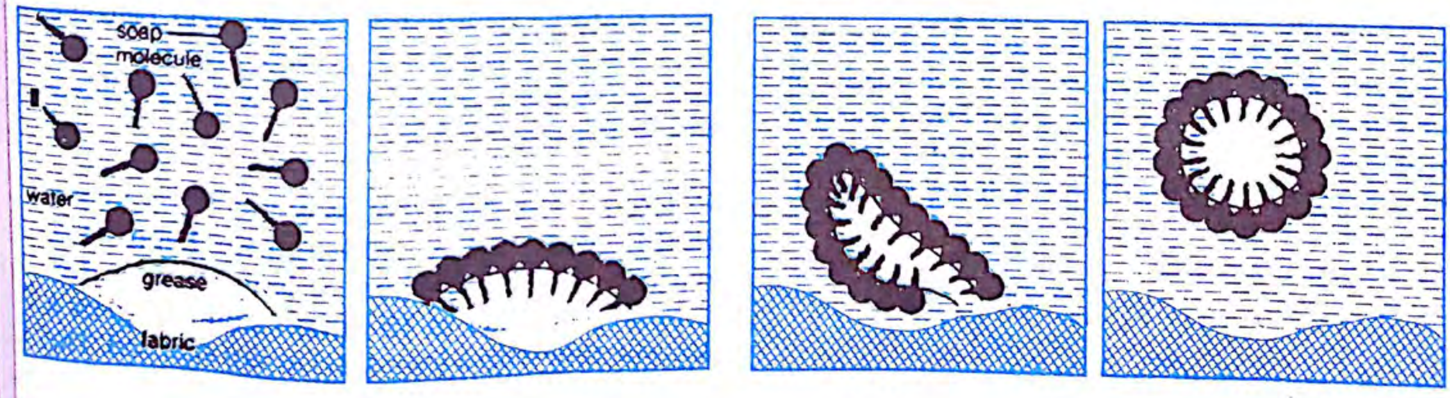
while the ionic heads project into the surrounding water. Electrostatic repulsion prevents the coalescing of the droplets into larger droplets, thus forming a stable emulsion of oil in water. Soap, therefore, acts as an emulsifying agent.

Cleansing action of soap When soap solution is applied to a grease-coated piece of fabric, the soap molecules first approach the grease spot. At the interphase of grease and water, the hydrophobic tails of the soap particles dissolve in grease while the hydrophilic heads dissolve in the water. The water molecules attract the polar ionic heads of the soap molecules. This action helps to lift the grease spot upwards, enabling more soap particles to dissolve in the grease. Eventually, with mechanical scrubbing, the grease patch is emulsified. On rinsing the fabric, the grease is removed.

Advantages and disadvantages of soap Soap is a good cleansing agent in soft water. In hard water, it forms scum. In acidic water, it reacts with the excess hydrogen ions to form unionized fatty acids. This lowers the cleansing effect of the soap, since it is the ionic polar heads of soap molecules that are chiefly responsible for its solubility in water.

Soap is also *biodegradable,* i.e. it can easily be decomposed by bacteria into simple inorganic substances. So it does not cause water pollution.

Fig. 30.9 Action of soap on a grease spot.



(a) Soap molecules approach the fabric.

(b) The hydrocarbon tails dissolve in the grease.

(c) The grease spot is gradually lifted off by the action of water molecules.

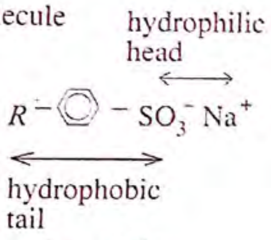
(d) The grease floats off as a globule surrounded by soap molecules.

Soapless detergents

Soapless detergents are the more favoured all purpose cleansing agents nowadays. They are available as liquids or solids. The most widely used soapless detergents are the alkyl benzenesulphonates, abbreviated as ABS. Like the soaps, they are sodium salts of an acid (e.g. a sulphonic acid in the case of ABS).

Structure The detergent molecule has a hydrophobic tail and a hydrophilic head. The hydrophobic tail is either a long chain hydrocarbon (usually 12 to 18 carbon atoms long) or a benzene ring with a long alkyl group attached. The hydrophilic head, unlike soap molecules, can be positively or negatively charged, or even neutral. The high solubility of soapless detergents in water is due to the $-SO_3^-Na^+$ group that is present in the molecules. Soapless detergents are also known as synthetic detergents because they are made by synthetically piecing various parts of the detergent molecule together. The raw materials are petrochemicals obtained from refining crude oil.

A detergent molecule



R is a long hydrocarbon chain.

Advantages and disadvantages of soapless detergents
Soapless detergents do not form scum or react with hydrogen ions. They retain their cleansing properties irrespective of the type of water used. In aqueous solution, detergents are neutral whereas soaps hydrolyze to give a slightly alkaline solution which may not be suitable for washing acid-sensitive fabrics.

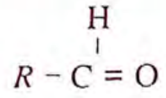
Soapless detergents can also be tailor-made for a specific purpose, such as breaking up oil slicks. As such, they have a wider application than soaps.

Certain soapless detergents are nonbiodegradable and so create water pollution problems when their foams clog up waterways. Nowadays, most detergents are manufactured with straight hydrocarbon chains, and so are biodegradable.

Commercial detergents (even soaps) also contain substances such as perfumes, brighteners, dyes and antiseptics. The most common of these is sodium tripolyphosphate. Since phosphates are good fertilizers, they cause the algae in waterways to multiply beyond control. This brings about water pollution by clogging up waterways.

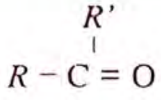
ALKANALS AND ALKANONES

Alkanals or aldehydes have the general formula *R*CHO while alkanones or ketones have the general formula *R*CO*R′* where *R* and *R′* may be alkyl or aryl groups.



$R-\overset{H}{\overset{|}{C}}=O$

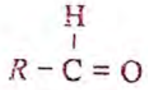
alkanal



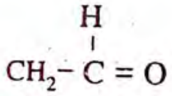
$R-\overset{R'}{\overset{|}{C}}=O$

alkanone

The main similarity between these two classes of compounds is the presence of the carbonyl group, >C=O. In alkanals, there is a hydrogen atom attached to the carbon in the carbonyl group while there is none in the alkanones. Some common alkanals and alkanones are given below.

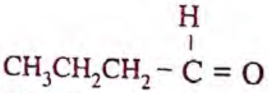


$R-\overset{H}{\overset{|}{C}}=O$



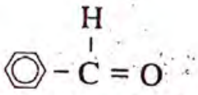
$CH_3-\overset{H}{\overset{|}{C}}=O$

ethanal

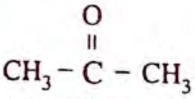


$CH_3CH_2CH_2-\overset{H}{\overset{|}{C}}=O$

butanal

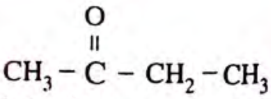


phenylmenthanal



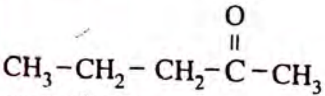
$CH_3-\overset{O}{\overset{||}{C}}-CH_3$

propan-2-one



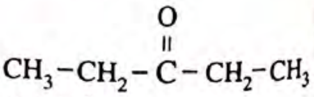
$CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3$

butan-2-one



$CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

pentan-2-one

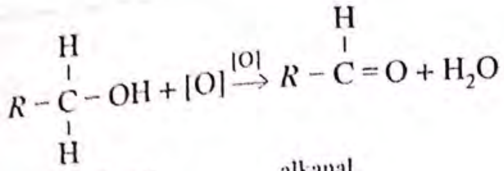


$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3$

pentan-3-one

Preparation

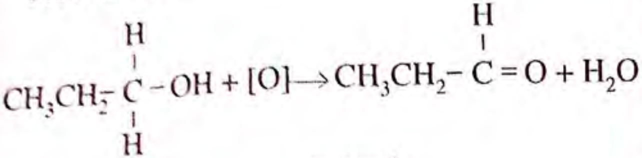
Alkanals Alkanals can be prepared by oxidizing primary alkanols, using acidified potassium tetraoxomanganate(VII), $KMnO_4$, or acidified potassium heptaoxodichromate(VI), $K_2Cr_2O_7$.



$$R-\overset{H}{\underset{H}{C}}-OH+[O]\xrightarrow{[O]}R-\overset{H}{C}=O+H_2O$$

primary alkanol alkanal

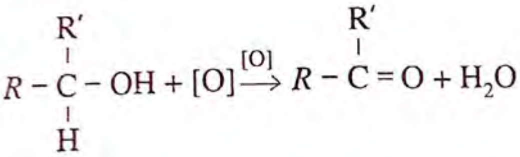
For example,



$$CH_3CH_2-\overset{H}{\underset{H}{C}}-OH+[O]\longrightarrow CH_3CH_2-\overset{H}{C}=O+H_2O$$

propan-1-ol propanal

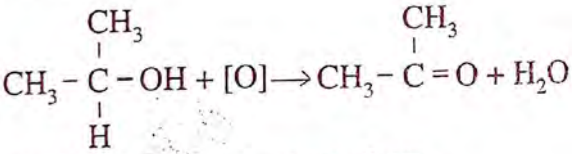
Alkanones Alkanones can be prepared by the oxidation of secondary alkanols using the same oxidizing agents as for alkanals.



$$R-\overset{R'}{\underset{H}{C}}-OH+[O]\xrightarrow{[O]}R-\overset{R'}{C}=O+H_2O$$

secondary alkanal alkanone

For example,



$$CH_3-\overset{CH_3}{\underset{H}{C}}-OH+[O]\longrightarrow CH_3-\overset{CH_3}{C}=O+H_2O$$

propan-2-ol propan-2-one

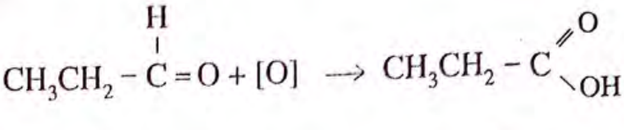
NOTE In the preparation of alkanals and alkanones, the alkanols are used in excess of the oxidizing agents as the alkanals and alkanones prepared can undergo oxidation reactions.

Physical properties

Only methanal and ethanal are gases at room temperature. Other low molecular mass alkanals and alkanones are liquids and the rest are solids. The hydrogen bonding in alkanals and alkanones accounts for their comparatively high boiling points with respect to molecular mass. The carbonyl group is polar while the alkyl group is non-polar. Therefore, alkanals and alkanones with short carbon chains (1C to 5C) are soluble in water but those with longer carbon chains are not. The latter, however, are soluble in non-polar (organic) solvents.

Chemical properties

Oxidation Alkanals are readily oxidized to alkanoic acids in the presence of strong oxidizing agents like acidified potassium tetraoxomanganate(VII) and acidified potassium heptaoxodichromate(VI).

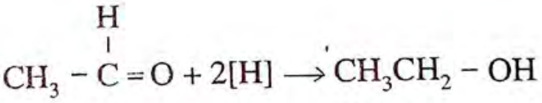


$$CH_3CH_2-\overset{H}{C}=O+[O]\longrightarrow CH_3CH_2-C\begin{matrix}{}^{\nearrow O}\\{}_{\searrow OH}\end{matrix}$$

propanal propanoic acid

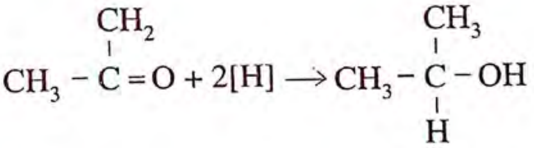
Alkanones undergo oxidation less readily since there is no oxidizable hydrogen attached to the carbonyl group. So a carbon-carbon bond has to be broken here. Only strong oxidizing agents like hot concentrated trioxonitrate(V) acid can oxidize alkanones. In the process, the alkanone molecule is broken up into two.

Reduction Alkanals are reduced to primary alkanols while alkanones are reduced to secondary alkanols by reducing agents like lithium tetrahydridoaluminate(III), $LiAlH_4$, and sodium tetrahydridoborate(III), $NaBH_4$.



$$CH_3-\overset{H}{C}=O+2[H]\longrightarrow CH_3CH_2-OH$$

ethanal ethanol



$$CH_3-\overset{CH_2}{C}=O+2[H]\longrightarrow CH_3-\overset{CH_3}{\underset{H}{C}}-OH$$

propan-2-one propan-2-ol

Tests to distinguish between alkanals and alkanones

Alkanones are less reactive than alkanals and are less easily oxidized.

Fehling's solution Fehling's solution is a mild oxidizing agent containing copper(II) complexes. Being mild, it only oxidizes alkanals but not alkanones.

In the process, the copper(II) complexes are reduced to copper(I) oxide which is brick-red in colour.

Add a few drops of Fehling's solution to 5 cm^3 of the test solution and boil the mixture. The formation of a brick-red precipitate indicates the presence of an alkanal.

Tollen's reagent Tollen's reagent is another mild oxidizing agent. It contains the complex ion, $Ag(NH_3)_2^+$, which is reduced to metallic silver by alkanals but not alkanones.

To 5 cm^3 of silver trioxonitrate(V) solution in a clean test-tube, add a few drops of dilute sodium hydroxide solution. A brown precipitate of silver oxide is formed. Dilute some aqueous ammonia to three times its volume with water. Add this solution to the test-tube drop by drop until the brown precipitate just dissolves. Then add two drops of dilute test solution. If an alkanal is present, a deposit of silver is formed as a mirror on the sides of the test-tube.

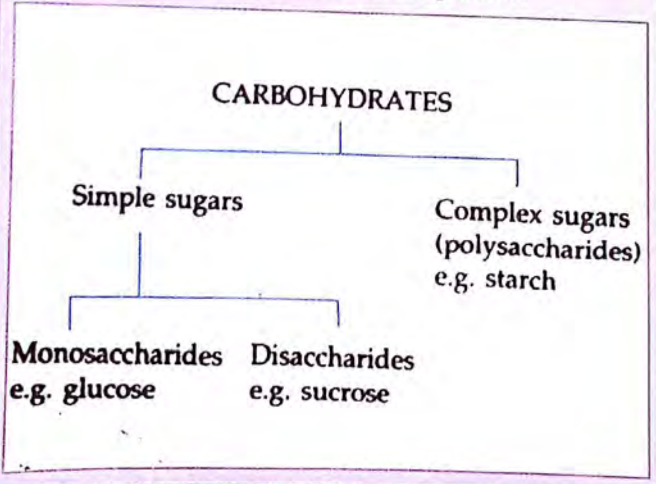
The reactions of alkanals with Fehling's solution and Tollen's reagent show that alkanals are good reducing agents, while alkanones are not. These help to distinguish between the two reaction groups of compounds.

CARBOHYDRATES

Carbohydrates are naturally occurring organic compounds containing carbon, hydrogen and oxygen, with the hydrogen and oxygen present in the ratio of 2: 1, as in water. The general molecular formula of carbobydrate is $C_x(H_2O)_y$ or $C_xH_{2y}O_y$.

Carbobydrates can be classified into *simple sugars* and *complex sugars*. Simple sugars are crystalline, soluble in water and have a sweet taste. Structurally, they can be further divided into *monosaccharides* e.g. glucose, and *disaccharides* e.g. sucrose. Disaccharides are derived from two molecules of monosaccharides.

Fig. 30.10 Classification of carbohydrates.

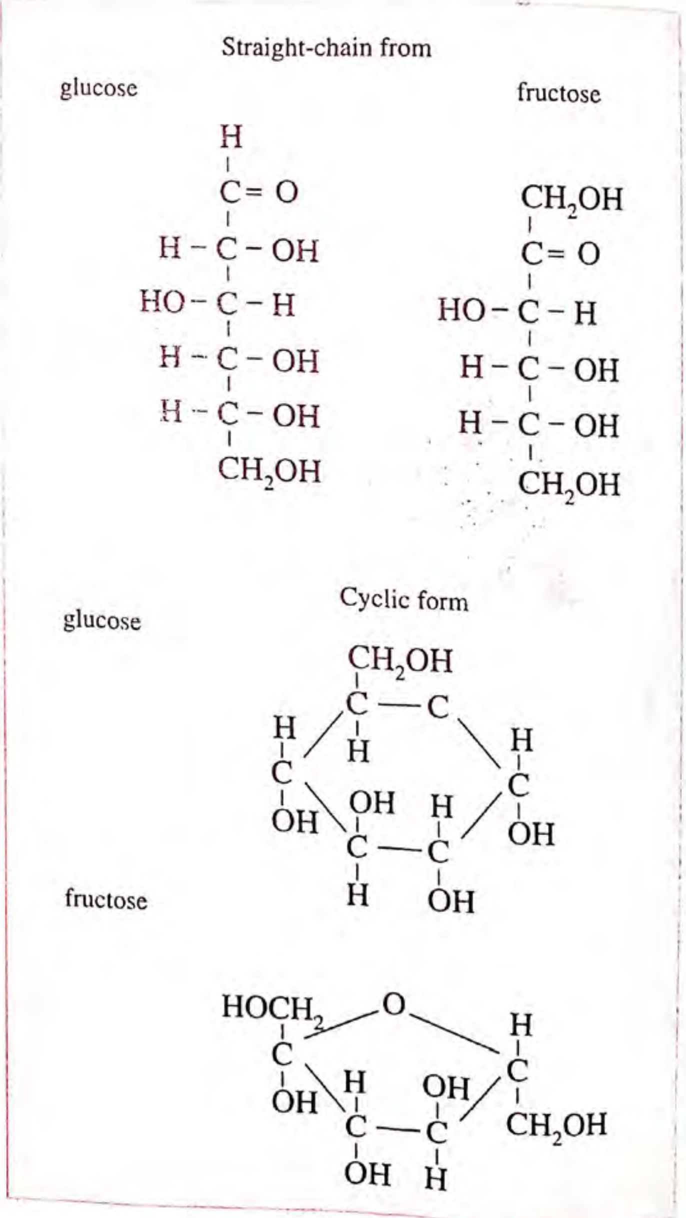


Complex sugars are also known as *polysaccharides*. They are non-crystalline, insoluble and tasteless substances, e.g. starch and cellulose. They have very high relative molecular masses and are polymers derived from monosaccharides.

Monosaccharides

Monosaccharides are simple sugars with three to six carbon atoms per molecule. However, the most common and important of these are the ones containing six carbon atoms per molecule, the *hexoses*, e.g. glucose, fructose, galactose and mannose. All hexoses have the same molecular formula, $C_6H_{12}O_6$, but possess different spatial arrangements.

Hexoses can exist both in the open chain and cyclic forms in solution. In solid crystals, they exist in the ring form.



Trioses and pentoses (sugars with three and five carbon atoms per molecule respectively) are also important monosaccharides. Trioses, $C_3H_6O_3$, such as 2,3-dihydroxypropanal (glyceraldehyde) and 1,3-dihydroxypropanone (dihydroxyacetone) are involved in muscle metabolism. Examples of important pentoses are ribose and deoxyribose (important constituents of the cell nuclei), arabinose (obtained from gum arabic and cherry tree gum), and xylose (obtained from the hydrolysis of wood, straw and corn cobs).

Sugars are also known as aldoses if they contain the alkanal (–CHO) group, and as ketoses if they have the alkanone (–CO–) group. Glucose is an aldose while fructose is a ketose.

Glucose

Glucose, commonly known as grape sugar or dextrose, is present in fruits such as grapes, in honey, and also in the sap of plants. It is the main source of energy for animal tissues and is present in the blood of animals. It is synthesized by plants during photosynthesis.

Preparation Glucose can be obtained by the hydrolysis of starch with dilute acid.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} \xrightarrow{+nH_2O} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

Heat starch with twice its mass of dilute tetraoxosulphate(VI) acid for two hours, replenishing the water as it evaporates. Neutralize the solution with solid sodium trioxocarbonate(IV), filter it and decolorize the filtrate by shaking it with pieces of charcoal. Concentrate the filtrate and cool it to crystallize the glucose as colourless solids.

Properties If glucose is heated with concentrated tetraoxosulphate(VI) acid, it will be dehydrated to form a black residue of carbon.

Note This dehydration reaction with concentrated tetraoxosulphate(VI) acid is characteristic of all carbohydrates.

$$C_6H_{12}O_6 \xrightarrow{-6H_2O} 6C$$

Glucose is a strong reducing agent because of the presence of the –CHO group. It reduces Fehling's solution to a red precipitate of copper(I) oxide on boiling. Glucose solution is readily fermented to ethanol and carbon(IV) oxide by the enzyme zymase in yeast.

Test Add a few drops of Fehling's solution to 5 cm^3 of glucose solution in a test-tube. A brick-red precipitate is obtained on boiling.

Uses Glucose is used as an immediate source of energy for sick people and sportsmen. It is also used in the manufacture of jam and sweets.

Fructose

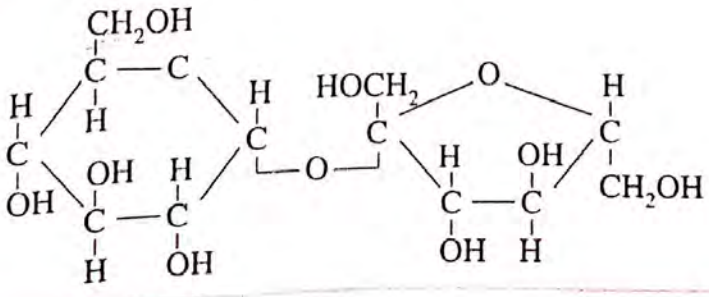
Fructose, commonly known as fruit sugar or laevulose, is usually found together with glucose in sweet fruit juices and honey. Fructose resembles its isomer, glucose, in many ways.

Disaccharides

A disaccharide is derived or condensed from two molecules of monosaccharides by the elimination of one molecule of water. The two component monosaccharides, which may be the same or different, can be recovered by the hydrolysis of the disaccharide.

$$\text{monosaccharide} + \text{monosaccharide} \underset{\text{hydrolysis}}{\overset{\text{condensation}}{\rightleftharpoons}} \text{disaccharide} + \text{water}$$

A sucrose molecule



Most common disaccharides are composed of two hexoses joined together by condensation. They possess a general molecular formula of $C_{12}H_{22}O_{11}$.

Table 30.3 The component monosaccharide in some important disaccharides.

Component monosaccharides	Disaccharides $C_{12}H_{22}O_{11}$
glucose + fructose	Sucrose (cane sugar)
glucose + galactose	Lactose (milk sugar)
glucose + glucose	Maltose (malt sugar)

Sucrose

Sucrose or cane sugar is the common granulated sugar which we use to sweeten food. It occurs naturally in many plants and fruits, e.g. pineapple, carrots, sorghum and the sap of the sugar maple tree. The main sources are sugar-cane and sugar-beet which contain as much as 15 to 20% sucrose.

NOTE Saccharin, the artificial sweetening agent which is commonly used, is not a sugar.

Preparation Sucrose is prepared chiefly from juices of sugar-cane and sugar-beet. The cane or beet is shredded and crushed between rollers and the juice is extracted with water warmed to about 80 °C. The solution is then purified by treatment with slaked lime and carbon(IV) oxide.

The purified solution is concentrated by distillation under reduced pressure. On cooling the concentrated solution, brown crystals of sugar separate out. The remaining liquid called *molasses* still contains a reasonable amount of sugar (about 60%) and is used for ethanol production by fermentation.

The brown sugar obtained is impure. It is refined by treatment with slaked lime and carbon(IV) oxide, and decolorized with animal charcoal.

Properties Sucrose is a colourless crystalline solid. It has a very sweet taste and dissolves readily in water but not in alkanol.

Sucrose chars on strong heating or warming with concentrated tetraoxosulphate(VI) acid. This is characteristic of all carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{-11H_2O} 12C$$

If sucrose is heated to a temperature of about 210 °C, which is above its melting point but below its charring temperature, a yellowish-brown substance, known as caramel, is obtained. Caramel is used for flavouring and in confectionery.

When sucrose is boiled with dilute tetraoxosulphate(VI) acid or hydrochloric acid, it is hydrolyzed to an equal mixture of glucose and fructose. This reaction is known as *inversion*. It can be effected by the enzyme *invertase* obtained from yeast.

$$\text{sucrose} + \text{water} \xrightarrow{\text{invertase}} \text{glucose} + \text{fructose}$$

Sucrose is not a reducing sugar since it does not have any free carbonyl group. So it does not have any effect on Fehling's solution. It gives a positive test with Fehling's solution only after hydrolysis.

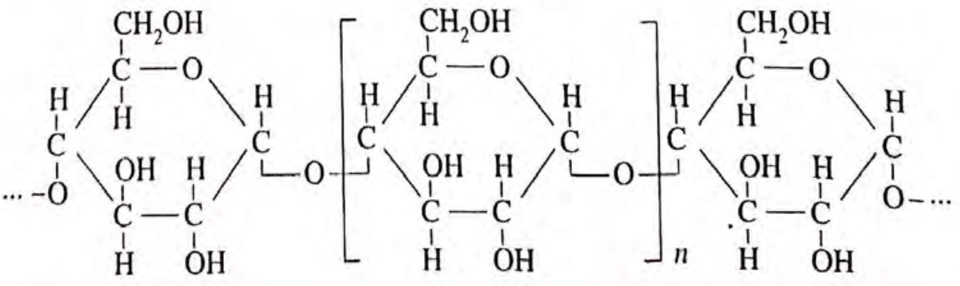
Test Add 5 cm^3 of freshly-prepared Seliwanoff's reagent to 1 cm^3 of sucrose solution. Warm in a water-bath. The mixture turns red after 10 minutes.

Uses Sucrose is used to sweeten food and beverages, and for preserving food. It is also used to produce ethanol by fermentation.

Polysaccharides

Polysaccharides are a group of complex carbohydrates composed of very long chains of monosaccharides

A starch molecule



linked together by condensation, i.e. by the elimination of one molecule of water for every bond formed between two monosaccharide molecules.

$$n \text{ monosaccharide} \xrightleftharpoons[\text{hydrolysis}]{\text{condensation}} \text{polysaccharide} + \frac{n}{2} \text{ water}$$

They can be hydrolyzed step by step by dilute acids to yield the component monosaccharides as the final products. Some important examples of polysaccharides are starch, glycogen (animal starch), cellulose and inulin. They are all polymers of hexoses and have the general molecular formula of $(C_6H_{10}O_5)_n$, where *n* is a very large number. Inulin is composed of repeating fructose units while the other three are composed of repeating glucose units.

Starch

Starch is a polysaccharide with a relative molecular mass of 15 000 to 300 000. It is composed of thousands of repeating glucose units linked together to form a giant branched molecule.

Starch occurs naturally in most plants as a storage carbohydrate, e.g. maize (corn), cassava, yam and cocoyam tubers, potatoes, rice, wheat, barley and oth cereals. They are all used as a source of starch (usua in the form of flour) in different parts of the wor

Preparation The raw materials used (e.g. potato cassava tubers) are first crushed to break the pla cells and release the starch granules. The crushed pu is then mixed with water to extract the starch. Tl water from the resulting starch suspension is remov either by evaporation or by centrifugation. In son countries, the water is decanted off after allowing tl suspension to stand for some time, leaving behind tl white starch residue in the container.

Properties Starch is a white powder with no taste c smell. It is insoluble in water. When an aqueou suspension of starch is warmed, it forms a colloida solution. This sets to a gel on cooling.

Starch is hydrolyzed by dilute acids to yield mixture of *dextrin* (a shorter chain intermediat product), disaccharides (mainly maltose) and glucose Further hydrolysis will eventually give glucose Hydrolysis of starch to dextrin and maltose can als be brought about by the enzyme amylase present i saliva and in malt.

Since starch does not contain any free carbony group, it does not reduce Fehling's solution.

Experiment 30.3 To study the hydrolysis of starch by an enzyme.

Metho Take two test-tubes *A* and *B* and put 3 cm³ of starch solution into each. Add 1 cm³ of saliva to test-tube *A*, *and 1 cm*³ of water to test-tube *B*. Mix the liquid in each tube thoroughly and place both tubes in a water-bath. Warm the water-bath until the solution in each tube is at a temperature of about 37 °C. Then stop the heating. At intervals of time shown in the table below, place a drop of solution from each test-tube on separate titles and add a drop of iodine solution to both.

At the end of the experiment, carry out the Fehling's test on the solutions in test-tubes *A* and *B*.

Time in minutes	0	2	5	10	15	20	25	30
Colour of I_2 + *A*								
Colour of I_2 + *B*								

Result The solution in test-tube A shows a gradual change in colour from dark blue to purple, and finally to yellow for the iodine test. The solution also gives a positive Fehling's test.

The solution is test-tube *B* acts as a control and shows a positive test for starch and a negative one for reducing sugars.

Conclusion The enzyme amylase, present in saliva, hydrolyzes starch to reducing sugars.

NOTE To show the acid hydrolysis of starch, repeat the above experiment using concentrated hydrochloric acid instead of saliva. Heat the solution to 70 °C. Before carrying out Fehling's test, neutralize the acid solution by adding sodium hydroxide solution.

Test Add a few drops of iodine to some boiled starch. A dark-blue coloration which disappears on heating and reappears on cooling results.

Uses Starch is used mainly as food. Industrially it is used to produce ethanol and glucose. In textile industries and in the laundry, it is used as a stiffening agent.

Cellulose

Cellulose is an unbranched polysaccharide with a relative molecular mass of 150 000 to 1 000 000. It is composed of glucose units which are linked in a slightly different way from that in starch.

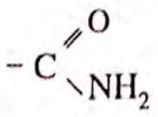
Cellulose is the main component of plant cell walls and plant fibres. It is found in the pure form in cotton wool. Hemp, jute, flax, sisal and straw are also composed mainly of cellulose. The principal industrial sources are cotton (98%) and wood (70%), each of cellulose.

Cellulose is a white solid which is not soluble in water and ordinary organic solvents. It is not easily hydrolyzed by dilute acids. Hydrolysis of cellulose can be carried out readily by the enzyme *cellulase* which is produced by microorganisms present in the digestive systems of termites and herbivorous animals. This enzyme is not present in our body, so we cannot digest cellulose. However, cellulose is necessary as it serves as roughage in our diet to promote the movement of the digestive tract.

Cellulose is the main raw material used for the manufacturing of paper, cellophane and rayon.

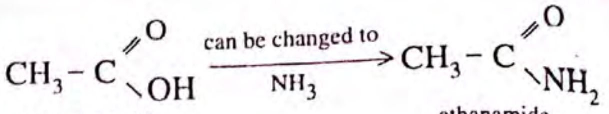
AMIDES

Amides are characterized by the presence of the functional carboxamide group.



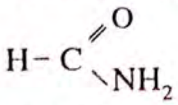
$$-C(=O)NH_2$$

They can be regarded as derivatives of monocarboxylic acids, where the hydroxyl group of the acid is replaced by the carboxamide group. Thus, ethanamide can be derived from ethanoic acid as follows:



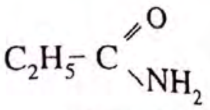
$$\underset{\text{ethanoic acid}}{CH_3-C(=O)OH} \xrightarrow[NH_3]{\text{can be changed to}} \underset{\text{ethanamide}}{CH_3-C(=O)NH_2}$$

Other examples of amides:



$H-C(=O)NH_2$

methanamide



$C_2H_5-C(=O)NH_2$

propanamide

Preparation

Amides are prepared by treating esters or acid chlorides with concentrated aqueous ammonia.

$$CH_3COOC_2H_5(aq) + NH_3(aq) \rightarrow CH_3CONH_2(aq) + C_2H_5OH(aq)$$

They are also prepared by dehydrating the ammonium salts of carboxylic acids.

$$CH_3COONH_4(aq) \rightleftharpoons \underset{\text{(ethanamide)}}{CH_3CONH_2(aq)} + H_2O(l)$$

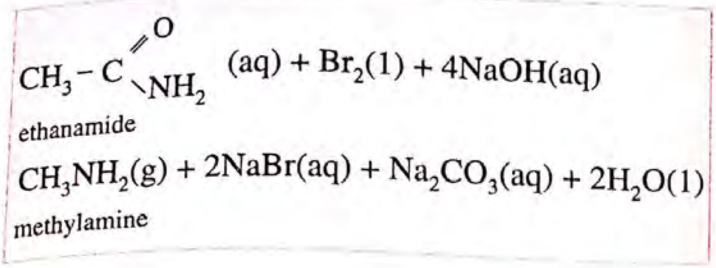
Physical properties

Methanamide is a liquid while the rest of the amides are crystalline solids. The melting points and boiling points of amides are much higher than would be expected from their relative molecular masses. This is due to the presence of hydrogen bonding between amide molecules. The bonding occurs between the hydrogen atom of the amino group and the oxygen atom of the carbonyl group.

Chemical properties

Amides undergo hydrolysis to give the corresponding monocarboxylic acids. This reaction is catalyzed by both mineral acids and alkalis.

With aqueous sodium hydroxide and bromine, amides yield the corresponding amines by eliminating the carbonyl group. This is an important reaction because it is a method whereby a carbon atom is eliminated from a molecule. Thus ethanamide (two carbon atoms per molecule) changes to methylamine (one carbon atom per molecule)–the Hofmann Reaction.



$$CH_3-C\overset{\displaystyle /\!\!/ O}{\underset{\displaystyle \setminus NH_2}{}}\,(aq) + Br_2(l) + 4NaOH(aq)$$

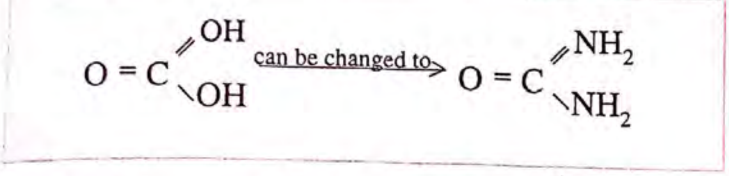
ethanamide

$$\longrightarrow CH_3NH_2(g) + 2NaBr(aq) + Na_2CO_3(aq) + 2H_2O(l)$$

methylamine

Carbamide (urea)

Carbamide or urea is an amide of hydrogen trioxocarbonate(IV) acid.



$$O=C\begin{matrix}\nearrow OH\\ \searrow OH\end{matrix} \xrightarrow{\text{can be changed to}} O=C\begin{matrix}\nearrow NH_2\\ \searrow NH_2\end{matrix}$$

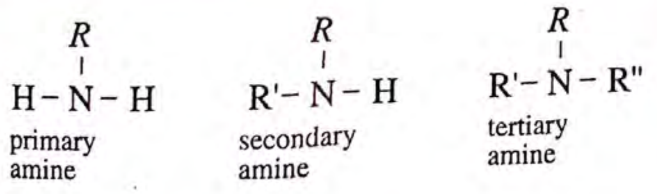
Urea is produced in large quantities by compressing carbon(IV) oxide and excess ammonia at a high pressure at 200 °C. It is used

- in the manufacture of synthetic resins and plastics, and
- as a fertilizer.

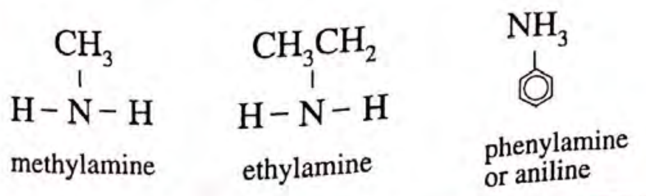
Urea is produced in our body as a waste product of protein breakdown. It is excreted mainly in the urine.

AMINES

Amines are characterized by the presence of the functional amino group, $-NH_2$. They can be regarded as derivatives of ammonia, where one or more hydrogen atoms have been replaced by alkyl or aryl groups. They can be classified into primary, secondary and tertiary amines according to the number of substituted hydrogen atoms.



Common examples of amines:



Properties and uses

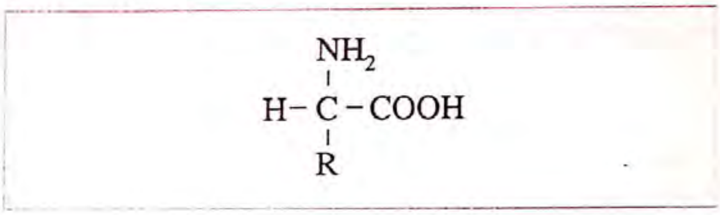
Amines are mainly gases and liquids with a fishy smell. They are polar compounds and are soluble in water. This is due to hydrogen bonding between the hydrogen atoms of the water molecules and the nitrogen atoms of the amino groups in the amines. Amines are bases. In water, they dissociate as follows:

$$RNH_2(aq) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$

The most important use of amines is in the making of polyamides or nylon.

AMINO ACIDS

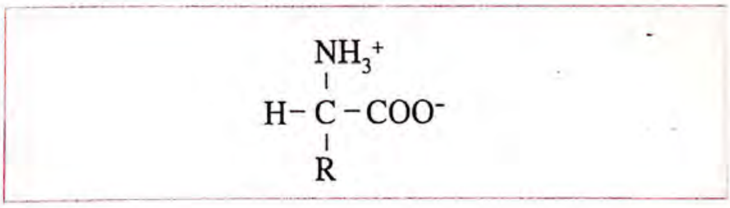
Amino acids are the basic structural units of proteins. Each amino acid contains an amino group ($-NH_2$) and a carboxyl group ($-COOH$) in its molecule. Its general structure is as follows:



$$H-\overset{\displaystyle NH_2}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-COOH$$

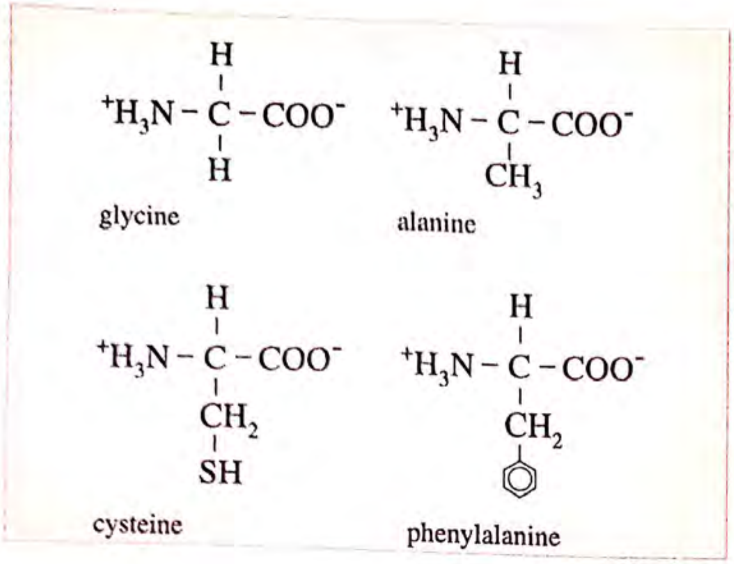
The carbon atom of the amino acid to which the functional groups are attached is known as the α-carbon.

In neutral solution, amino acids are mainly in the form of dipolar ions called *Zwitterions*.



$$H-\overset{\displaystyle NH_3^+}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-COO^-$$

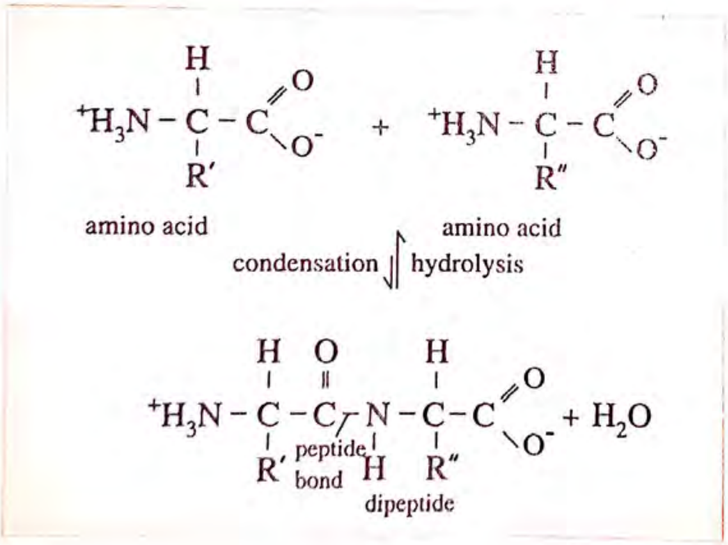
There are twenty naturally occurring amino acids of biological importance. All proteins found in living organisms are combinations of these amino acids. Some of these amino acids are known as *essential amino acids* because they cannot be synthesized in our body. Thus, these amino acids must be present in our dietary proteins. Some examples of amino acids are as follows:



Peptides

Peptides are amides formed by the interaction between amino groups and carboxyl groups. The bond joining the α-amino group of one amino acid and the α-carboxyl group of another amino acid is known as the *peptide bond.*

Two amino acids react to form a dipeptide; three amino acids to form a tripeptide; and so on.



If a number of amino acids are linked by peptide bonds, a *polypeptide* is formed. A polypeptide chain has an amino end and a carboxyl end. It consists of a regularly repeating part or main chain and a variable part (indicated by R) or side chain.

NOTE *R* will be different depending on the amin acids which make up the polypeptide.

PROTEINS

Proteins are made up of polypeptide chains. Som proteins, like myoglobin, consist of only on polypeptide chain. Others may consist of more tha one like or unlike polypeptide chains. For exampl haemoglobin is made up of four chains, two of on kind and two of another. The amino acid sequence i the polypeptide chains of a protein is specified b genes. This sequence is important since it determine the three dimensional structure of the protein an hence its biological function.

Examples of proteins are

- insulin (a hormone),
- haemoglobin (oxygen-carrying pigment in blood)
- ribonuclease (an enzyme), and
- collagen (a muscle protein).

Occurrence

Proteins are found in all living systems as structural components and as biologically important substances such as hormones, enzymes and pigments.

Proteins in our food can be divided into *first class proteins* and *second class proteins*. First class proteins contain essential amino acids. These are mainly of animal origin. Examples of foods which contain first class proteins are lean meat, fish, eggs, milk and cheese. Second class proteins are mainly vegetable proteins which are found in vegetables such as peas and beans.

Structure and shape

Proteins have well defined structures. The primary structure of a protein refers to the way in which the atoms of the protein molecule are joined to one another by covalent bonds to form chains and cross-linkages between chains.

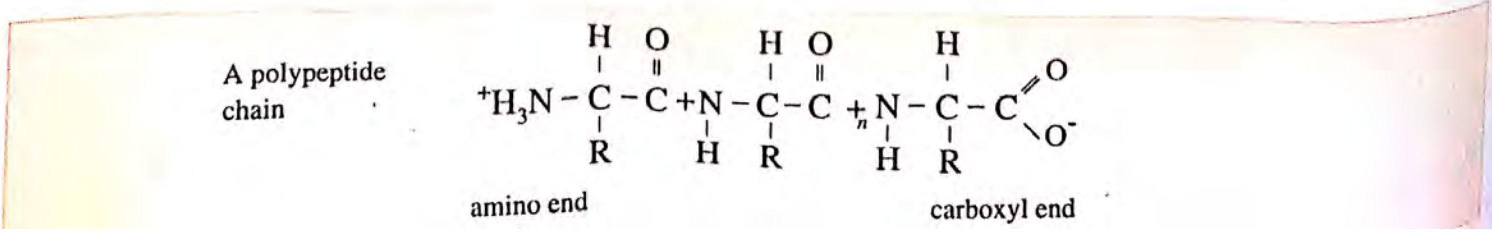
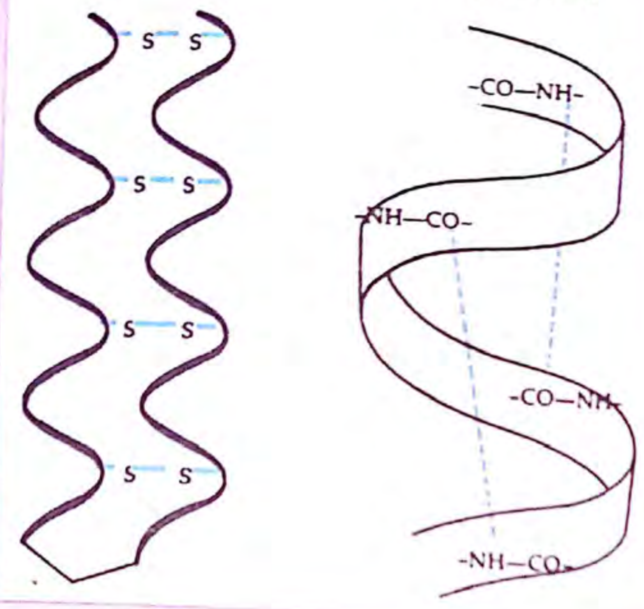


Fig. 30.11 a-Helical structure of polypeptide chains.



a) Two adjacent a-helical coils with disulphide cross-linkages.

(b) Hydrogen bonding in an a-helical polypeptide chain.

The cross-linkages between chains may be *disulphide bridges* (–S–S–) or they may be ionic bonds between the basic amino and the acidic carboxyl groups.

The three dimensional structure refers to the way the polypeptide chains of a protein are arranged in space to form coils and sheets (fibrous proteins) or compact spheroids (globular proteins). These shapes are maintained partly by hydrogen bonds and partly by cross-linkages which occur between the polypeptide chains.

X-ray crystallography shows that many of the polypeptide chains in proteins have an α-helical structure.

The shape of a protein molecule is important for its biological function. For example, an enzyme protein must come in close contact with its substrate to bring about chemical change. This can only happen if the shape of the enzyme molecule allows the enzyme to fit into the substrate molecule.

Properties

Denaturation Proteins usually form colloidal solutions. When such solutions are heated, the proteins precipitate or coagulate. This is due to irreversible changes in the molecular shapes of the proteins, and the proteins are said to be denatured. Proteins are easily denatured by

- temperatures above 40 °C,
- certain organic solvents and chemical reagents, and
- variations in pH.

Since the function of a protein is related to its shape, a denatured protein loses its biological activity. This is why living systems operate within narrow temperature and pH ranges.

Hydrolysis Proteins can be hydrolyzed to give amino acids by boiling them with solutions of hydrochloric acid or sodium hydroxide. Hydrolysis can also be carried out by using suitable enzymes. The amino acids obtained on hydrolysis can be separated and identified by using paper chromatography. This is the procedure that was used in identifying the amino acid sequence in the polypeptide chains of many proteins.

Tests for proteins

Biuret test Add about 1 cm^3 of dilute caustic soda solution into a test-tube containing some dilute egg-white solution. Then add 1% copper(II) tetraoxosulphate(VI) solution drop by drop. The test solution is shaken thoroughly after each drop. The formation of a violet coloration is a positive test for proteins.

Millon's test Add a drop or two of Millon's reagent to some egg-white solution in a test-tube. The formation of a white precipitate which turns brick-red on heating indicates the presence of proteins.

Trioxonitrate(V) acid test Add three or four drops of concentrated trioxonitrate(V) acid to 2 cm^3 of egg-white solution. The formation of an intense yellow colour indicates the presence of proteins.

NOTE A solution of egg-white is prepared by mixing egg-white with three times its volume of water. Add a little common salt to make the egg-white dissolve.

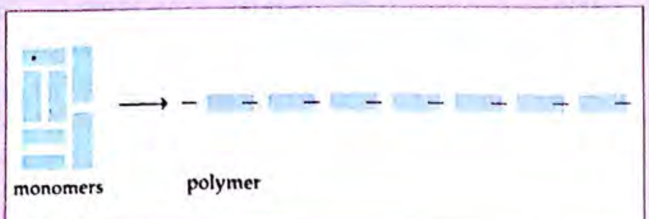
POLYMERS

Many organic compounds contain thousands of atoms per molecule. Such large molecules are known as giant molecules or macromolecules.

We may regard any molecule with a relative molecular mass of 5 000 or more as a macromolecule.

Certain macromolecules are formed by joining

Fig. 30.12 Monomers join to form a polymer.



together a large number of much smaller molecules to form a long chain. The starting material is known as a *monomer* (*mono* means one; mer means part or unit). The final product which is a macromolecule of high molecular mass is called a *polymer* (poly means many).

Thus, a polymer consists of a repeating unit and its general molecular formula may be represented simply as $+$ repeating unit $+_n$ where n is a very large whole number. The molecular size of a given polymer is not fixed, i.e. *n* is a range of numbers. Polymers may be natural or artificial.

NOTE All polymers are macromolecules but not all macromolecules are polymers, e.g. diamond is macromolecular but it is not polymeric.

Natural Polymers

All living things contain important organic compounds which can broadly be grouped into fats and oils, carbobydrates and proteins.

Fats and oils are not large enough to be grouped as giant molecules and hence are not polymers. However, certain carbohydrates such as starch and cellulose and all proteins are giant molecules that are polymers. Rubber and many resins are also natural polymers found in plants.

Chemists subjected natural polymers like cellulose to chemical treatment in order to produce polymers with certain desired qualities. This led to artificial polymers like cellulose acetate and viscose rayon. However, once chemists discovered that polymers were made up of repeating units of monomers, they were able to synthesize polymers from small organic molecules. This led to the production of a whole range of very useful synthetic polymers.

Synthetic Polymers

Synthetic polymers are commonly called *plastics*. The term *plastic* comes from the Greek word *plastikos*, which means to mould. Nowadays, plastics refer to synthetic materials which can be softened by heat or pressure, and then moulded into any desirable shape.

Thermoplastics and thermosets

Plastics are either

- *thermoplastics*, or
- *thermosets.*

Thermoplastics can be softened repeatedly by heat and remoulded. Thermosets, however, cannot be softened or melted by heat and remoulded once they are formed or *set*.

Table 30.4 Thermoplastics and thermosets.

Thermoplastics	Thermosets
Polythene	Bakelite
Polypropene	Urea-methanal
Polystyrene	
Nylon	
Terylene	
Perspex	

Desirable properties of plastics

Practically everything around us is made of some type of plastic. The following factors have made our present *plastic age* possible.

1 Plastics have properties which make them suitable for many purposes. Plastics are strong but light; inert to air, water, and other chemicals; resistant to fungal and bacterial attacks; and good insulators of heat and electricity.

2 Plastics can be tailor-made to our exact requirements. They can be made into hard, rigid blocks; thin, flexible sheets; fibres that can be made into ropes and fabrics; and very light foams. They have wide applications.

3 Raw materials for the manufacture of plastics are readily and cheaply available from the refining of crude oil. The boom of the oil industry has contributed greatly to the growth of the plastics industry.

4 Plastic items can be manufactured at very low costs by using moulds and automated manufacturing processes.

Problems with the use of plastics

There is a heavy dependence on crude oil, since petrochemicals provide the bulk of the raw materials needed for making plastics. This poses a problem as the world's supply of crude oil is limited. Alternative energy sources that are being explored do not provide the raw materials needed for making plastics.

Most plastic materials are non-biodegradable and cannot be broken down by microbial action into simple inorganic forms. Therefore, they cause severe land pollution problems since they are not easily disposable. Burning plastic objects would not be a good alternative as this would liberate toxic vapours or gases into the atmosphere.

Making Polymers

Synthetic polymers are made by the *polymerization* of monomers. For polymerization to occur, heat and the presence of a chain-initiating substance called an initiator are required.

Polymerization is the process whereby two or more monomers link together to form a compound of high molecular mass called the polymer.

There are two kinds of polymerization–

- *addition polymerization,* and
- condensation polymerization.

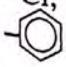
Addition polymerization

In addition polymerization, the monomers simply join together to form the polymer which has the same empirical formula as the monomer, but is of a higher molecular mass. The polymerization may be represented as follows:

$nA \rightarrow (A)_n$ where A is the monomer.

The monomers must be simple, unsaturated molecules with double bonds, e.g.

- ethene and propene, or
- substituted ethenes of the type, $CH_2 = CHX$ where X can be
  - –H,
  - –R,
  - –Cl, –CN, or



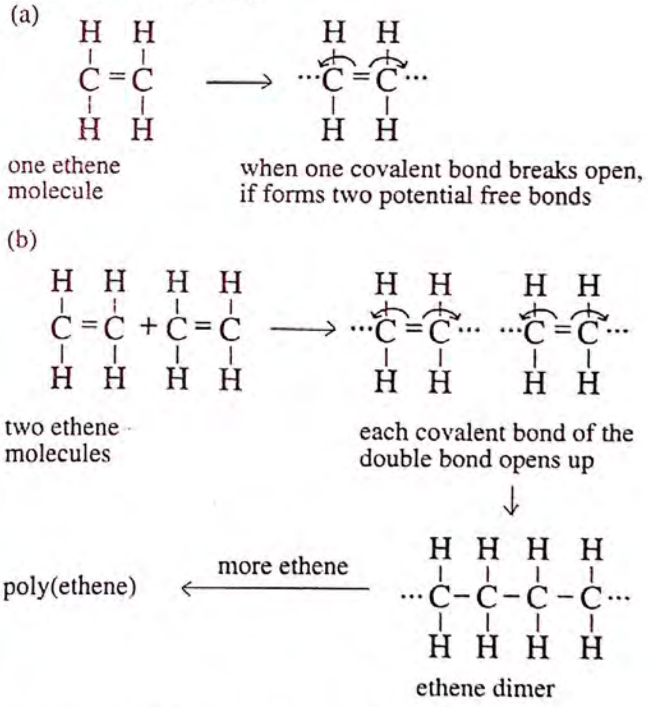
Addition polymerization is the process whereby two or more of the same monomers link together to form the polymer without elimination of any small molecules.

Most monomers are derived from petrochemicals. The cracking process in oil refineries produces a number of unsaturated hydrocarbons. Of these, ethene, CH_2CH_2, is the most important (the group, $CH_2 = CH–$ was formerly known as vinyl). Polymers made from ethene or its derivatives are called vinyl-type polymers.

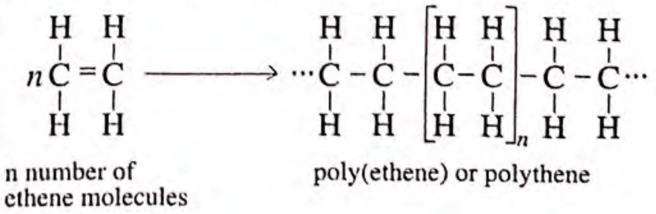
Addition polymers include

- poly(ethene),
- poly(chloroethene),
- poly(phenylethene),
- perspex, and
- poly(propenonitrile).

Ethene molecules undergo polymerization in the following way:



Thus, the formation of ploy(ethene)can be summarized as shown:



OR

$n\,CH_2 = CH_2 \rightarrow \cdots CH_2 - CH_2 \left[CH_2 - CH_2 \right]_n CH_2 - CH_2 \cdots$

Where $CH_2 - CH_2 -$ is the repeating unit.

Poly(ethene) If ethene is subjected to a high temperature of about 250 °C and pressure above 1 500 atm, together with traces of oxygen (as an initiator), it polymerizes into poly(ethene). This polymer, which is also known as *polythene*, can be represented as $[CH_2–CH_2]_n$, where n = 1 000 to 10 000.

The poly(ethene) obtained by the above method is called low *density poly(ethene)*. There is also a *high density poly(ethene)*, prepared at a lower temperature and pressure by using catalysts.

Low density poly(ethene) is used in making a wide range of products. The most important ones are plastic bags, bottles, kitchen wares, and transparent films for packaging garments and foodstuff. It is also used as wire and cable insulators because of its insulating properties.

High density poly(ethene) is used for making large boxes, crates, detergent bottles dustbins and harder plastic bags than-those made from low density poly(ethene).

Poly(chloroethene) Poly(chloroethene) is also known as *polyvinyl chloride* or PVC. It is manufactured from either ethene or ethyne. Ethene is first chlorinated to form chloroethene (vinyl chloride), $CH_2{=}\ CHCl$, which is the starting monomer. Chloroethene is polymerized at about 55 °C under pressure in the presence of hydrogen peroxide as catalyst.

$$n\,CH_2=CHCl$$

chloroethene

$$\downarrow$$

$$\cdots CH_2-CHCl-[CH_2-CHCl]_n-CH_2-CHCl\cdots$$

poly(chloroethene) or polyvinyl choride

Experiment 30.4 To prepare perspex.

Method Add about 0.1 g of an organic peroxide (catalyst) to 10 cm^3 of methyl 2-methyl-propenoate in a test-tube. Immerse the test-tube in a water-bath at 60 to 70 °C for about an hour. The liquid monomer will polymerize to a solid polymer. To get the polymer out, it is necessary to break the test-tube.

Result A glassy, transparent solid is obtained on warming the methyl 2-methylpropenoate.

Conclusion Perspex is obtained by warming methyl 2-methylpropenoate in the presence of an organic peroxide catalyst.

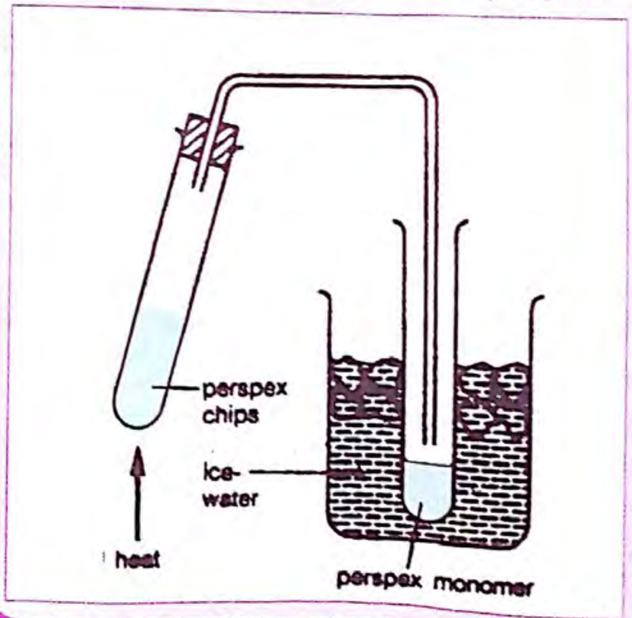
Experiment 30.5- To depolymerize perspex.

Method and Results Place some perspex chips in a hard glass test-tube. Heat the chips carefully with a strong Bunsen flame. Immerse the test-tube for collecting the products that form on heating the perspex chips in a beaker of ice-water as shown. A clear liquid condenses in the cooled test-tube. This is the monomer that gives rise to perspex on polymerization.

NOTE A strong Bunsen flame is used as it will keep carbonization to a minimum and inhibit subsequent repolymerization.

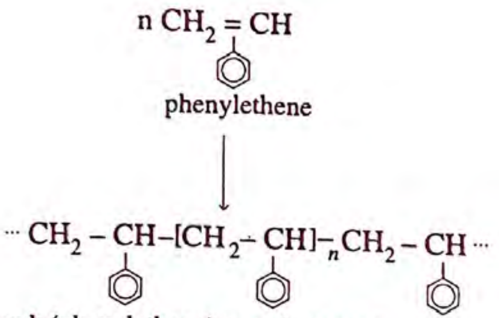
Conclusion Perspex can be easily depolymerized.

Fig. 30.13 The depolymerization of perspex.



Specially hardened poly(chloroethene) is used for making tough plastic pipes, cable coverings, artificial leather cloths, records and even tiles. Plasticised poly(chloroethene) is quite soft and flexible and is used for making things like shower curtains, table clothes, raincoats and hand gloves.

Poly(phenylethene) Commonly known as *polystyrene,* poly(phenylethene) is made from the monomer phenylethene (or styrene) by refluxing, using a solution of benzoyl peroxide as catalyst.



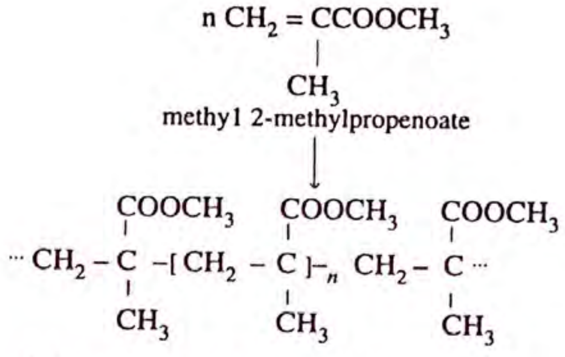
poly(phenylethene) or polystyrene

Polystyrene is a clear transparent plastic which is hard but brittle. When air, coupled with a foaming agent, is blown into heated polystyrene, it expands into a light, white, opaque solid that floats in water. This is known as expanded polystyrene or *styrofoam.*

Polystyrene is used for making *see-through* containers and lighting fixtures since it is a good electrical insulator. Expanded polystyrene is used as ceiling tiles and lamp shades because of its lightness. Due to its high compressibility, it is widely used as packing materials or as shock absorbers for fragile objects during transportation. It is also used for making disposable cups and food containers, especially in fast-food shops.

Perspex If the disubstituted ethene, methyl 2-methyl-propenoate, is heated, it polymerizes to give poly(methyl 2-methylpropenoate) or PMMA for short. This material is commonly known as *perspex.* An organic catalyst, lauryl peroxide, is used in this process.

Perspex is a strong, hard, transparent thermoplastic with a glossy surface. Because ot its glasslike appearance, it is often used as a replacement for glass. Unfortunately, unlike glass, it is easily scratched.



$$n\,CH_2=\underset{CH_3}{C}COOCH_3$$

methy1 2-methylpropenoate

$$\downarrow$$

$$\cdots CH_2-\overset{COOCH_3}{\underset{CH_3}{C}}-[CH_2-\overset{COOCH_3}{\underset{CH_3}{C}}]-_n\,CH_2-\overset{COOCH_3}{\underset{CH_3}{C}}\cdots$$

poly(methy1 2-methylpropenoate) or perspex

Perspex is used to make car rear lights, wind-shields, window-panes, fish tanks, contact lenses, street-lamp housing and others.

Poly(propenonitrile) Propenonitrile is the starting monomer for preparing the polymer poly-(propenonitrile). It is derived from ethene by substituting one of the hydrogen atoms with a –CN group. The polymer formed is commonly known as *polyacrylonitrile.* The catalyst for this polymerization is an organic peroxide.

$$n\,CH_2=CHCN$$

propenonitrile

$$\downarrow$$

$$\cdots CH_2-[CHCN-CH_2]-_n\,CHCN\cdots$$

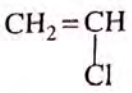
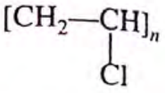
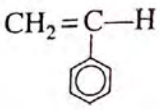
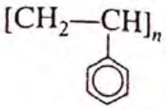
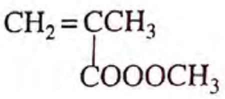
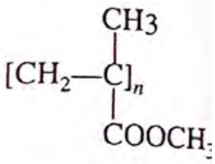
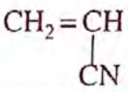
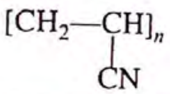
poly(propenonitrile)

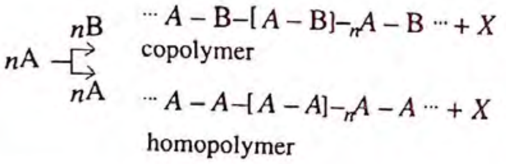
Poly(propenonitrile) is used chiefly for making textile. It is spun into threads and used for making *woolly* garments. One such material is popularly known as *Orlon.*

Condensation polymerization

Condensation polymerization differs from addition polymerization in that small molecules such as water, ammonia or hydrogen chloride are eliminated during the formation of the polymer. If the two condensing monomers are of different types, the resultant polymer is called a *copolymer.* If they are the same, then the resultant polymer is a *homopolymer.* Generally, the reaction is represented as follows:

Table 30.5 Some common addition polymers.

Name	Common name	Monomer	Repeating Unit
Poly(ethene)	Polythene, polyethylene	$CH_2{=}CH_2$	$[CH_2—CH_2]_n$
Poly(chloroethene)	Polyvinyl chloride (PVC)	 $CH_2{=}\underset{Cl}{CH}$	 $[CH_2—\underset{Cl}{CH}]_n$
Poly(phenylethene)	Polystyrene		
Poly(methyl 2-methyl propenoate)	Perspex	 $CH_2{=}\underset{COOCH_3}{CCH_3}$	 $[CH_2—\overset{CH3}{\underset{COOCH_3}{C}}]_n$
Poly(propenonitrile)	Polyacrylonitrile, acrylic fibre, Orlon	 $CH_2{=}\underset{CN}{CH}$	 $[CH_2—\underset{CN}{CH}]_n$



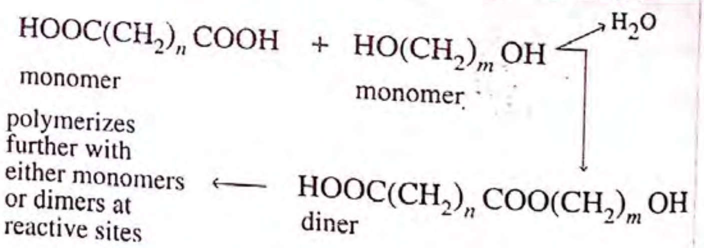
NOTE *X* is a small molecular by-product like H_2O, HCl or NH_3.

Condensation polymerization is the process whereby two or more monomers link together to form the polymer with the elimination of a small molecule.

In the esterification reaction studied earlier, the acid and the alkanol condense to give a dimer with the elimination of a water molecule. Since each monomer has only one active functional group, i.e. a hydroxyl group, –OH, and a carboxylate group, –COOH, the reaction stops once the ester is formed.

$$\underset{\text{monomer}}{RCO\boxed{OH}}\ +\ \underset{\text{monomer}}{\boxed{H}OR'} \xrightleftharpoons{H^+} \underset{\text{dimer}}{RCOOR'} + \underset{\text{by-product}}{H_2O}$$

For further condensation to occur, each monomer must have at least two active functional groups. Examples of such monomers are dicarboxylic acids and diols. Reactions between two such monomers results in a dimer with two reaction sites, one at each end of the molecule. This dimer is able to undergo further condensation with more monomers to give rise to a longer chain polymer.



NOTE The condensation polymers have parent chains made up of carbon and some other atoms. The polymer formed in this reaction is known as a polyester because there are many ester linkages.

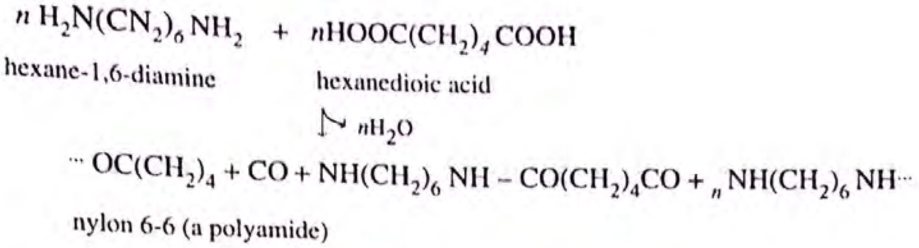
The relative molecular mass of a condensation polymer is not an exact multiple of the monomers as in an addition polymer. This is because there is a loss in mass during the condensation process.

The two most important condensation polymers are

- *nylon,* and
- *terylene.*

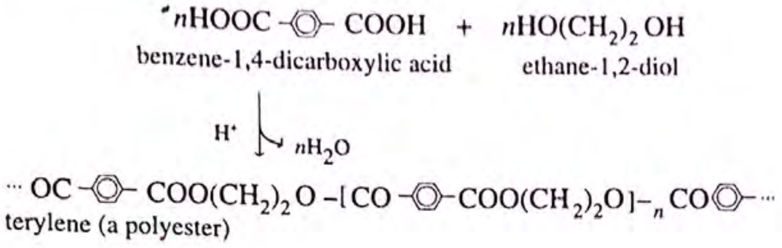
The former is a *polyamide* and the latter a *polyester.*

Preparation of nylon 6-6



$$n\,H_2N(CN_2)_6NH_2 + nHOOC(CH_2)_4COOH \xrightarrow{-nH_2O} \cdots OC(CH_2)_4 + CO + NH(CH_2)_6\,NH - CO(CH_2)_4CO +_n NH(CH_2)_6\,NH\cdots$$

Preparation of terylene



Nylon This is a general term that refers to a group of synthetic fibres. There are many types of nylon. In nylon 6.6, the two monomers are hexane-1,6 diamine, $H_2N-(CH_2)_6-NH_2$, and hexanedioic acid (adipic acid), $COOH-(CH_2)_4-COOH$. Both monomers are bifunctional. In the initial condensation, the –COOH group of the acid reacts with the $-NH_2$ group of the amine, with the elimination of water, to form the amide linkage group, –CO–NH–.

Nylon 6.6 can be prepared by mixing an aqueous solution of hexane-1,6-diamine to hexanedioic acid in tetrachloromethane.

Nylon is extensively used as a synthetic fibre because of its very high tensile strength. Thus nylon fibres are ideal for making ropes, fishing lines, nets and racquet strings. Nylon is also used to replace many steel parts in machines like gears and bearings. These parts are not only hard but also smooth so that they do not need lubrication.

Nylon is used for making all kinds of clothing. Such clothing *drip-dry* easily, and are crease-free and resistant to fungal and moth attacks. However, nylon clothing do not absorb moisture and are uncomfortable to wear in warm weather. This property is common to clothing made of other synthetic fibres as well. Nowadays, most clothing made of nylon and other synthetic fibres contain a certain amount of natural fibres like cotton which can absorb moisture.

Terylene This is a polyester that is also known as *dacron* in the U.S.A. It is formed by the condensation of benzene-1,4-dicarboxylic acid (terephthalic acid) and ethane-1,2-diol, using an acid catalyst.

Terylene is another synthetic fibre which is mainly used in the manufacture of synthetic textiles. It is soft and is capable of retaining an almost permanent crease. Woven terylene is used for making the sails of boats where a strong rot-proof material is required.

Phenol-methanal, urea-methanal and melamine-methanal Phenol-methanal is commonly known as *bakelite*. This is a hard plastic or resin. It is formed by condensing hydroxybenzene (phenol), and methanal in the presence of an acid or an alkali as catalyst.

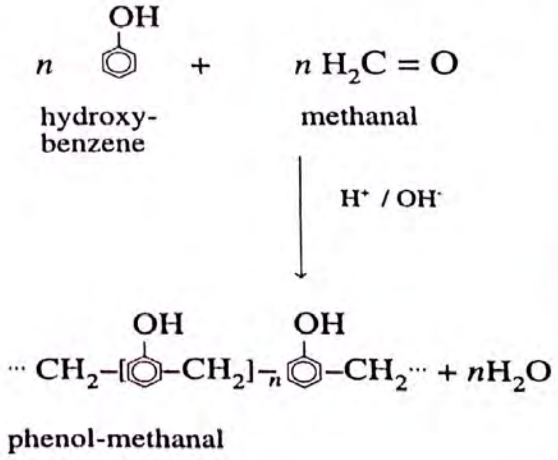
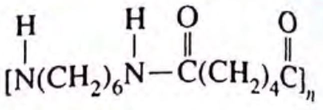
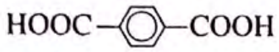
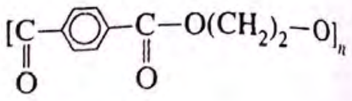
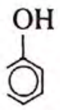
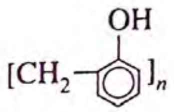


Table 30.6 Condensation of polymers.

Name	Monomers	By-product	Repeating unit
Nylon 6.6	$H_2N(CH_2)_6NH_2$ hexane-1,6-diamine $HOOC(CH_2)_4COOH$ hexanedioic acid	H_2O	 $[\overset{\text{H}}{\text{N}}(\text{CH}_2)_6\overset{\text{H}}{\text{N}}-\overset{\text{O}}{\text{C}}(\text{CH}_2)_4\overset{\text{O}}{\text{C}}]_n$ a polyamide
Terylene	 benzene-1,4-dicarboxylic acid $HO(CH_2)_2OH$ ethane-1,2-diol	H_2O	 a polyester
Phenol-methanal	 hydroxy-benzene $H_2C=O$ methanone	H_2O	

Various other synthetic resins may be produced using compounds other than phenols. For example,

- urea condenses with methanal to form urea-methanal resins, and
- melamine condenses with methanal to form melamine-methanal resins.

Phenol-methanal is a dark-brown polymer which is often used to make plugs, switches, utensil handles, telephone casings, radio housing and sockets. Its excellent electrical insulating property, together with its non-combustible quality, makes it an ideal material for the electrical industry.

Urea-methanal is similar to phenol-methanal except that it is transparent and can easily be coloured with pigments. It is used for making electrical fittings and kitchenware. This plastic is also prepared as a foam, which is commonly used as a heat insulator.

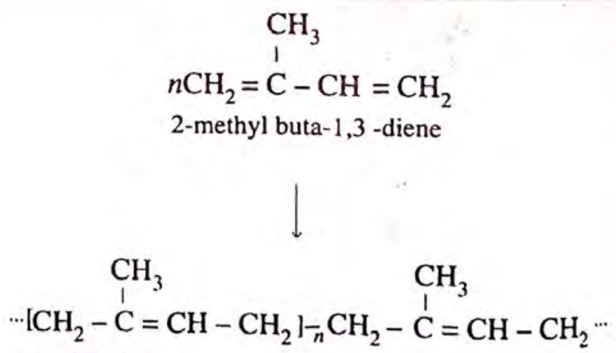
Melamine-methanal is similar to urea-methanal. It can be produced in attractive colours and is used mainly to make unbreakable, heat-resistant cups, plates and bowls.

Rubber

Rubber is another group of important polymers. Both natural rubber and synthetic rubber are now available.

Natural rubber

Rubber is obtained from the rubber tree, *Hevea brasiliensis*. When the bark of the tree is cut, a thick white liquid called latex oozes out. If the latex is collected and heated, it changes into an elastic solid called *rubber*. This rubber is of little use because it is soft and sticky. Chemically, it consists of 2-methyl buta-1,3-diene monomers known previously as *isoprene*.



$$n\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$$

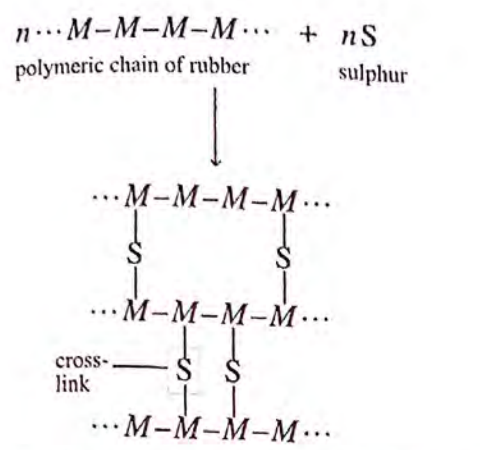
2-methyl buta-1,3 -diene

$$\downarrow$$

$$\cdots[\text{CH}_2-\overset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2]_n\text{CH}_2-\overset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2\cdots$$

natural rubber

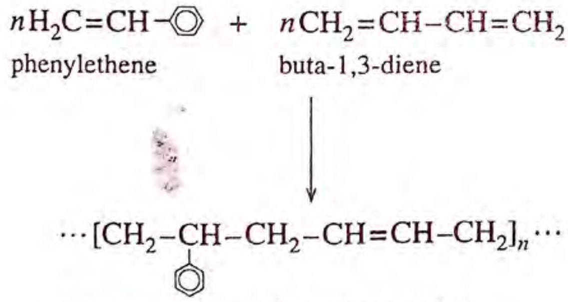
When the monomers polymerize, they form long polymeric chains which have only a limited number of cross-links between them. By adding sulphur and heating, the soft rubber becomes hard. This process is known as *vulcanization*. The sulphur atoms form strong cross-linkages which hold the long rubber chains together. This gives rubber greater tensile strength, durability and elasticity over a wide range of temperatures.



where M = $[CH_2(CH_3)C{=}CHCH_2]_n$

Synthetic rubber

The first synthetic rubber was poly(2-chlorobuta1,3-diene) or *neoprene*. Later, styrenebutadiene rubber (SBR), thiokol, poly(buta-1,3-diene) and poly(2-methyl propene) were invented. Of these, SBR is the most useful all-purpose synthetic rubber.

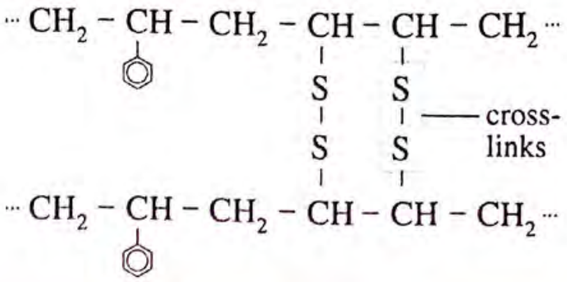


a polymeric chain of synthetic rubber

SBR is obtained by the copolymerization of phenylethene (styrene) with three parts of aqueous buta-1,3-diene. It is vulcanized by carefully heating it with about 3% by mass of sulphur. As a result, bridges of sulphur atoms are formed between adjacent polymeric chains at the double bond positions. This gives SBR and synthetic rubber its elasticity and hardness.

SBR rubber is often used in making vehicle tyres and footwear because of its high resistance to abrasion.

SBR rubber (a copolymer)



POLYMERS IN LIVING SYSTEMS

Natural polymers are found widely in living things where they play important structural and functional roles. The main polymers are carbohydrates and proteins. Carbohydrates and proteins, together with fats and oils, are the main classes of foods that are necessary to sustain life.

NOTE Fats and oil will be considered in this section as they are important large molecules in living systems.

Carbohydrates

Carbohydrates such as starches, glycogen and cellulose are the energy sources of living things. These polymers are made up of simple sugars such as glucose.

Glucose is the first product of photosynthesis, the process whereby green plants manufacture food. In this process, carbon(IV) oxide, CO_2, and water, H_2O, are combined to form glucose $C_6H_{12}O_6$. The energy for the reaction comes from sunlight. The green pigment, chlorophyll, plays an important role in trapping the sun's energy.

During the process, water molecules are split to provide the reducing agent that is needed to reduce carbon(IV) oxide to glucose. Many reaction steps are involved in this process.

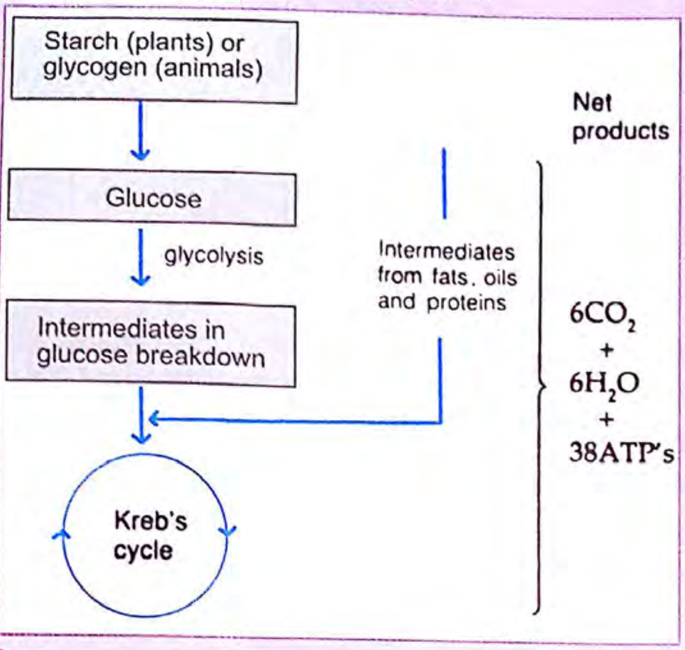
Splitting of water $$2H_2O \rightarrow \underset{\text{R.A.}}{4[H]} + O_2$$

Reduction of CO_2 $$CO_2 + 4[H] \rightarrow \underset{\text{sugar}}{CH_2O} + H_2O$$

The overall reaction can be written as follows:

$$12H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6H_2O + 6O_2$$

Fig. 30.14 Scheme showing the breakdown of carbohydrate in living cells.



In plant cells, thousands of glucose molecules are linked to form starch and cellulose molecules. Cellulose is found only in plants. It is used as a building material and is the main component of plant cell walls and fibres. Starch is stored in the seeds and various other parts of the plant. It acts as a store of energy-rich food.

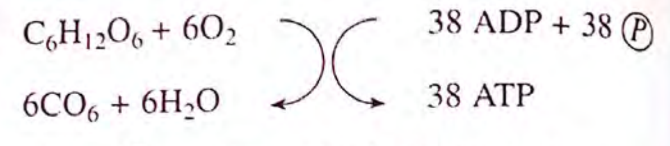
When a plant is eaten by an animal, the starch is broken down to glucose units in the digestive system of the animal. This is because the molecule of starch is too big to diffuse through the living cell membranes of the digestive system. Glucose is a small molecule and is soluble in water. Therefore, it is absorbed into the body of the animal easily. In most animals, the glucose is carried by the blood to the liver to be recombined to form *glycogen* or animal starch.

All living organisms use stored glycogen and starch mainly as a source of energy for their various biological activities. The energy is obtained by the step by step breakdown of glucose, which comes from the hydrolysis of starch or glycogen. This process is known as *cellular respiration*.

The first few steps in the breakdown of glucose do not require oxygen and are referred to as glycolysis. Further breakdown involves oxygen. This pathway is known as the *Kreb's citric acid cycle*. The complete breakdown of glucose to carbon(IV) oxide, water and energy involves both glycolysis and Kreb's cycle. This process is often called the *oxidative metabolism of glucose* and can be represented as follows:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2 + \text{energy}$$

The energy released in the various steps in the breakdown of glucose is linked to the production of high energy adenosine triphosphate (ATP) molecules. ATP is an organic compound which is made up of three tetraoxophosphate(IV) groups. It is formed from adenosine diphosphate (ADP) and a tetraoxophosphate(IV) group.



where Ⓟ represents hydrogentetraoxophosphate(IV) acid.

A total of 38 ATP molecules are produced by the complete oxidation of one molecule of glucose.

ATP is the most important immediate source of energy in all living cells. The energy in ATP is released when it is hydrolyzed to ADP. Some of this energy can be used directly by the cell for its biological activities, the rest is lost as heat.

$$\text{ATP} + H_2O \rightarrow \text{ADP} + H_3PO_4 + 34\ \text{kJ}$$

Many intermediate products in the breakdown of sugar are used to produce other useful substances, such as fats, oils and proteins, that are needed by living organisms.

Fats

Fats and oils are important energy stores in living things. In animals, fats are stored in fat storage cells which are usually found under the skin.

To liberate their store of energy, fats and oils are first broken down to intermediate products which then enter the Kreb's cycle to give rise to the production of ATP molecules. Certain fats are important structural components of living cells.

Proteins

Proteins are mainly used as building materials by living things, especially animals. Important substances in living systems like enzymes, hormones and immunoglobins are proteins.

Proteins may be used as a source of energy. This happens during starvation. The proteins in muscles are first broken down to amino acids. These are then broken down further to produce intermediates that can enter the Kreb's cycle and lead to the production of ATP molecules.

Enzymes

Enzymes are protein molecules secreted by special cells in a living organism. They are organic catalysts responsible for the metabolic reactions that take place in living organisms. Thus, glycolysis, synthesis of proteins and photosynthesis are mediated by numerous enzymes.

NOTE Metabolic reactions include both the building up processes and breaking down processes that take place in living organisms.

Enzymes may be classified according to the type of reactions they catalyze. Thus, enzymes that catalyze hydrolytic reactions are known as *hydrolases*. Examples are amylase which digests starch, protease which digests protein and lipase which digests fat. Another type of enzyme is the *oxidation-reduction enzyme* which is concerned with the oxidation of food substances. Examples are oxidase, dehydrogenase and oxygenase.

Properties Common characteristics of enzymes are as follows:

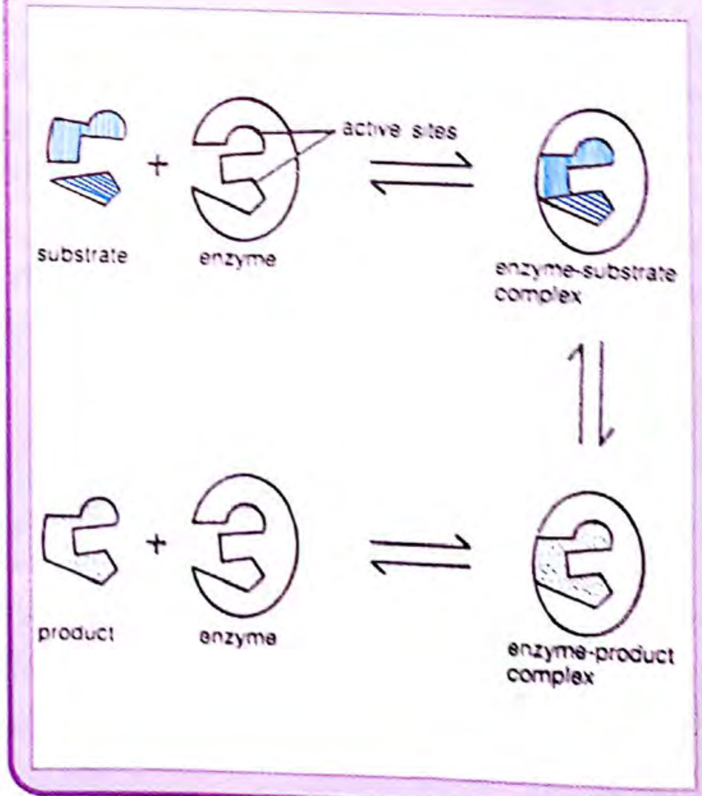
1 Enzymes are soluble. This is important since biochemical reactions occur in an aqueous medium.
2 Enzymes are proteins. Some enzymes require certain substances called *coenzymes* to activate them. These coenzymes are non-proteins.
3 Enzymes are specific, i.e. each enzyme can act only on a specific substrate or a group of substrates. No two different enzymes can act on the same substrate in the same way.
4 Enzymes are temperature-sensitive. They work best between 33–40 °C with the optimum temperature being 37 °C. At temperatures above 40 °C, their activities decrease as they tend to become denatured.
5 Enzymes are pH-sensitive. Different enzymes require different ranges of acidity and alkalinity to be active.
6 Enzymes can be inactivated by inhibitors, such as cyanides and compounds of lead and mercury.
7 An enzyme can catalyze reversible reactions in either direction depending on the conditions. The enzyme, however, only speeds up the reaction until equilibrium is reached. It has no effect on the equilibrium point.
8 Enzymes work very rapidly.

How enzymes work The *lock-and-key hypothesis* is used to explain enzyme-controlled reactions. Briefly, the following steps are assumed to occur during such reactions.

1 The enzyme and substrate molecules come together to form an *enzyme-substrate complex*.
2 The substrates in the complex react together to form an *enzyme-product complex*.
3 The enzyme-product complex splits to give the enzyme and the product.

The unchanged enzyme goes on to form another enzyme-substrate complex. Thus, the enzyme is used over and over again. The regions on the enzyme into which the substrate molecules fit are known as the *active sites* of the enzyme. This is why the shape of the enzyme molecule is important for its biological function.

Fig. 30.15 Lock-and key hypothesis to show how enzymes work.



Uses

Enzymes have many uses in adidition to their vital biochemical functions.

Industrially, enzymes are used in the manufacture of ethanol from sugars and starches, and in cheese making. They are also used in some detergents to help break down biological substances, like blood, which cause stains. Other products that contain enzymes are meat tenderizers and vitamins. Doctors use medicines containing enzymes to clean wounds of dead tissues and to dissolve blood clots.

SUMMARY

- Alkanoic acids form a homologous series represented by the general molecular formula $C_nH_{2n+1}COOH$. Alkanoic acids with two and three carboxyl groups are known as dicarboxylic and tricarboxylic acids respectively.
  - (a) Alkanoic acids can be prepared by the oxidation of the corresponding alkanol, for example ethanoic acid is prepared from ethanol.
  - (b) Alkanoic acids dissolve in water to form weak acids.
  - (c) Solubility of alkanoic acids in water and their acidic nature decreases as the number of carbon atoms in the alkyl group (R) increases.
- Esters, $RCOOR^{/}$, are salts formed by the reaction between alkanoic acids and alkanols.

$$\text{alkanoic acid} + \text{alkanol} \underset{\text{hydrolysis}}{\overset{\text{esterification}}{\rightleftharpoons}} \text{ester} + \text{water}$$

- Fats and oils are naturally occurring esters. Fats, usually of animal origin, are solids while oils, usually of plant origin, are liquids. Oil can be converted to fat by hydrogenation. Fats and oils undergo hydrolysis in a process called saponification to form soaps.
- Soaps are made from fats and oils while detergents are synthetic substances built from petroleum products. But both soap and detergent molecules have hydrophilic heads and hydrophobic tails. Therefore, both help in the action of cleansing.
- Alkanals have the general molecular formula $RCHO^{/}$, while alkanones have the general formula $RR'CO$.
  - (a) Alkanals are readily oxidized, while alkanones are not.
  - (b) Alkanals and alkanones are reduced to primary and secondary alkanols respectively.
- Carbohydrates have the general formula $C_x(H_2O)_y$. Carbohydrates can be classed into
  - (a) monosaccharides or simple sugars (glucose and fructose),
  - (b) disaccharides consisting of two simple sugar units (sucrose), and
  - (c) polysaccharides (starch and cellulose) which are polymers with a simple sugar as a monomer.
- Amides have the general molecular formula $RCONH_2$. They react with aqueous sodium hydroxide and bromine to give the corresponding amines, RNH_2.
- Amino acids are the basic components of proteins. There are twenty kinds of naturally occurring amino acids.

  (a) Amino acids have the general structure $H_2NRCHCOOH$.
  (b) The carboxyl group of one amino acid reacts with the amino group of another with a loss of one molecule of water to form a peptide. The bond formed is the peptide bond.
  (c) A polypeptide chain consists of many amino acids linked together by peptide bonds.

- A protein consists of one or more polypeptide chains.
  (a) The amino acid sequence in a polypeptide chain is important in determining the three-dimensional structure of the protein molecule.
  (b) The shape of a protein molecule is important for its biological function.
  (c) Proteins are denatured by heat. This is due to an irreversible change in their shape which results in a loss of their biological function.

- Polymerization is a process whereby two or more simple molecules link together to form a much larger molecule. The simple molecules are known as the monomers, and the complex molecule formed by the linking of the monomers is known as the polymer.
  (a) In addition polymerization, two or more of the same monomers link together to form the polymer without elimination of any small molecules. Poly(ethene), poly(chloroethene) and poly(phenylethene) are examples of such polymers.
  (b) In condensation polymerization, two or more monomers link together to form the polymer with the elimination of a small molecule, such as water or ammonia. Synthetic fibres like nylon and terylene are examples of such polymers.

- Rubber is a natural polymer obtained from the latex of the rubber tree. Synthetic rubber is also available.

- Important natural polymers in living systems include carbohydrates, proteins and enzymes. Fats and oils, though not giant molecules, are biologically important large molecules.
  (a) Fats and carbohydrates are the main sources of energy for biological activities. This energy is liberated in the form of ATP molecules by the step by step breakdown of a simple sugar like glucose. The process is known as cellular respiration.

  $$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2 + \text{energy}$$

  (b) Proteins are used as building materials in living systems and as components of substances with important biological functions.
  (c) Enzymes are the organic catalysts of biochemical reactions.

- Enzymes are proteins which catalyze biochemical reactions by forming enzyme-substrate complexes. The shape of an enzyme is very important as it has to fit into the substrate molecules exactly to form the complex

EXERCISES

1. The name of $(CH_3)_2$ $CHCOOH$ is
A propanoic acid.
B 2-methyl propanoic acid.
C dimethyl butanoic acid.
D 2, 2-dimethyl propanoic acid.

2. Citric acid appears in unripe orange while ethanoic acid appears in
A unripe pawpaw. B carrot.
C vinegar. D ethanol soured.

3. From $HCOOH(aq) + C_2H_5OH(aq) \rightleftharpoons HCOOC_2H_5(l) + H_2O(l)$
Which of these is/are acids?
A $HCOOH$
B $HCOOH + C_2H_5OH$
C $HCOOC_2H_5$
D $HCOOH$ and $HCOOC_2H_5$

4. Esters are employed in the following except
A making perfumes.
B making cement.
C making solvents for cellulose trioxonitrate V.
D nail varnishes.

5. Oil can be changed into fat in the presence of nickel at 180°C through a process called
A alkylation. B polymerization.
C hydrogenation. D substitution.

6. "Lux", "omo", washing liquids are all
A soaps.
B emulsifying and curdy agents.
C detergents.
D all contain synthetics and oil.

7. Most non-soapy detergents are
A biodegradable.
B non-degradable.
C alkoxides.
D scum.

8. Major advantages of non-soapy detergents over soap-detergents is that
A they form scum.
B they do not form scum and are capable of reacting with hydrogen ions.
C they do not form scum but reacts with hydrogen ion.
D they do not retain their cleansing power after washing.

9. All carbohydrates contain
A carbon and oxygen.
B carbon, hydrogen and sulphur.
C carbon, oxygen and hydrogen.
D carbon, water and phosphorus.

10. Monosaccharides are
A hydrolysable.
B non-hydrolysable.
C sweet but sometimes non-sugary.
D not soluble in water.

11. Sucrose is different from starch in that sucrose is
A hydrolysable.
B reacts with iodine solution.
C reacts with seliwanoff's reagent.
D sucrose reacts with both iodine solution and seliwanoff's reagent.

12. Cellulose, starch, fructose and glucose are all
A alkanols. B alkanones.
C proteins. D carbohydrates.

13. Proteins hydrolyse to
A polypeptides. B monopeptides.
C colloids. D peptide linkages.

14. Most enzymes are
A inorganic catalysts.
B proteins.
C carbohydrates.
D amines.

15. Rubber latex is converted to tough rubber by the addition of
A sulphur.
B cross linkers and phosphorus.
C polymers and carbon.
D isoprene.

16. These are condensation polymers except
A nylon.
B terylene.
C phenol-methanol.
D esters.

17. An alkanoic acid reacts reversibly with an alkanol to produce.
A a salt.
B an ester
C a sugar
D an amide.
E an acid anhydride.

18. Ethanedioc acid is
A a mineral acid.
B a dicarboxylic acid.
C commonly known as citric acid.
D a common fatty acid.
E an aromatic carboxylic acid.

19. Natural rubber is a polymer of
A 2-methyl buta-1,3-diene or isoprene.
B methanal.
C phenylethene or styrene.
D propenonitrile.
E hydroxybenzene.

20. (a) Give the formula of ethanoic acid and indicate its functional group.
(b) Ethanoic acid reacts with both sodium hydroxide and ethanol. Using equations, compare the two reactions and classify the products.
(c) What happens when ethanoic acid is heated strongly with soda-lime?

21. (a) Give the experimental details of how you would prepare ethyl ethanoate.
(b) Using an equation, describe the hydrolysis of ethyl ethanoate.
(c) What happens when ammonia gas is bubbled through ethyl ethanoate?

22. (a) What do you understand by the term *saponification*?
(b) Outline how a sodium soap may be prepared in the laboratory.
(c) Write briefly on detergents and explain their advantages over soap.

23. (a) What is obtained when a carbohydrate is completely dehydrated?
(b) What are monosaccharides? Give examples and show how they differ structurally.
(c) How would you obtain glucose from starch?

24. (a) What are disaccharides? The various disaccharides are said to differ mainly in their component monosaccharides. Give the component monosaccharides of the following.
(i) Maltose (ii) Sucrose
(iii) Lactose
(b) How would you identify the following?
(i) Glucose (ii) Starch
(iii) Sucrose

25. (a) Using an equation, explain how the structure of amino acids is suited for the formation of a polymeric chain.
(b) Describe the hydrolysis of proteins.

26. (a) Write briefly on the nature and properties of enzymes.
(b) Explain how enzymes work using the lock-and-key hypothesis.

27. One desirable property of plastics is that they can be made into very complicated shapes. Explain how this is done.

28. When a strong solution of tin(IV) bromide is added to a 50% solution of phenylethene in 1,2 dichloroethane, it is found that the volume of the mixture decreases with time and that the viscosity of the mixture increases with time.
(a) Draw the structural formula of phenylethene.
(b) Why do we use 1,2-dichloroethane and not water to dissolve phenylethene?
(c) How would you explain the visible change in appearance of the mixture with time? What could be the final product?

29. (a) Write out part of the structure of the product formed when the monomers, urea, H_2NCONH_2, and methanal, HCHO, undergo polymerization.
(b) Is urea-methanal an addition polymer or a condensation polymer?
(c) On heating some poly(methyl 2-methylpropenoate) chips, a liquid distillate is obtained. What could be the distillate?

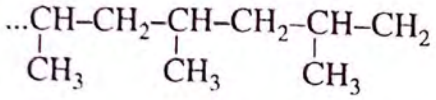
30. Part of the structure of some polymers are represented below. For each,

(a) draw the structural formula of the repeating unit.

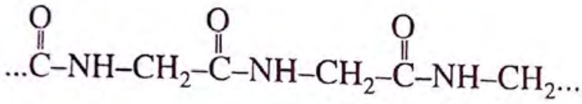
(b) the IUPAC name and structural formula of the monomer(s).

(c) identify if they are addition polymers or condensation polymers. If it is the latter, name the by-product that is eliminated.

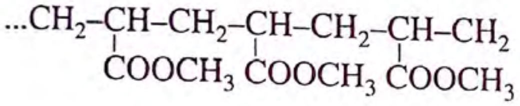
- $\ldots CF_2-CF_2-CF_2-CF_2\ldots$

- 

  $\ldots\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2$

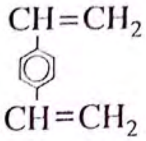
- 

  $\ldots\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{O}{\|}}{C}-NH-CH_2\ldots$

- 

  $\ldots CH_2-\underset{COOCH_3}{\underset{|}{CH}}-CH_2-\underset{COOCH_3}{\underset{|}{CH}}-CH_2-\underset{COOCH_3}{\underset{|}{CH}}-CH_2$

31. Poly(phenylethene) is a thermoplastic with linear polymeric chains. If traces of a compound like 1,4-diethenyl benzene is introduced to poly(phenylethene), some crosslinking occurs. Draw the structural formula of the copolymer and indicate its repeating units.



32. Write short notes on

(a) addition polymers,

(b) condensation polymers,

(c) synthetic rubber,

(d) thermoplastics and thermosets.

Give an example in each case.

33. Discuss the importance of polymers in living systems.

SECTION
FIVE

APPLIED CHEMISTRY

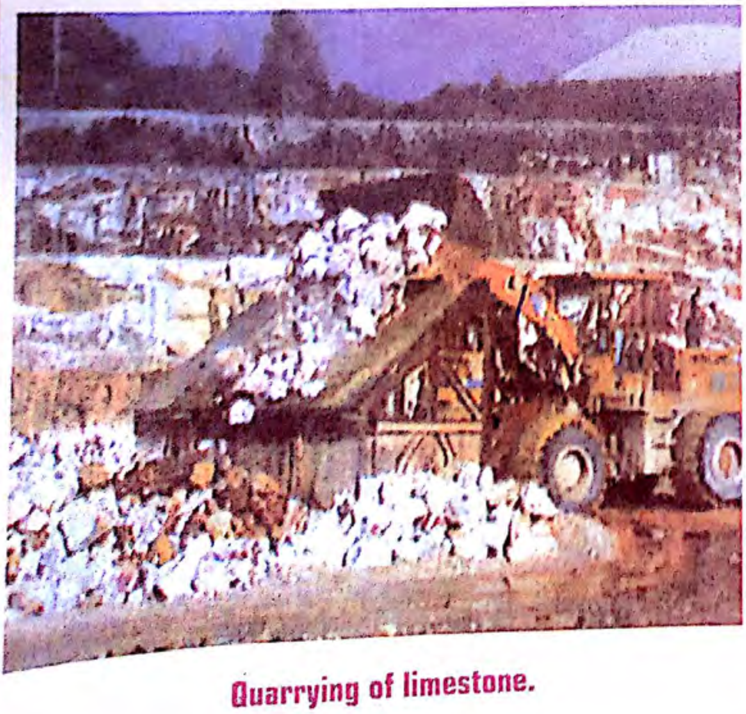
31

INDUSTRIAL CHEMISTRY

DEVELOPMENT OF THE CHEMICAL INDUSTRY

The development of the chemical industry had important effects on chemistry. Soon after the Middle Ages, factories supplying soap, alum, acids and other basic chemicals were set up. As society became complex, the need to develop and produce important chemicals grew. Chemists set to work to fulfil these needs. Wars also served as a force in accelerating these developments.

In 1749, the Lead Chamber process for the commercial manufacture of hydrogentetraoxosulphate(VI) was developed. This initiated a whole new range of other chemical industries. Later, in 1791, the Leblanc process for the making of trioxocarbonate(IV) was invented. Extensive industrial chemical research, however, was not in full swing until 1856 when William Perkin discovered the first aniline dye. Then, research by teams of scientists became the norm in chemical industry. The Haber process for the manufacture of ammonia was developed under such conditions. This led to an increase in the demand for trained chemists.



Quarrying of limestone.

IMPORTANT RAW MATERIALS

To find out more about the various chemical industries, it is a good idea to visit such industries sited in your community. You will be able to see the raw materials used and how they are converted into the various products that are in great demand by society.

The important raw materials are coal, natural gas, petroleum, limestone, salt or sodium chloride, metallic ores, sulphur and air. All except air are mined from the earth's crust. Salt is obtained mainly from sea water. Many other raw materials are derived from these main raw materials.

We have already discussed the formation and sources of coal. Chemicals derived from coal are by-products of the process by which bituminous coal is converted into coke. The gas and vapours are led to special equipment to yield fuel gas, ammonia and coal tar. Coal tar contains a number of chemicals such as benzene, toluene, phenol, naphthalene and cresols.

Petroleum, natural gas and their derivatives are discussed in chapter 28. The industrial uses of coal and petroleum are summarized in fig. 31.1.

Mining salt.

Limestone rocks, caves and cliffs exist in many parts of the world. From limestone we get lime or calcium oxide which is used for making cement and concrete.

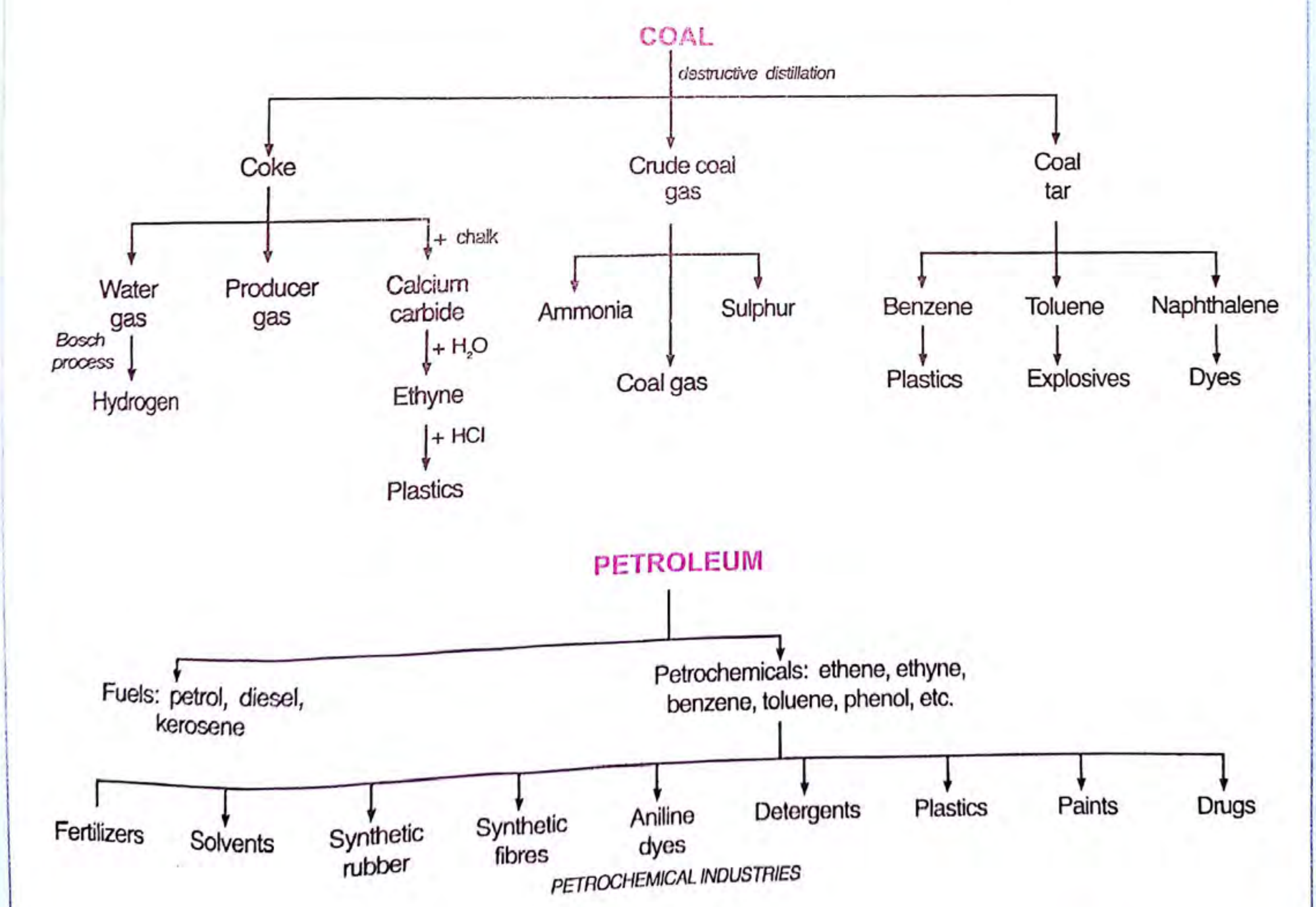
Salt or sodium chloride occurs as rock salt in underground deposits and in sea water. Electrolysis of sodium chloride produces chlorine. The other main product is sodium hydroxide which is used in the manufacture of soap and textile, and in petroleum refining. The chlorine produced can be made to react with hydrocarbons obtained from fossil fuels. These chlorohydrocarbons are versatile raw materials. They are used in the making of synthetic rubber, paint removers, refrigerants and several types of insecticides, and in dry cleaning.

Sulphur occurs naturally in some places. It is also obtained as a by-product when sulphide ores of copper or zinc are treated. Most of the sulphur is converted into hydrogentetraoxosulphate(VI) acid. This acid is manufactured in much greater quantities than any other chemicals. It is used in many chemical processes and in the manufacture of fertilizers, paints, dyes, explosives, synthetic fibres and accumulators.

Important metals such as iron, aluminium and copper are extracted from their respective mineral ores. This has given rise to the metal extraction industries in countries where the ores are available. The metals are used mainly in the construction of buildings and bridges, and in making machines, vehicles, ships and aircraft.

Air is the chief source of oxygen and nitrogen. The latter is used in the manufacture of ammonia by the Haber Process. Ammonia is used mainly in the production of fertilizers and trioxonitrate(V) acid.

Fig. 31.1 Industrial uses of coal and petroleum.



DIVISIONS OF THE CHEMICAL INDUSTRY

The chemical industry is founded on a wide variety of raw materials. Amongst the most important are coal, molasses, salt, mineral ores, water, air and fats and oils of animal and plant origin. Petroleum is a fairly recent addition to the list.

Since the chemical industry produces a variety of products, it is useful to classify the industry on the basis of its products. We have chemical industries which produce

- basic chemicals such as acids, alkalis, salts and organic chemicals;
- chemical products that are used in the manufacture of artificial fibres and plastics;
- chemical products used as starting materials in other industries that manufacture substances such as paints, fertilizers and explosives; and
- chemical products such as cosmetics, drugs and soap for our personal use.

The chemical industry is now defined as *one that uses chemistry to make chemicals from other chemical substances.*

Hydrocarbon chemical plant for the manufacture of basic organic chemicals.

Heavy Chemicals

The most useful basic chemical that the chemical industry makes is hydrogentetraoxosulphate(VI) acid. It is used in many chemical processes — from making fertilizers to cleansing (pickling) steel. Sodium hydroxide for making soap and other things is also produced in large quantities. Ammonia is another chemical that is manufactured in large quantities. It is used to make fertilizers as well as explosives. These and other chemicals are called *heavy chemicals* because they are made in very large quantities.

Fine Chemicals

Drugs and chemicals produced in relatively small amounts are referred to as *fine chemicals*. These are also produced to a very high degree of purity.

Drugs used in medicine have to be manufactured in a very pure form.

Fertilizers

The fertilizer industry is an important one. Fertilizers are needed to increase crop yield to feed the world's rapidly increasing population.

Three important elements have to be provided in suitable form in fertilizers. They are nitrogen, phosphorus and potassium (commonly referred to as N.P.K.). Nitrogen is supplied mainly in the form of ammonia which in turn is obtaind from fossil fuels. The ammonium compounds used are ammonium trioxonitrate(V) and ammonium tetraoxophosphate(V). Some sodium trioxonitrate(V) is also used as a source of nitrogen. Sometimes, ammonium tetraoxosulphate(VI), recovered as a by-product from the conversion of coal into coke, is also used.

Phosphorus is obtained in nature as rock phosphate. It has to be treated with hydrogentetraoxosulphate(VI) acid to get it into a form that can be used in fertilizers. The phosphorus can be converted into superphosphates, triple superphosphates and tetraoxophosphate(V) acid. This acid can then be converted into ammonium tetraoxophosphate(V).

Potassium, in the form of its several salts, is mined from underground deposits. Potassium compounds, nitrogen compounds and phosphorus compounds are mixed together in most of the fertilizers used nowadays. The proportions in which they are mixed are usually given as the N.P.K. values. In many cases, small quantities of trace elements (such as zinc, boron, copper and molybdenum) are added, depending on their need in certain regions.

Plastics

The modern plastics industry developed to a great extent out of a search for a substitute for rubber during World War II. In the nineteenth and early twentieth century, the four main sources of raw materials for the plastics and synthetic organic chemical industries were *coal*, *limestone*, *cellulose* and *molasses*.

Coal yielded

- benzene for the synthesis of poly(phenylethene), commonly known as polystyrene;
- phenol, methanal and urea for the syntheses of a range of thermosetting plastics.

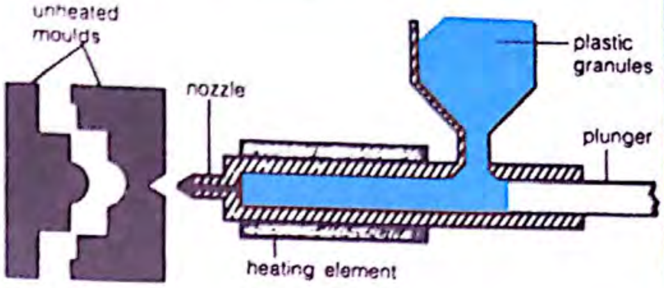
Limestone, when heated with coal produced calcium carbide, which yielded ethyne under suitable treatment. The ethyne is used in the manufacture of poly(chloroethene), commonly known as polyvinyl chloride.

Molasses yielded ethanol from which ethene is produced. The ethene is used to produce a range of poly(ethene) plastics.

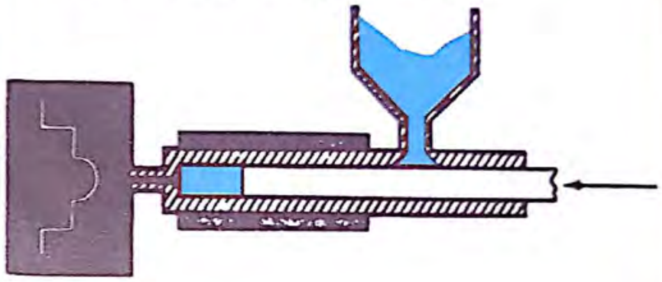
Nowadays, starting raw materials are obtained by the fractional distillation of crude oil or petroleum. The plastics are manufactured in their raw form as granules or powder. These are then exported to fabrication plants to be manufactured into various products.

Fig. 31.2 Injection moulding.

(a) Plastic granules are first melted.

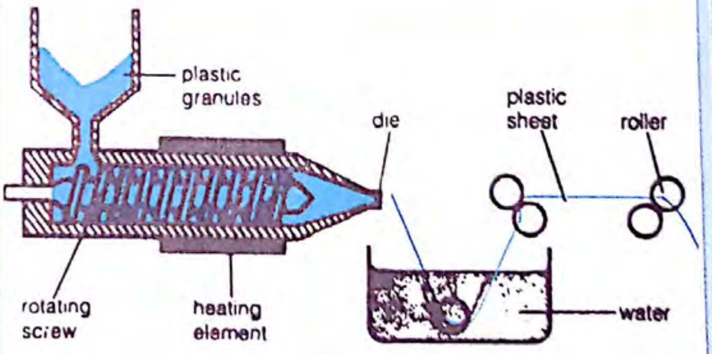


(b) The molten plastic is injected into a mould.



(c) Finished product.

Fig. 31.3 Extrusion.



Most plastic processing methods involve heating the raw material (in the form of granules or powder) until it softens, shaping the softened material and then setting it. Two important processes used are *injection moulding* and *extrusion*.

In injection moulding, the plastic granules are heated until they are soft enough to flow. The softened plastic is then forced under pressure into a closed mould cavity where it can cool to form the shape of the mould. Since the cavity is filled under pressure, every detail of the mould would be faithfully reproduced in the finished part.

In the extrusion process, a continuous flow of molten plastic is forced through a shaped opening called a die, and the plastic is then cooled. Depending on the shape of the opening, many different parts can be made. If the opening is like a ring, a tube or pipe can be made. If the opening is a long thin slit, a sheet may be formed. One application of extrusion is in the plastic covering of wires and cables for insulation purposes. Another adaptation is in extrusion coating. Paper, fibreboard and aluminium foil are coated with polymers by the direct extrusion process. The plastic coating enhances the packaging properties. For example, plastic coated paper is impermeable to water and oil and is hence used in the packaging of food products.

The plastic industry is divided into four categories — bags, household and kitchen wares, industrial plastic supplies ard miscellaneous items. The industrial plastic supplies cover items such as casings for radios, cassette recorders and TV sets; and PVC pipes and fittings for the building industry. The miscellaneous items include precision-moulding of plastics to produce gears and bobbins for digital clocks; and rollers, hubs and clamps for audio and video cassettes.

The plastics industry has achieved remarkable success by widening the use of its products as well as by diversifying its applications.

Rolls of steel sheets in an iron and steel plant.

Metallurgy

Metallurgy is the science of extracting metals from their ores and preparing them for practical and commercial use. Metallurgical processes include the refining of metals and the manufacture of alloys for special purposes. The manufacture of steel is especially important because of its wide application. Details are given in chapter 26.

Pharmaceuticals

Since ancient times, we knew that some substances had the power to heal certain diseases. Many plant extracts had such medicinal properties. In the beginning, chemists concentrated their attention on isolating the active components in such extracts and using them. Nowadays, chemists are involved in the synthesis of such compounds. The discoveries of sulphonamides and antibiotics have led to a great improvement in the quest for a better life. Drugs of today have conquered many diseases considered incurable in the past. They include

- quinine for the treatment of malaria, and
- insulin for the treatment of diabetes.

The majority of the drugs manufactured nowadays are synthetic. Some of them are identical to natural substances found in plants and animals, while others are entirely new. Especially useful are the sulpha drugs which are used to treat pneumonia and other serious illnesses. The most widely used drug is aspirin. It was discovered in coal tar but nowadays it is manufactured synthetically.

Glass

Sand appropriately blended with various other substances has given us glass. Window panes, mirrors, bottles, fruit jars, drinking glasses and dishes are made of glass. Lenses for still and television cameras are made of glass. Chemists use a large number of test-tubes, beakers and other apparatus made of glass for their experiments.

There are many kinds of glass. They may be transparent, translucent or coloured, depending on the purpose for which they are used. Glass used in ovenware has to be heat resistant. The glass used in test-tubes and beakers must be resistant to chemicals. To produce these different properties, the composition of glass and the heat treatment have to be varied.

In nature, glass is formed during volcanic eruptions. The Egyptians were the pioneers in the art of making glass, but the foremost glassmakers of the olden days were the Romans. Today, the industry is almost completely mechanized, though hand operations are still used in some small-volume specialized fields. The chief processes used for making glass are much the same as they have been in the past. Sand, soda, lime and other materials are mixed together and melted in a furnace at a very high temperature to produce molten glass. While the glass is molten, it is shaped and made to cool so as to form a rigid piece. The glass piece is annealed by reheating it and then gradually cooling it. In modern glass manufacturing factories, machines do a lot of work that were done by hand previously.

Ovenware, heavy tumblers and many other kinds of glassware are shaped entirely by pressing. A quantity of hot glass of the right size and shape is delivered to a metal mould which is set in position under a plunger. The plunger forces the hot glass into the space between the mould and the plunger and holds it there until it has solidified.

Window glass is made by drawing a continuous vertical sheet from a pool of molten glass. Plate glass is made by rolling.

Massive shapes such as architectural blocks and mirror banks used for big telescopes are made by casting. For this purpose, heat-resistant moulds are used and molten glass is poured into them.

Like most materials, glass contracts on cooling. Furthermore, glass is a poor conductor of heat. Thus, it is quite possible that during the forming process, various parts of the glass may be at different temperatures and will solidify at different times. Each part will tend to contract by different amounts as it cools to room temperature. Since cold glass is rigid, the difference in contraction will cause internal stress to develop. To prevent this, the glass must be annealed. Most glass today is annealed in continuous furnaces called *lehrs*. The glassware is placed on a metal belt that conveys it through a tunnel. The temperature along the tunnel is graduated so that after passing through a hot zone, the glassware is slowly cooled to a safe handling temperature at the end of the belt.

Annealing of bottles at a glass factory.

Ceramics

The art of processing earthy materials into useful or ornamental objects through the application of high heat is known as *ceramics*. The art of making ceramic products goes back beyond the era of recorded history. Up to the early years of the twentieth century, ceramics were produced by trial and error.

In recent years, chemistry and physics have joined hands to unravel the secrets of ceramic materials. This has resulted in better products and more varied uses.

Scientists can now produce ceramics that can withstand the stress and heat imposed by the supersonic speeds of aircraft and by nuclear reactors. They are also used in critical parts of rockets and spacecraft, such as the nose cones, rocket exhaust nozzles and heat-resistant windows.

The raw materials used are silica and oxides of magnesium, aluminium, zirconium, thorium, titanium and boron. Some artificial carbides and nitrides are also used nowadays. The raw materials are ground to a uniform consistency and mineral impurities are removed. The cleaned materials are then heated to temperatures between 500 °C and 3 000 °C. During these processes, certain physical and chemical changes are brought about. These changes make the ceramics strong and durable.

Paints

Paint is a fluid mixture which contains suspended colouring material. When it is applied as a thin layer on a surface, it produces an opaque solid film. Although its early use was chiefly decorative, protection against weathering and corrosion is an equally important use in the modern times.

Most paints are applied by brushing, but other methods such as spraying, dipping and roller coating are also used.

Cement

Cement is made by heating a mixture of powdered lime (calcium oxide) and clay. When mixed with water, it can be used to fasten stones and bricks together. The mixture (called *mortar*) hardens like stone when it dries.

The most popular cement is known as *Portland cement*. This type of cement is made by heating a mixture of limestone and clay, and grinding the products. It consists of calcium silicates (as a result of the reaction between silica and calcium oxide) and calcium aluminates (formed by the reaction between calcium oxide and aluminium oxide present in clay). Complex chemical changes occur during setting, resulting in a hard mass.

Portland cement is mainly used as a component of *concrete*. Concrete is made by mixing cement, sand and broken stones or gravel. The sand and gravel must be clean and free from soft particles and vegetable matter. Water is then added to the mixture which forms a rock-like mass when it hardens. In the late nineteenth century, it was found that concrete can be reinforced with steel rods. *Reinforced concrete* revolutionized the building industry. It is used in highways, bridges and dams. It is also used in virtually all large buildings. One of the advantages of concrete is that it can be poured into forms, and it hardens in place so that the whole structure is like one huge stone. There are no joints to worry about.

Soaps and Detergents

Soap is defined as a chemical compound or a mixture of chemical compounds resulting from the reaction between fatty oils, or fats, and alkalis.

It is manufactured by introducing melted fats into an excess of sodium hydroxide solution and boiling the mixture. The pasty boiling mixture is then treated with brine. This causes the contents to separate into two layers. The upper layer contains impure soap. This is then washed to remove the excess alkali and salt and treated in various ways to give the desired product.

Detergents are synthetic cleansing products. They are often made from petrochemicals. Detergents are used to wash dishes, laundry, walls and floors.

Soaps and detergents have the property of reducing the surface tension of water. They are able to lift dirt from greasy surfaces thereby reducing the spread of germs.

Food and Drinks

Chemical and biochemical processes are used in preserving, flavouring and enriching the nutrient content of food and drinks. The production of alcoholic drinks such as beer involves fermentation processes, which have to be carefully controlled.

In the preparation of food and drinks, certain specified standards have to be met. Chemists analyze samples of food and drinks routinely to ensure that these standards are met.

ECONOMICS OF INDUSTRIAL PROCESSES

The economics of an industrial process is mainly linked to

- raw materials, energy requirements and transport;
- use of by-products and recycling; and
- supply and demand.

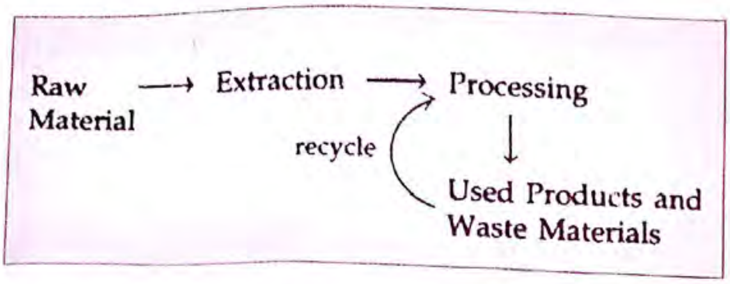
(See the table on page 581.)

Raw materials, energy requirements and transport

Raw materials should be easily and cheaply obtainable. Fuel supplies are very expensive. So the energy requirements of an industrial process has to be taken into consideration before starting a particular chemical industry. Road, rail and sea links should be present to transport both raw materials and finished products. These three factors should be taken into account in the siting of a chemical factory. Only then can the industrial process be economically feasible.

Use of by-products and recycling

Where possible any chemical produced as a by-product should be used so that it does not form uneconomic waste. An industrial process should also ensure that used products and waste materials can be returned to the processing stage, i.e. recycled. Recycling conserves the world's supply of non-renewable raw materials such as metals. It is also economical as the recycled material does not pass through the energy-demanding extraction stage.



Supply and demand

The demand for a certain substance may change suddenly so that the basic process of a chemical industry has to be altered for it to be economical. For example, in the past, the heavy fractions of crude oil were in great demand. Now, the lighter petrol and natural gas fractions are in demand. Crude oil industry is meeting this demand by cracking chemicals in the heavier fractions to produce the smaller molecules found in the lighter fractions.

IMPORTANCE OF INDUSTRIAL CHEMISTRY IN NIGERIA

Chemical industries require:

- raw materials,
- energy,
- water,
- machinery,
- labour, both skilled and unskilled,
- transportation for the raw materials and products, and
- markets for the products.

Nigeria has a rich supply of petroleum, natural gas and coal which are important raw materials needed in chemical industries. Other important inorganic raw materials include limestone, tin, columbite, clay and iron ore. Raw materials of plant and animal origins include rubber, palm oil, oils from groundnut and cotton seed, and cellulose. Nigeria uses these raw materials for her own chemical industries as illustrated by the following examples.

1 Refineries, such as the one at Port Harcourt, use petroleum to produce many products like fuel gases, kerosene, petrol and diesel oil.
2 Soap and margarine are made from vegetable oils.
3 Cement is made from limestone at factories located at Nkalagu, Ewekoro, Calabar and Benue.
4 Glass is produced from silica at Port Harcourt.
5 Steel is manufactured from iron ore and scrap iron at the iron and steel works at Ajaokuta.
6 Cosmetics, plastic goods and paints are produced from petrochemicals at factories in Lagos.

A cement plant – the site was chosen because of the availability of limestone shale, coal and water.

Nigeria exports raw materials to countries which need them for their own industries.

Chemical industries require energy. The amount and type of energy needed will depend on the chemical process. Nigeria has its own supply of energy from fossil fuels like petroleum, natural gas and coal, and also from moving water (hydroelectric power). The power plants which supply electrical energy to the chemical industries use mainly petroleum and natural gas. The Nkalagu Cement Factory uses coal as its major source of energy.

Most chemical industries need plenty of water, especially for cooling. Very pure water is needed for certain chemical processes like dyeing. Nigeria, with its many rivers, has a plentiful supply of water.

Nigeria has to spend money to import machinery that is needed in chemical industries.

Chemical industries need highly skilled chemists, chemical engineers and technicians. Our schools, colleges and universities have the facilities to train such people. The requirement for unskilled labour is not high in chemical industries as in other industries like building and food processing industries.

Nigeria has adequate road and railway transportation. Industries which use heavy raw materials like cement and iron ore are usually located in the areas where the raw materials are produced. Chemical industries that use imported raw materials or which export a greater part of their products are built near coastal towns and ports like Lagos and Port Harcourt.

Nigeria exports both raw materials for chemical industries and products from her own chemical industries to other countries. The chemical industries also supply many products for domestic use. Thus, we see that chemical industries

- provide earnings from foreign trade;
- improve the standard of living by providing many materials for domestic use (which would be too expensive if they were imported); and
- provide employment.

Many chemical industries in Nigeria are carried out on a large scale. There are also small scale chemical industries such as pottery, dyeing and tanning of leather.

SUMMARY

- A chemical industry is one that uses chemistry to make chemicals from other chemical substances (raw materials).
- The most important basic raw materials for the chemical industry are petroleum, natural gas, coal, limestone, sodium chloride and sulphur.
- The chemical industry can be classified according to the products produced. We have industries that produce
  - (a) heavy chemicals,
  - (b) fine chemicals,
  - (c) fertilizers,
  - (d) plastics,
  - (e) metals from ores,
  - (f) pharmaceuticals,
  - (g) glass,
  - (h) ceramics,
  - (i) paints,
  - (j) cement, and
  - (k) soaps and detergents.
- The economics of an industrial process is linked to raw materials, energy requirements, transport, use of by-products, recycling, and supply and demand. The economic feasibility of some important industrial processes is given below.

Process/Industry	Economic feasibility
• Liquefaction of air to produce oxygen (see page 362)	• Clean process; the raw material (air) is readily available; low energy demand; gases are useful.
• Solvay process for the manufacture of sodium trioxocarbonate(IV) (see page 443)	• The starting materials, sodium chloride and calcium trioxocarbonate(IV) are cheap and readily available; by-products can be reused; energy demand is fairly high but is compensated by the high demand for the products.
• Electrolysis of brine to produce sodium hydroxide, chlorine and hydrogen (see page 211)	• Three commercially important products are obtained; raw material is cheap and readily available; energy demand is high but is compensated by the high demand for the products.
• Contact process for the production of tetraoxosulphate(VI) acid (see pages 263 and 384)	• Exothermic reactions reduce energy demand and produce enough excess energy for use by other processes.
• Haber process for the production of ammonia (see pages 262 and 396)	• Highly efficient; exothermic reactions produce enough energy for the process to be feasible.
• Manufacture of trioxonitrate(V) acid (see page 405)	• Exothermic reaction provides enough energy for the process to continue after the initial energy supply to start the process.

- The chemical industries are of economic importance as they provide foreign trade earnings and employment, and improve the standard of living.

EXERCISES

1. Fine chemicals have the following characteristics except
   A they are chemically pure.
   B they are produced by batch process.
   C they are produced in large quantity because of high applicability.
   D they are produced in small quantity because of limited applicability.

2. Examples of heavy chemicals include
   A $NaOH$
   B perfumes.
   C H_2SO_4
   D NH_3

3. Plastics are polymers whose production technique involves, except
   A high pressure.
   B low temperature.
   C high temperature.
   D setting.

4. Metallurgy is a scientific process which involves the following except
   A manufacture of alloys.
   B manufacture of both natural and artificial catalysts.
   C refining of metals.
   D grading of metals.

5. Ceramics have the following characteristics except
   A heat and chemical resistant.
   B amenable to corrosion since they are of earthly impurities.
   C it withstands stress.
   D they are strong and durable.

6. The major difference between cement and mortar is that
   A mortar hardens by giving off water.
   B cement hardens by giving off water.
   C mortar is always white.
   D cement is always coloured because of superheating.

7. These are examples of chemical industries except
   A photosynthesis.
   B solvay process.
   C electrolysis of brine.
   D contact process.

CHEMISTRY OF EARTH AND SPACE

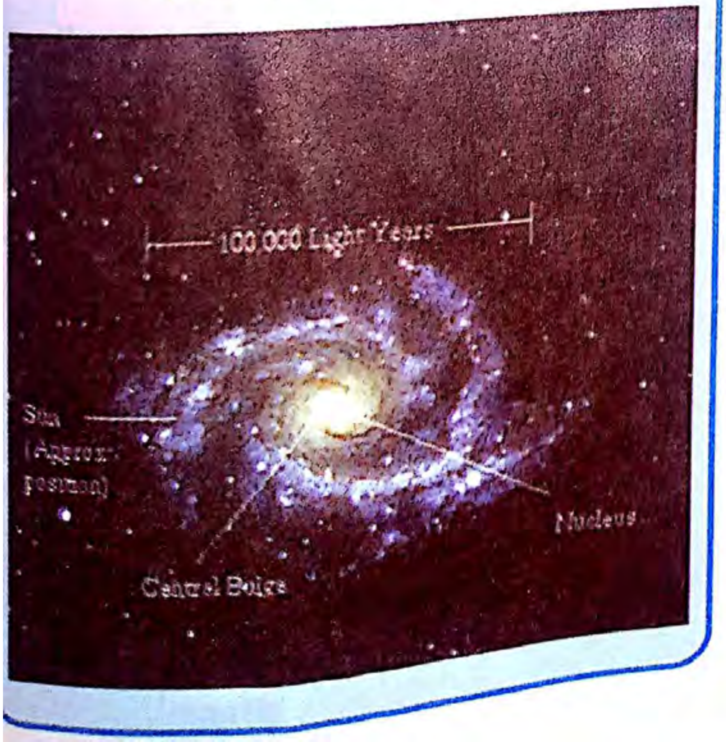
32

EARTH

The Universe includes everything we know but no one knows its size, how it began or when it will end. Some astronomers say that the Universe was formed in the distant past when a single body of matter exploded to form galaxies which spread out through space.

A galaxy is a huge collection of stars, gas and dust. Our own star, the Sun, is one of the more than 100 000 million stars that make up our galaxy, the Milky Way. For a long time, astronomers thought that our galaxy was the whole universe. We now know that a large number of other galaxies exist beyond our own. Earth is one of the planets that orbit round the Sun. It is the only planet that is known to have life.

Fig. 32.1 The Milky Way is a spiral, disc-shaped galaxy. It is about 100 000 light years across and about 13 000 light years thick at its centre. Our Solar System is located near the edge of this galaxy, about 30 000 light years from its centre.



Age of Earth

Various methods were used in the past to find out the age of Earth. The most exact method is based on the study of the radioactivity of certain minerals in which one or more radioactive elements decay to form other elements.

A radioactive element decays to a daughter element at a constant and known rate that is known as its *half-life*. The half-life is not affected by external conditions. As the radioactive element decays, its quantity in a particular rock decreases while the quantity of the daughter element increases. Scientists are able to calculate the age of the rock or mineral from

- the decay rates of the radioactive element (which are known), and
- the ratios of the parent and daughter elements.

The radioactive isotopes most commonly used for these studies include carbon-14, rubidium-87, potassium-40, uranium-235, uranium-238 and thorium-232. The quantities are measured by radiation detectors. The method is not exact and the ages obtained may vary by as much as several hundred million years.

Studies using the above method show that the oldest known rock on Earth was formed nearly 4.0 x 10^9 years ago. Based on this, we can say that Earth is between 4.5×10^9 to 5.0×10^9 years old.

Structure of Earth

Earth is made up of three parts:

- the *atmosphere* which is the layer of air that surrounds the planet;
- the *hydrosphere,* which is the part composed of water; and
- the lithosphere, which is the solid part

Atmosphere

The air surrounding Earth is composed of about 78% nitrogen, 21% oxygen and 1% other gases including carbon(IV) oxide, water vapour and the rare gases. Dust and air pollutants are also present in the atmosphere, especially in the big cities, and industrial and agricultural areas. The atmosphere extends to a height of more than 450 km from the surface of Earth.

The lower layer (up to about 10 km at the poles and about 17 km at the equator above the Earth's surface) is known as the *troposphere*. This is the region where great changes in temperature and water vapour content of the air take place. It is the part of the atmosphere which determines the weather–clouds form here, and the rains, thunder and lightning occur here.

The next atmospheric layer, extending from about 10 to 17 km to about 45 km above the surface of Earth is known as the *stratosphere*. This is the zone of horizontal air movements. The fast moving currents of air travel at speeds of up to 400 km h^{-1} The temperature in the stratosphere rises from –60 °C at an altitude of about 10 km to 0 °C at about 45 km. This increase in temperature is due to the absorption of ultraviolet radiation by the ozone layer in the stratosphere.

NOTE The build-up of the ozone layer in the stratosphere is due to the photo-dissociation of oxygen molecules, O_2, into single oxygen atoms, O, by the Sun's ultraviolet rays. When an atomic oxygen collides with an oxygen molecule, an ozone molecule, O_3, is formed. Ozone molecules can dissociate to give ordinary oxygen molecules.

The next layer of the atmosphere is known as the *mesosphere*. It extends from about 45 km to about 75 km. The air of the mesosphere is less dense than that of the stratosphere. The temperature varies from 0 °C at an altitude of about 45 km to –90 °C at about 75 km.

The region of the atmosphere extending from about 75 km to about 400 km is known as the *thermosphere*. The air in the thermosphere is thin. This layer is also referred to as the *ionosphere* because many of the molecules and atoms in this region are ionized by the radiation from space and the Sun. The region beyond 400 km is known as the *exosphere*. The air in this layer is extremely thin and consists mainly of hydrogen. The exosphere continues indefinitely into space and eventually merges with the Sun's atmosphere.

Hydrosphere

Water forms a discontinuous layer over about 71% of the Earth's surface. Approximately 98% of the total mass of water is in the form of salt-water in the oceans and seas. Fresh water is present in inland lakes, in the soil (as ground water) and in the pores of rocks. Ground water flows to the surface of Earth as spring water and flows into streams and rivers. The permanent regions of snow, at the poles and at high altitudes, consist of frozen water. Earth is the only planet in the Solar System that contains large amounts of water. This water is continuously circulated through the hydrosphere with the oceans acting as reservoirs. Thus, water evaporates from the surfaces of the water bodies and precipitates as rainfall (or snow).

Many substances are found dissolved in water. The most abundant of these is sodium chloride. The others are composed mainly of the chlorides and tetraoxosulphates(VI) of magnesium, calcium and potassium. Dissolved gases such as nitrogen, oxygen and carbon(IV) oxide are also present, with the last two being important for biological activity.

Lithosphere

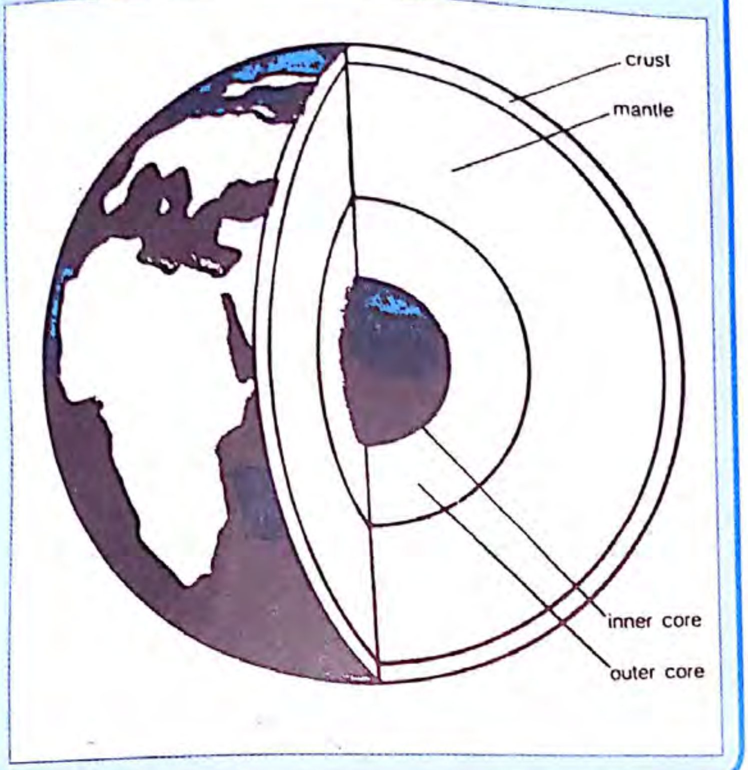
The lithosphere is composed of rocks and soil. It may be considered to be made up of three parts: the crust, mantle and core.

The outermost part is called the crust and extends to a depth of about 30 km in the continental areas and about 8 km in the main ocean floors.

The portion below the crust is known as the interior of Earth. From studies of earthquakes, volcanic activities and other phenomena, scientists think that it consists of a nickel-iron (or possibly pure iron) *central core*, surrounded by a mantle. The *mantle* which is about 2 900 km thick is thought to be plastic, i.e. neither solid nor liquid. The nickel-iron central core consists of a solid inner core and a liquid outer core. The diameter of the whole core is about 7 000 km.

About a hundred different elements may be listed as components of the Earth's lithosphere. Of these,

Fig. 32.2 Earth's structure.



oxygen is the most abundant. It exists in combination with other elements, mainly as oxides. The next most abundant element is silicon, which is found commonly as silicon(IV) oxide.

Most of the other elements are also found as compounds although a few exist in the pure state.

The compounds of the lighter elements are found mainly in the Earth's crust and include oxides, trioxocarbonates(IV) and tetraoxosulphates(VI) of sodium, magnesium, aluminium and calcium. The interior of Earth is composed mainly of heavier elements and their compounds, e.g. the dense rocks in the mantle are composed of trioxosilicates(IV) of iron and magnesium.

Table 32.1 The eight most abundant elements in the Earth's crust.

Element	Percentage by mass
Oxygen	46.71
Silicon	27.69
Aluminium	8.07
Iron	5.05
Calcium	3.65
Sodium	2.75
Potassium	2.58
Magnesium	2.08

USING SPECTROSCOPY TO STUDY THE PLANETS AND STARS

When sunlight passes through a prism, It is dispersed to give a band of coloured lights known as a *spectrum.* Prisms are used in spectroscopes to disperse all types of electromagnetic radiation to give spectra. Nowadays, diffraction gratings are used in most spectroscopes instead of prisms since they give very sharp spectra.

NOTE A diffraction grating, used in a spectroscope, is a polished metal or mirror surface on which is ruled a large number of fine, equidistant, closely packed parallel lines.

There are two types of spectra:

- *emission spectra,* and
- *absorption spectra.*

Emission spectra These are observed when light from a source undergoes dispersion directly. For example, when light from a glowing sodium source is examined through a spectroscope, we see a line emission spectrum which consists of two bright yellow lines very close together in a dark background. A glowing hydrogen source emits a spectrum with red, blue-green and violet lines.

Usually, line emission spectra are emitted by atoms and ions which are not interacting. Band emission spectra which is composed of groups or bands of lines are emitted by molecules of glowing gases or vapours. Continuous emission spectra are emitted by hot solids, liquids and gases at high pressures where the molecules are close enough to interact.

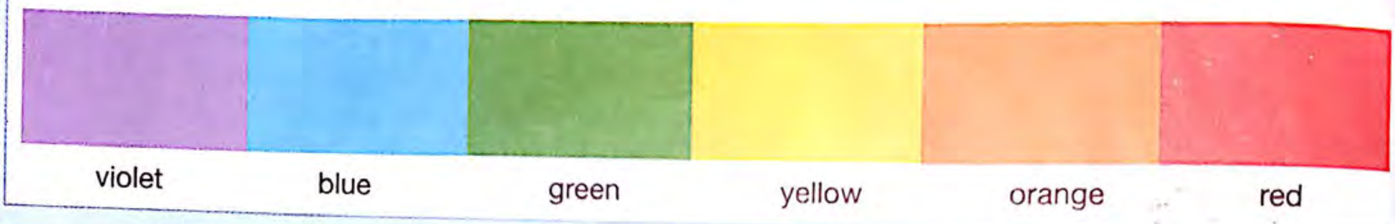
Absorption spectra These are observed when the emitted light passes through a material that partially absorbs it before it is dispersed. For example, when white light passes through a cool gas or vapour, a line absorption spectrum is obtained. Dark lines occur in the continuous spectrum of white light. These lines occur at exactly the same positions as the coloured lines in the emission spectrum of the gas or vapour. Thus, the emission and absorption spectra of an element are the same except that in the former the spectrum consists of bright coloured lines in a dark background, while in the latter it consists of dark lines in a bright background. As in the emission spectra, band and continuous absorption spectra are also obtained.

Fig. 32.3 Types of spectra.

(a) Sodium line spectrum

(b) Band spectrum

(c) Continuous spectum ot white light



Each element emits a characteristic line emission or absorption spectrum which can be used to identify it. Thus, by using a spectroscope, the chemical composition of the source that emits a particular radiation or the material that absorbs the radiation can be identified. Spectroscopic methods are extremely sensitive and can detect the presence of minute quantities of materials.

Spectroscopy is used to analyze the light from stars and the reflected sunlight from planets to get information about the chemical composition of these heavenly bodies. Sophisticated astronomical spectroscopes and spectrographs (instruments which take photographs of spectra) are used for such stellar and planetary spectroscopic studies.

A star's spectrum provides information about its temperature, luminosity and chemical composition. The chemical composition includes the identity of the elements present and whether they are present as compounds, molecules, atoms or ions.

Spectroscopic studies of sunlight reflected by a planet provide

- characteristics of the constituents of the atmosphere of the planet through which the solar radiation travelled; and
- the nature of the solid surface or cloud material from which the radiation is reflected.

THE SOLAR SYSTEM

The Sun and all the bodies orbiting round it make up the Solar System. The Sun is a *star* because it glows all the time giving off its own heat and light. The *planets* and their *moons* are the main bodies that revolve round the Sun. These bodies shine because they reflect the Sun's light that falls on them. Other bodies in the Solar System are the *asteroids, comets* and *meteoroids.*

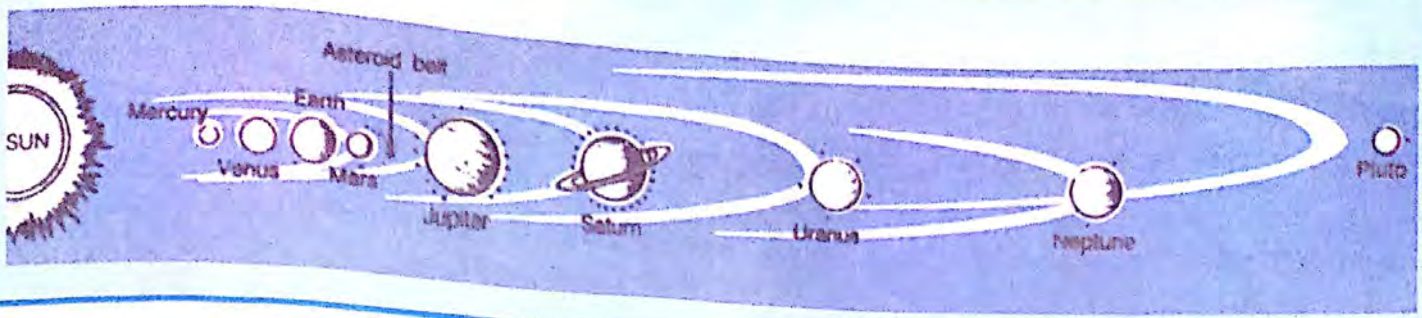
Nearest the Sun is Mercury, the smallest of the planets. Then come Venus, Earth, Mars, Jupiter, Saturn, Uranus, Neptune and Pluto. The distance across the Solar System is about 12 000 million kilometres.

The Sun

The Sun is a vast ball of hot glowing gas. It has a diameter that is more than 100 times that of Earth and a mass about 333 400 times that of Earth. It has an enormous gravitational pull about 28 times stronger than that of Earth. Thus, the Sun controls the movements of all the bodies in the Solar System, except those of the moons.

The density of the Sun is only 1.4 times that of water, while Earth has a density that is 5.5 times that of water. This is because Earth is composed of dense

Fig. 32.4 The Solar System.

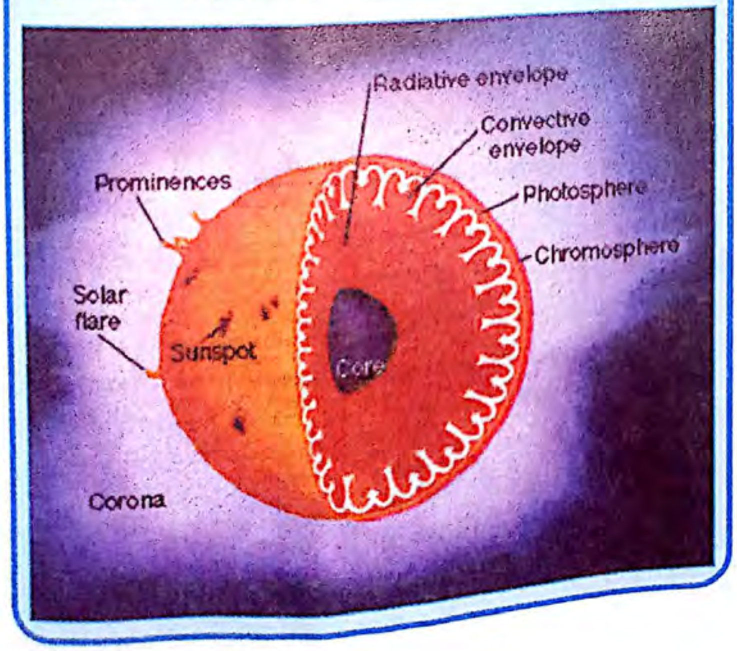


rocks while the Sun consists mainly of very light elements.

The solar atmosphere is composed of two layers– the lower layer is the *chromosphere* and the higher layer is the *corona*. The bright disc of the Sun from which light and heat are given off is the *photosphere*. Clouds of burning gas shoot up into space forming *prominences*. The dark spots on the Sun's surface are the *sunspots*.

Analysis of the solar spectra from the Sun's corona and photosphere shows that the bulk of the solar gases is made up of hydrogen. Helium makes up about 15% of the solar gases and a very small amount is composed of the other elements such as boron, carbon, nitrogen, oxygen, fluorine, neon, sodium, magnesium. aluminium, silicon, phosphorus, calcium and iron found on Earth. Most of the elements are present predominantly as atoms and positive ions in various stages of ionization. The emission spectra show that many electron transitions occur within atoms, especially of argon, calcium and the transition metal group (chromium, manganese, iron, cobalt and nickel), which are practically impossible to achieve on Earth. Molecules are relatively rare because of the high temperature. They may be observed on spectra from sunspots which have ternperatures that are lower than the other parts of the Sun.

Fig. 32.5 The structure of the Sun.



The Sun has a temperature of about 6 000 °C at its surface and about 15 000 000 °C at its core. This heat is produced by nuclear fusion reactions. The most important fusion process is the fusion of the nuclei of two hydrogen atoms (i.e. proton-proton reaction) to produce a deuterium atom, with a simultaneous release of a positron and a neutrino. The deuterium atom may collide with another hydrogen atom to form a helium isotope with an atomic mass of 3 and gamma-rays. Two such helium isotopes may collide to produce a stable helium atom with an atomic mass of 4, while releasing two protons and gamma rays. All these nuclear fusion reactions release an immense amount of energy.

$$
\begin{aligned}
{}^1_1\text{p} + {}^1_1\text{p} &\rightarrow {}^2_1\text{D} + {}^{0}_{+1}\text{e} + \text{v} \\
{}^2_1\text{D} + {}^1_1\text{p} &\rightarrow {}^3_2\text{He} + \gamma \\
{}^3_2\text{He} + {}^3_2\text{He} &\rightarrow {}^4_2\text{He} + 2{}^1_1\text{p} + \gamma
\end{aligned}
$$

NOTE A positron is a positive electron (e^+). A neutrino (v) is a particle without charge, of negligible mass and with a great penetrating power.

The Moon

The Moon is Earth's natural satellite and our nearest neighbour in space. It is about 384 400 km away from Earth. The diameter of the Moon is about one-quarter that of Earth. Its gravity is only one-sixth that of Earth.

The Moon revolves around Earth once every 27.32 days. In the same period, it completes one rotation on

Some of the other planets in the Solar System.

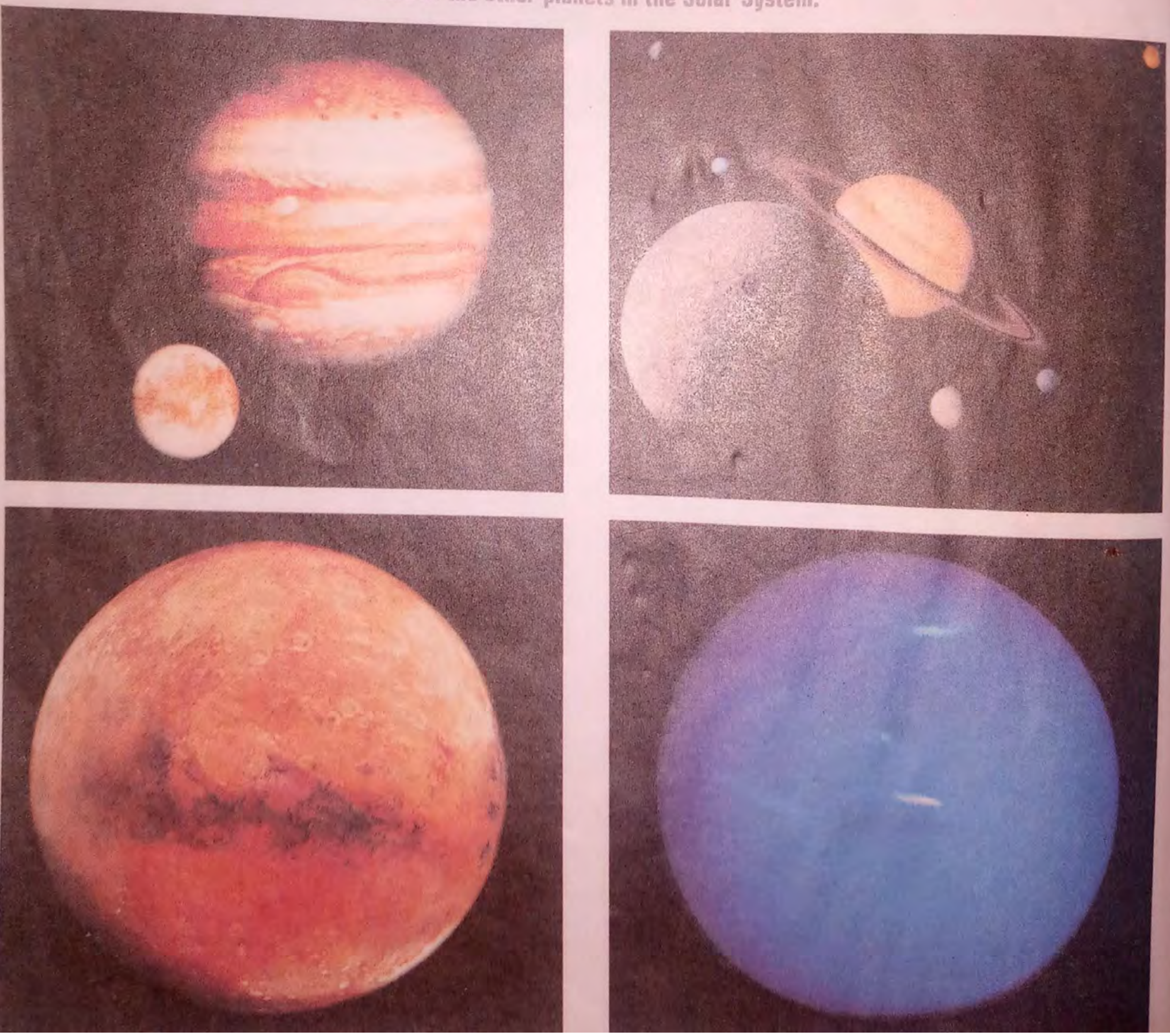


Table 32.2 *Planetary data.*

Name	Diameter in km	Distance from the Sun (in million km)	Density (in Earth day/years)	Time of revolution on its axis (in Earth hour/day)	Time of rotation of moons	Number
Mercury	4 878	58	5.44 g cm^{-3}	87.97 days	58.5 days	0
Venus	12 103	108	5.10 g cm^{-3}	225 days	243 days	0
Earth	12 756	150	5.52 g cm^{-3}	365.25 days	23.95 hours	1
Mars	6 794	228	3.93 g cm^{-3}	1.9 years	24.1 hours	2
Jupiter	142 740	778	1.33 g cm^{-3}	11.9 years	9.83 hours	16
Saturn	120 672	1 427	0.70 g cm^{-3}	29.46 years	10.65 hours	20+
Uranus	52 427	2 870	1.23 g cm^{-3}	84.01 years	23.90 hours	15
Neptune	49 493	4 486	1.66 g cm^{-3}	164.8 years	16.00 hours	8
Pluto	3 827	5 952	0.90 g cm^{-3}	248.5 years	6.39 days	1

Name	Chemical composition
Mercury	Terrestrial planet with mineral-rich rocks. Very thin atmosphere of hydrogen, helium and neon.
Venus	Terrestrial planet with mineral-rich rocks. Thick, dense atmosphere of carbon(IV) oxide (96%). nitrogen (3.5%) and traces of other gases including acidic ones.
Earth	Terrestrial planet with mineral-rich rocks and water. Atmosphere of nitrogen (78%), oxygen (21%) and 1% other gases.
Mars	Terrestrial planet with mineral-rich rocks. Thin atmosphere of carbon(IV) oxide (96.5%), nitrogen (1.5%), argon (1.5%) and traces of other gases.
Jupiter	Gaseous planet composed mainly of hydrogen, with some helium, methane and ammonia. System of faint rings, composed of dark grains of sand and dust, present.
Saturn	Gaseous planet composed mainly of hydrogen and helium, with traces of methane and ammonia. System of seven large rings, each camposed of thousands of ringlets, present. Rocks, dust and lumps of ice make up ringlet.
Uranus	Cold gaseous planet with atmosphere of hydrogen and helium, and with methane, ammonia and water in a frozen form. System of ten narrow, dark rings present.
Neptune	Cold gaseous planet with an atmosphere of hydrogen and helium, and some frozen methane. System of five narrow rings, with broad dust bands, present.
Pluto	Frozen planet, probably composed of solid methane.

its own axis. Therefore, the same side of the Moon is always facing Earth. There is no water or air on the Moon. As a result, it is very hot (about 120 °C) when lit by the Sun and very cold (about –180 °C) when it is not. The Moon's surface has many craters, jagged mountains and flat dustcovered plains known as seas.

Studies of the rocks, brought back from the Moon, show that the Moon is as old as Earth, i.e. about 4 800 million years old. Although lunar rocks look similar to those on Earth, their chemical compositions are different.

The Planets

Mercury, Venus, Earth and Mars are known as the *terrestrial* planets. They are all about the same size and mass. They are dense because they are rich in rocks and minerals. Jupiter, Saturn, Uranus and Neptune are much larger than the terrestrial planets. They are also less dense because they are made up of light gases such as hydrogen, helium, ammonia and methane. Pluto is less dense like the other outer planets, but unlike them, it is small.

All the planets revolve around the Sun and at the same time rotate on their axes from west to east except for Venus, which rotates in the opposite direction.

Mercury

Mercury is a small, rocky, sun-scorched planet whose surface is similar to that of the Moon. The temperature of the side facing the Sun is so high that even lead would melt, while the other side is extremely cold. Mercury's scanty atmosphere is composed mainly of hydrogen, helium and neon. Its mass and volume are about one-sixteenth those of Earth. Although Mercury is a smaller planet, its density is nearly the same as the Earth's. This indicates that it may have a core of dense metals.

Venus

Venus is similar to Earth in size, mass and density. The planet is completely covered with opaque white clouds. The atmosphere of Venus consists of 96% carbon(IV) oxide, 3.5% nitrogen and traces of other gases such as sulphur(IV) oxide, argon, carbon(II) oxide, oxygen, hydrogen chloride, hydrogen fluoride and water. Its atmospheric pressure is 60 to 100 times that of Earth, while its surface temperature is about 460 °C.

Earth

Earth is a rocky planet that is almost spherical, with a polar radius of 6 356 km and an equatorial radius of 6 378 km. Earth is the only planet in the Solar System that lies in a region with a temperature that can support life. In addition, it has an abundance of oxygen and water on its surface—two substances that are essential for life.

Mars

Mars is a dry cold planet with temperatures at its equator that vary between 25 °C in the afternoon to –40 °C at night. Mars has many earthlike features such as clouds, mountains, craters, deserts and polar ice-caps. These led astronomers to believe that intelligent beings lived on Mars. These ideas had to be abandoned after studies showed that most parts of Mars do not have water. The polar caps are a frozen mixture of water and carbon(IV) oxide. The clouds are composed of dust, not water vapour. Great dust storms sweep through the airless deserts at high speeds.

Mars has a thin atmosphere, which consists of about 96.5% carbon(IV) oxide, 1.5% nitrogen, 1.5% argon, and traces of oxygen, carbon(II) oxide and water. The mean density of Mars is lower than that of Earth. This means that it may have a richer content of the lighter elements or a lower nickel-iron content than Earth. Studies indicate that it may have a solid core.

Jupiter

Jupiter, the largest of the nine planets, has a diameter that is more than eleven times the size of Earth. Its mass is 318 times that of Earth, hence it has an enormous gravitational pull. However, the mass of Jupiter is small compared to its size. This is because Jupiter is composed mainly of hydrogen. The hydrogen exists as a gas in its thick atmosphere and probably as a liquid underneath the atmosphere. The next most abundant substance is helium, followed by methane, ammonia and other simple molecules.

Jupiter has belts of colourful clouds in its atmosphere. The clearly visible Great Red Spot is now known to be a huge hurricane that has been blowing for years. Jupiter also has a faint ring system composed of dark sand grains and dust.

Jupiter gives off a lot more heat than it receives from the Sun. This indicates an intensely hot and active core. Jupiter's mean surface temperature is around −140 °C, although the temperature at its core is estimated to be about 30 000 °C.

Jupiter has 16 moons. Io, one of its large moons, has eight active volcanoes.

Saturn

Saturn is the second largest planet in the Solar System. It is a very cold planet with a surface temperature of about −182 °C. It has an atmosphere of mainly hydrogen and helium with traces of ammonia and methane. Saturn is one of the least dense planets despite a rocky core slightly bigger than Earth. A series of cloud belts surround the planet. These are similar to but paler than those of Jupiter.

Saturn, encircled by its series of rings, is one of the most beautiful planets in the Solar System. There are seven large distinct rings. The rings are made up of thousands of separate ringlets and dark grooves. These ringlets consist of rocks, dust and lumps of ice of various sizes. Most of the ringlets are about a few hundred metres thick.

Saturn has many moons. To date 20 have been recorded.

Uranus

Uranus is a very cold planet as it receives only $^{1}/_{350}$ as much sunlight as Earth. Uranus is an unusual planet because its axis of rotation is tilted sideways until it is almost horizontal.

Uranus' atmosphere is made up of mainly hydrogen and helium with traces of methane, ammonia and water. However, it is so cold that all the last three compounds probably form a frozen mixture. The maximum surface temperature of the planet is about −185 °C. The planet probably has a solid core surrounded by ice and liquid hydrogen.

Uranus has 15 moons to date. It also has ten narrow, black rings made up of dark "boulders".

Neptune

Neptune is about the same size as Uranus. It has a thick stormy atmosphere of hydrogen and helium with white clouds of frozen methane around the equatorial region. Its Great Dark Spot is a huge hurricane about the size of Earth. It is also encircled by five narrow rings.

Neptune is very cold with a temperature of −205 °C. It may have a solid core surrounded by a thick layer of ice.

Triton, one of its moons, is volcanic with a temperature of −240 °C, the coldest recorded for any of the bodies in the Solar System.

Pluto

Pluto is the smallest planet as well as the farthest from the Sun. Pluto probably has a surface temperature of about −220 °C on the sunlit region, and about −253 °C on the dark side. All substances would have been liquefied or frozen at this temperature. Its body probably contains a large amount of solid methane.

Asteroids, Comets and Meteoroids

Asteroids These are small rocky bodies, usually found between Mars and Jupiter. This region is known as the "asteroid belt". There are thousands of asteroids of varying sizes. They could be the remains of heavenly bodies that broke up long ago. Most asteroids move along circular orbits. Asteroids are rich in elements similar to those on Earth. Efforts are being made to tap these mineral resources to sustain industries on Earth.

Comets These are frozen collections of ice, dust and gases which move in elongated, irregular orbits around the Sun. Far from the Sun, a comet consists of a small body (or a collection of small bodies) which reflects sunlight and is called the *nucleus*. The nucleus is composed of compounds such as frozen water, ammonia, methane, and other heavier hydrocarbons. As the comet approaches the Sun, it becomes heated, melts and the compounds in it dissociate to produce a cloud of gaseous molecules, atoms and ions which shroud the nucleus. The doud, together with the *nucleus*, forms the *head* of the comet. When dose to the Sun, a bright *tail* (which may be long) may develop. This tail always points away from the Sun because of the solar wind, which is a stream of energetic ions and electrons from the Sun.

A comet may make only one appearance or it may appear regularly. A spectacular comet, the *Halley's comet*, is seen every 76 years. It was last seen in 1986.

Fig. 32.6 A comet.

Meteoroids These are small fragments of stone flying through space at very high speeds. They are usually the remains of comets and asteroids. Millions of meteoroids travel around the Sun. When the meteoroids enter our atmosphere, they are known as *meteors*. They travel at great speeds and the air friction heats them up. They glow and disintegrate, forming a bright flash of light, known as a *shooting star.* Occasionally, pieces of meteors land on Earth. These are called *meteorites*. A large meteorite can cause a big crater if it falls on land. Meteorites are composed of many elements, such as iron, magnesium, sodium, calcium, aluminium, nickel, silicon and hydrogen, found on Earth. Spectroscopy of meteors also shows a similar composition.

STARS

Stars are self-luminous objects, shining by radiation obtained from energy sources within themselves (by nuclear fusion). By contrast, planets shine by reflected light. Stars vary in age, size, temperature, luminosity (brightness), colour and chemical composition. The Sun is a typical star.

Classification of Stars

Stars are grouped according to their spectra, which give information on their temperature, luminosity and chemical composition. These spectral classes are given the letters *O, B, A, F, G, K* and *M*. They are arranged in order of decreasing temperature, from the hottest to the coolest stars. Stars in classes *O* to *M* are said to belong to the main sequence group. Other stellar classes which are outside the main sequence include the *C* stars and the *S* stars, which are the giants and the supergiants, and the white dwarfs.

The stars in the main sequence have essentially the same chemical composition but their surface temperatures and atmospheric pressures are different. In addition, these stars also show a colour sequence—from the very hot (20 000 °C) bluish-white *O* and *B* stars, to the moderately hot (6 000 °C) yellow *G* stars, to the the cool (3 000 °C) red *K* and *M* stars.

Like the Sun, the stars in classes *O* to *M* are composed mainly of hydrogen, helium and small amounts of other elements found on Earth. However, stellar spectra show that the particulate nature of these elements varies with the temperature of the stars.

In cool stars, simple molecules and neutral atoms of elements are abundant, while in hot stars highly ionized atoms of elements predominate. Thus, spectra of the cool stars of class *M* show the presence of simple molecules like titanium oxide and neutral atoms of metals like iron, calcium and magnesium.

The spectra of the slightly hotter *K* stars show that molecules like titanium oxide are not present although stable pieces of molecules like the hydroxyl radical are present.

The spectra of the G stars are characterized by emission lines showing the presence of ionized atoms of metals like iron and calcium.

The spectra of *F* stars indicate the presence of more ionized metal atoms than neutral atoms.

Class *A* stars have spectra showing strong hydrogen emission lines (indicating unionized hydrogen atoms), while in the spectra of class B stars, these lines are faint indicating that most of the hydrogen atoms are ionized.

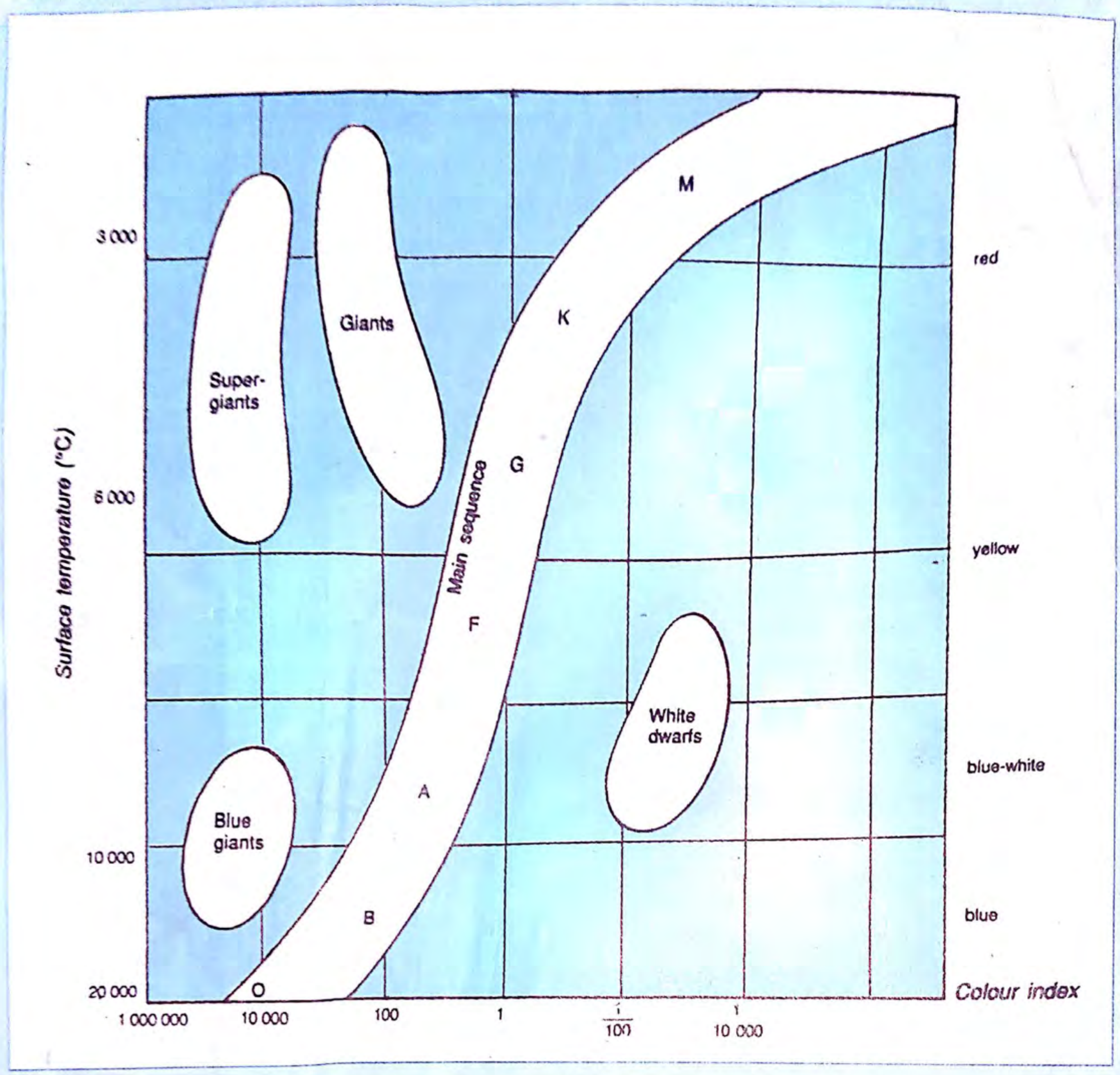
The spectra of the very hot *O* stars show that even helium atoms are ionized, while oxygen, nitrogen and carbon are doubly ionized.

Life History of Stars

Stars are formed from massive clouds of dust and gas (mainly hydrogen) that are found in space. The particles in a cloud are attracted to one another by the force of gravity. As millions of particles come together, the cloud shrinks, its density increases and heat is generated. As the temperature at the core increases to over 1 000 000 °C, nuclear fusion reactions begin. Vast amounts of energy are released and a glowing ball of gas appears, marking the birth of a star.

Most stars are formed in this way but their life histories vary according to their sizes at birth. The small stars live the longest; the medium-sized stars live for about 10 000 million years; while large stars live for about a few million years.

Fig. 32.7 Number of times brighter than the Sun.



A star that is small at birth does not produce much nergy. Its size or brightness does not change ppreciably during its lifetime and it fades away when ts store of hydrogen is used up.

A medium-sized star is very bright when young. The hydrogen atoms at its core fuse to form helium hereby liberating a large amount of energy. It cools slightly and enters its *middle age*, which is its most active period. As the hydrogen at its core is used up, the hydrogen in the outer layer (shell) of the star undergoes fusion reaction. This causes the star to expand into a luminous red giant. Meanwhile, the core contracts, becomes denser and the temperature starts to increase. At about 100 000 000 °C, the helium nuclei begin to fuse to form the nuclei of heavier elements like carbon-12, oxygen-16, neon-20 and magnesium-24 in reactions similar to the following

$$^{4}\text{He} + {}^{4}\text{He} \rightarrow {}^{8}\text{Be}$$
$$^{4}\text{He} + {}^{8}\text{Be} \rightarrow {}^{12}\text{C}$$
$$^{4}\text{He} + {}^{12}\text{C} \rightarrow {}^{16}\text{O}$$
$$^{4}\text{He} + {}^{16}\text{O} \rightarrow {}^{20}\text{Ne}$$
$$^{4}\text{He} + {}^{20}\text{Ne} \rightarrow {}^{24}\text{Mg}$$

These reactions stop when the store of helium in the core is used up. The outer layer or shell of the star usually drifts away to leave a small star, the white dwarf (the core), which cools and fades away eventually

On February 23, 1987 a supernova was seen in the Large Megellanic Cloud. It caused a great deal of excitement as it is the brightest exploding star seen on earth in over 380 years.

A star that is large at birth produces much larger amounts of energy than the medium-sized star. Such a star often becomes a supergiant. When the hydrogen and helium in its core are used up in fusion reactions, he nuclei of heavier elements like carbon-12 undergo fusion to form much heavier elements such as sodium. This happens at temperatures of about 700 000 000 °C. At higher temperatures than this, the nuclei of the transition group of elements (such as nickel, chromium, manganese and cobalt) are formed. If the temperature continues to rise, the nuclei of the transition group of elements tend to break down to helium nuclei in processes which use up enormous amounts of energy. The star collapses suddenly and explodes as a *supernova*. During this explosion, many types of nuclear reactions occur. A supernova is a rare phenomenon. If sufficient mass is left behind after the explosion, a white dwarf may form.

The Sun

The Sun was born as an average-sized star and probably will have a life span of about ten billion years. It is now a yellow G star which is in its *middle age*. It will slowly expand to form a red giant which may extend up to Earth. Then it will become a white dwarf when its shell drifts away. This marks the beginning of the end of its life as it slowly cools and fades into a cold black dwarf.

Light years

Astronomers measure stellar distances by light years. One light year is the distance travelled by light in one year, i.e. about 9.24×10^{15} m. So when we look into space to see a star, we are really looking back in time. Most of the starlight we see started on its journey a long long time ago. For example, light from Sirius (the brightest star) takes 87 years to travel to us on Earth. Light from our star, the Sun, takes only $8\frac{1}{2}$ minutes to reach us.

SPACE TRAVEL

On October 4, 1957 Russian scientists and engineers shook the world by placing into orbit the first man-made satellite, Sputnik 1. Sputnik 1 had a mass of 82.8 kg and a diameter of 0.58 m. The polished aluminium sphere orbited Earth at heights ranging from 228 km to 946 km for 92 days, completing a total of 1400 orbits.

No sooner had the world recovered from the excitement of this first achievement than it was again shaken by the launching of Sputnik 2 on November 3, 1957. Sputnik 2 weighed 508.5 kg and carried a living animal, a husky dog named Laika.

Since the early launchings, many types of artificial Earth satellites have been successfully placed in orbit. These include weather satellites, Earth satellites, communications satellites, and scientific and astronomical satellites.

In April 1961, the first man, Yuri Gagarin was launched into space. He orbited Earth for 108 minutes and returned safely to Earth.

Advances made in radio, telemetering and television made it possible to guide unmanned spacecraft. It also enabled the transmission of all kinds of scientific data and pictures to ground stations. Thus, many unmanned spacecraft were sent out to study the planets in the Solar System. These probes include the Mariners and Vikings (to study Mercury, Mars and Venus), and the Pioneers and the Voyagers (to study the outer planets).