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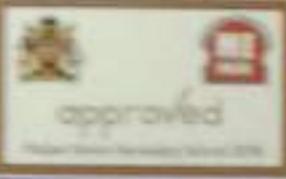
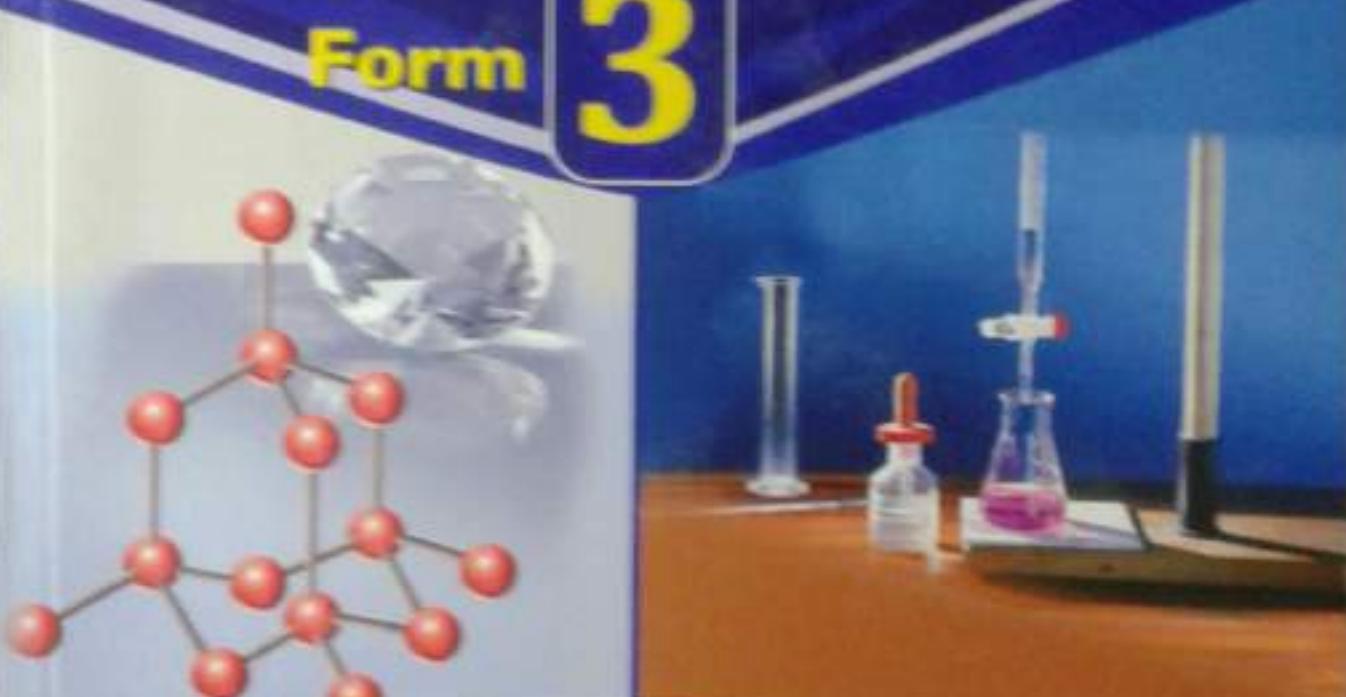
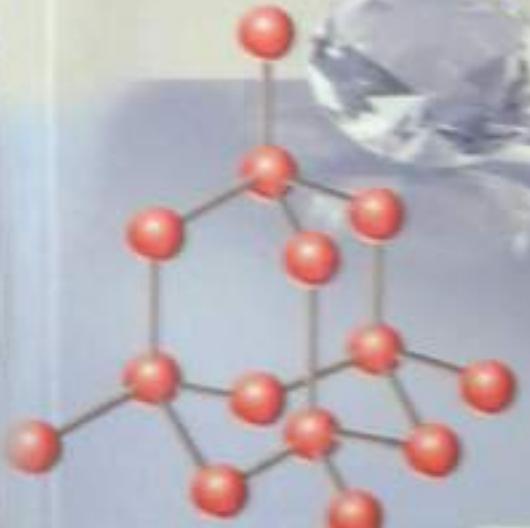
Excel & Succeed



Senior Secondary
Chemistry
Student's Book

Form

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grey matter

Cedric Mipaso
Lameck Kaonga

LONGHORN

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Topic 1: Experimental techniques

Success criteria

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



- (a) Describe safe ways of disposing chemical wastes in the laboratory.
- (b) Design scientific investigations.
- (c) Carry out an investigation to determine the purity of a substance.
- (d) Describe simple tests for water, ions and gases.

1.0 Introduction

Study of science involves conducting carefully planned investigations on a matter of interest to determine an outcome expected i.e. whether it is true or false. There are many experiments undertaken in the course of study of chemistry and other sciences. These investigations (experiments) are systematic and standardized to minimize individual subjectivity and bias. In order to achieve this, valid and suitable experimental techniques are adopted and adhered to, which promote the acceptance of the results into scientific consensus among the scientists universally.

1.1 Laboratory wastes

Most chemical reactions in the laboratory leave us with quite some amount of wastes. These laboratory wastes must be safely disposed to ensure safety in the laboratory and good environmental hygiene in the school and the surrounding community.

Examples of laboratory wastes are:

- Unused chemicals or reagents e.g. acids, alkalis, solid chemicals and detergents among others.
- Soluble inorganic salts e.g. calcium chloride (CaCl_2), phosphorus pentaoxide (P_2O_5) and sodium sulphate (Na_2SO_4).
- Broken laboratory glasswares, sharp objects etc.
- Mineral oils, carcinogenic solids, paraffin and other sources of fuels.
- Plastics, waste papers and rubbers.
- Gloves, wipes, tissue papers.
- Poisonous gases from chemical reactions.

Class activity

1. From the above list can you identify waste products from chemical reactions.
2. Give five more examples of waste products from chemical reactions that are not listed above.

Safe ways of disposing laboratory wastes

The general principle for safe disposal of laboratory wastes requires separation of the wastes into different categories and disposing each category of waste using acceptable method(s). The following are various of disposing wastes.

1. Draining using a lot of water

The following wastes can be safely washed down the drain (sinks) with the use of excess water.

- Harmless soluble inorganic salts such as magnesium sulphate, sodium sulphate, potassium chloride among others.
- Contaminated and unused acids, alkalis, detergents.

But the following substances should never be washed down the drain: arsenic and arsenic compounds, compounds of boron, cobalt, lead, copper, organo phosphorus and organo nitrogen pesticides, mineral oils, hydrocarbons, nitrites and fluoride compounds.

2. Use of normal waste bins

This is for disposal of controlled wastes. Controlled wastes include non-recycle plastics, piece of wood, rubber and dirty papers.

3. Use of special controlled waste containers

Sharp metal objects e.g. scalpel, broken laboratory glassware, fine powders inside a bottle, sample tube and items highly contaminated with hazardous chemicals are placed in these containers. However, syringes and needles must not be put here. The containers must be regularly emptied and not allowed to overflow.

Remember! Sharp objects should be handled carefully during disposal to avoid cuts and pricks. This ensures prevention of possible transmission of deadly diseases such HIV and AIDS, herpes, tetanus among others.

4. Incineration

Wastes are put in an incinerator (Fig. 1.1) where they are burned. Wastes that are incinerated include: syringes and needles, all organic solvents, soluble organic wastes, paraffin and mineral oils.



Fig 1.1: Burning wastes in an Incinerator

5. Use of fume chambers

This is used for experiments involving poisonous waste gases such as chlorine, sulphur dioxide, hydrogen chloride and other carcinogenic solids.

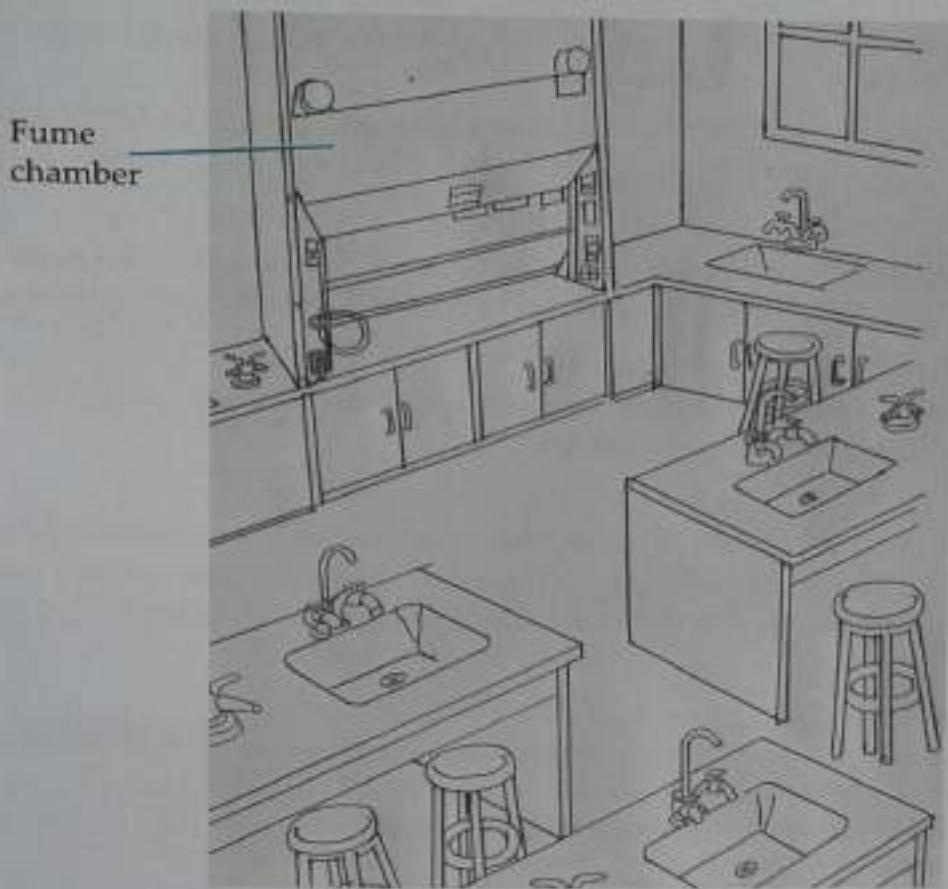


Fig 1.2: Fume chamber in a laboratory setting

6. Recycling

Some wastes in the laboratory can be recycled. Each laboratory should have a bin for recyclable materials such as unbroken glass, packing waste and papers. The recycling bin should be clearly labelled indicating what items to be placed there.

1.2 Designing scientific investigations

We mentioned earlier that scientific investigations must be systematic and use validated methods which are verifiable by other researchers in order for the results obtained to be acceptable. To do this, there is a standard procedure to be followed as outlined below.

(a) Problem identification

This is the first step where a problem is recognized. In today's life one often comes across happenings which require explanations. Such questions or problems may be interests to a scientist who will seek to provide answers to them e.g. what causes rusting? Why plastics do not decompose easily?

(b) Formulation of hypothesis

A hypothesis is either a tentative theory or a tentative explanation for the observation made. In a nutshell, a hypothesis is an intelligent guess which the researcher considers as the possible cause of the problem on the basis of facts the researcher has or thinks of. As more and more evidence is obtained, the hypothesis gains increasing acceptance and eventually is promoted to the rank of theory.

A theory is a set of scientific assumptions consistent with one another and supported by evidence but not fully proved. For example, Dalton Theory of Atomic mass.

(c) Experimentation

An experiment is a series of investigations intended to discover certain facts, which may lead to either the acceptance or modification or sometimes rejection of a hypothesis.

(d) Observation and data collection

After setting up an experiment, a researcher makes careful observations and recording of all events that he or she considers important.

(e) Interpretation of data

Once a researcher has collected data he or she must try to explain the meaning of the data in relation to the aim of the experiment. This is an attempt to interpret the data. In other words this is explaining the result of what is found from the data.

(f) Conclusion

A researcher must draw conclusions at the end of the investigations based upon collected data. The conclusion is either a confirmation or rejection of the hypothesis under investigation. If the hypothesis is true it is confirmed and adopted and if false it is declared null and void hence rejected. When a hypothesis is rejected another one is formulated and tested.

Sample Scientific investigation

Problem identified

Many objects are wearing out due to rusting. Therefore, there is a concern about causes of rusting. The research question to be answered are:

- (i) What causes rusting?
- (ii) What conditions are necessary for rusting to take place?

Hypothesis

The researcher formulated following hypothesis

- (i) Heat causes rusting.
- (ii) Water (moisture) causes rusting.
- (iii) Air (oxygen) must be present for rusting to occur.

Experimentation

The following experiment has been designed to investigate conditions necessary for rusting to take place.

Experiment 1.1

Aim: To investigate conditions necessary for rusting
Requirements

- Four test tubes
- Test tube rack
- Boiling tube
- Paraffin wax
- Cotton wool
- Emery paper
- Rubber bung
- Anhydrous calcium chloride
- Iron nails
- Distilled water and tap water
- Source of heat

Procedure

1. Label four test tubes A, B, C and D.
2. Clean four iron nails thoroughly with emery paper.
3. Put one nail in each test tube and place the test tubes in the test tube rack.
4. Do not add anything to test-tube A.
5. Add tap water to cover the nail in test tube B.
6. Push a plug of cotton wool above the nail in test tube C. Add anhydrous calcium chloride. Put another plug of cotton wool to cover anhydrous calcium chloride. Close the test tube with a rubber bung.
7. Add boiled or distilled water to test tube D. Add a layer of paraffin wax and close the tube as in Fig 1.3.
8. Leave the test tubes undisturbed for one week. Make your observations.

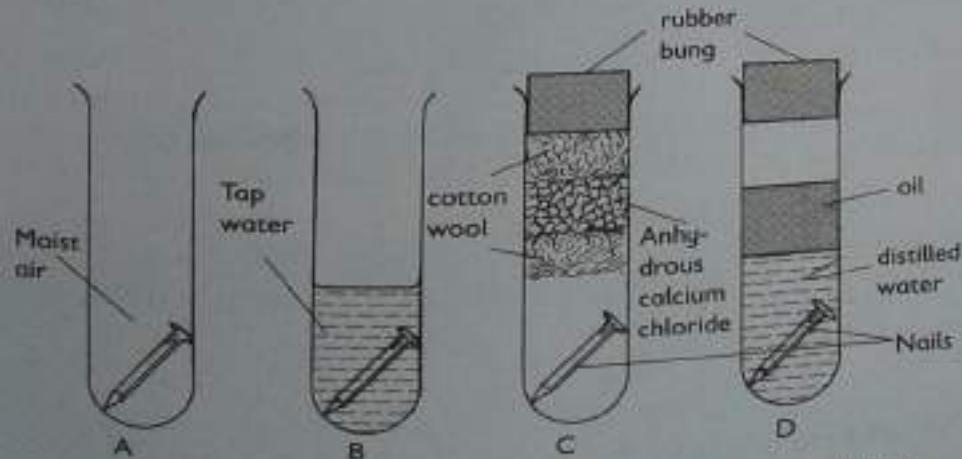


Fig 1.3: Set up for investigating conditions necessary for rusting

Observations, data recording and presentation

Data presented in the table 1.1 clearly shows what conditions must be present in order for rusting to take place.

Table 1.1: Summary of conditions necessary for rusting

Test tube	Conditions present	Observations made
A	Air + water	Nail rusted
B	Water + Air	Nail rusted
C	Air only	Nail remained shiny (No observable change)
D	Water only	Nail remained shiny (No observable change)

Therefore, a researcher must design the experiment in such a way that the conditions being investigated are independently verifiable.

Data interpretation

It would be observed that nails in test tube C and D remained bright shiny while those in test tube A and B rusted.

Nail in test tube A, was exposed to air containing moisture (water vapour) causing the nail to rust. In test tube B, there is dissolved air in the water, hence rusting occurred. Rusting occurred in A and B because both air (oxygen) and moisture were present. Nails in test tube C and D did not rust. In test tube C fused calcium chloride absorbed any water vapour present in the air inside the test tube. Hence no rusting could take place in absence of moisture. In test tube D, boiling the water drove out all dissolved air, water being the only condition present could not allow rusting to take place.

Therefore from the experiment it is true **water** (moisture) and **air** are necessary conditions for rusting. However, both must be present for rusting to take place.

1.3 Determining purity of substances

Substances have characteristic properties unique to each of them in their pure state i.e. their **melting** and **boiling** points. This has been used by chemists in verifying purity of substances in the fight against counterfeits.

Pure substances have fixed melting and boiling points. That is, they have sharp boiling and melting temperatures i.e. melt or boil completely at specific temperature. Impure substances melt or boil over temperature range. **Impurities** causes rise in boiling points particularly for liquids while reduces melting points for most solid substances depending on the quantity of impurities present.

However, for liquids the boiling points also depend on the prevailing atmospheric pressure which must be taken into consideration when such investigations are being carried out.

Effects of impurities on boiling points of water

Experiment 1.2

Aim: To investigate the effect of impurities on the boiling point of water.

Requirements

- Pure water
- Boiling tubes
- Stirrer
- Thermometer
- Delivery tube
- Sodium chloride
- Clamp and stand

Procedure

1. Arrange your apparatus as shown in Fig.1.4 below

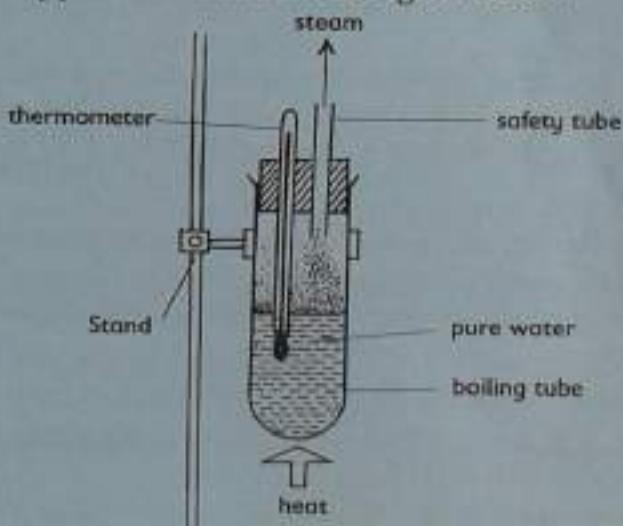


Fig 1.4: Apparatus for measuring boiling points of water

2. Put some water in a boiling tube. Heat until it boils. Record its temperature.
3. Pour some water in another clean boiling tube. Add a spatulaful of sodium chloride and stir until all dissolves. Heat this solution until it starts to boil. Record its temperature.
4. How do the two temperatures compare? What is your conclusion?

Discussion

It would be observed that the two temperature readings obtained are different. When sodium chloride solids were added to water, the boiling point of the solution was raised. Therefore we can conclude that impurities increases boiling points of pure substances. Pure water boils at 100°C.

Melting points of pure naphthalene and impure naphthalene

Experiment 1.3

Aim: To determine the melting points of pure naphthalene and impure naphthalene.

Requirements

- Boiling tube
- Thermometer
- Stirrer, beaker
- Naphthalene, camphor
- Clamp stand
- Water
- Melting point tube
- Rubber band
- Mortar and pestle
- Source of heat

Procedure

1. Grind some pure naphthalene in a mortar using a pestle. Scoop some of it and place it into the melting point tube; tap the tube to ensure the powder move down to the bottom end. Ensure the length of powder in the tube is about $\frac{1}{2}$ cm.
2. Using a rubber bung, attach the thermometer to the melting-point tube and place them in a water bath as shown in Fig. 1.5. Ensure both the rubber bung and the open end of the tube are well clear of the water surface level.

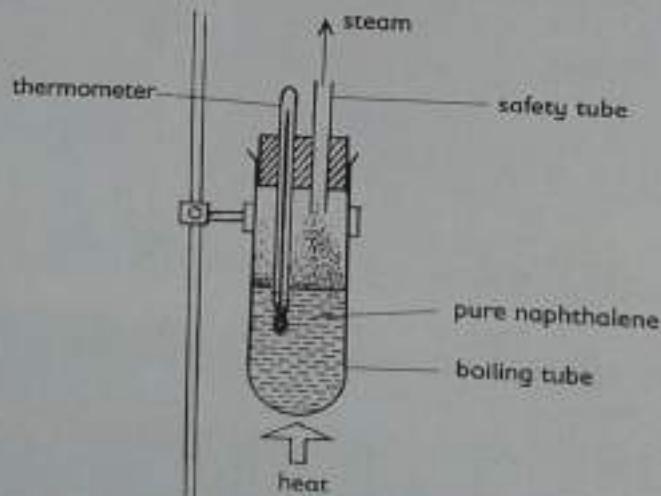


Fig 1.5: Apparatus for measuring the melting of naphthalene

3. Heat the water bath gently while stirring slowly and continuously. When the temperature reaches $65^{\circ}\text{C} - 75^{\circ}\text{C}$, remove the burner at intervals so that the temperature rises slowly.

- Note and record the temperature at which naphthalene melts. This is the point at which the white powder suddenly shrinks and forms a clear liquid. Does the temperature remain constant at this point?
- Repeat the experiment using a mixture of naphthalene and camphor. (Camphor is an impurity in this case). Record this melting point. What do you notice about this melting point?
- Copy Table 1.2 below and fill in temperature readings obtained.

Table 1.2: Investigation of effects of impurities on melting point of naphthalene

Melting point	Temperature (°C)
Naphthalene	
Naphthalene + camphor	

What effect does camphor have on melting point of naphthalene?

Discussion

When naphthalene is melting, the temperature stops rising. It will only rise again when all naphthalene has melted. Naphthalene as a single pure substance melts at 80°C. An impure substance would melt over a **range of temperatures**. The impurities reduce the "sharpness" of the melting point or boiling point. Pure substances have **definite** (fixed) melting and boiling points. Adding of impurities to naphthalene would lower its melting point. This is true for most substances.

If a solid to be investigated has a melting point above 100°C, an oil-bath is used instead of a water bath. This allows for such temperatures to be measured. Note that the melting point and boiling point of a pure substance are definite while that of an impure substance is a range of temperatures.

It is possible to follow the temperature of a solid before and after melting. The results can then be used to plot a graph and produce a heating curve as shown in Fig 1.6.

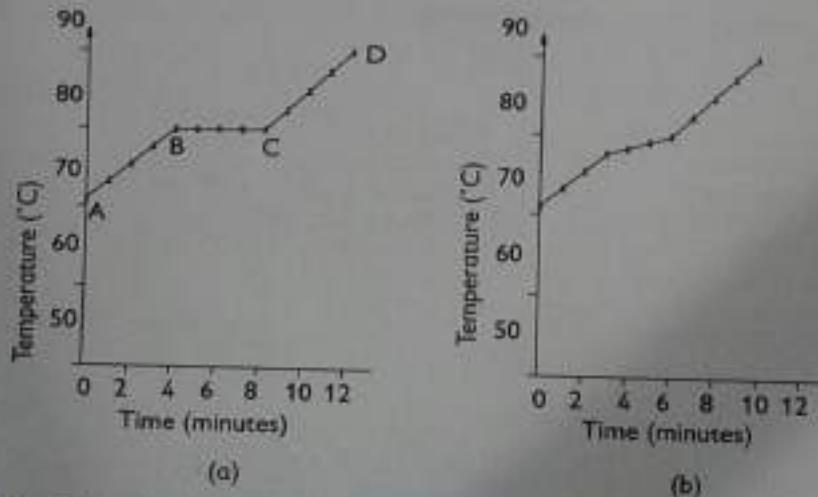


Fig 1.6: Plotted curve of heating a pure naphthalene and an impure naphthalene

Portion AB: Naphthalene absorbs heat energy and the temperature increases steadily.

Portion BC: Pure naphthalene changes its state from solid to liquid. The temperature stays constant at 80°C until all naphthalene melts. All the heat absorbed is used to change solid naphthalene into liquid therefore no temperature rise. This heat is called **latent heat of fusion**.

Portion CD: The liquid absorbs more heat energy. The temperature rises. It stops rising when the boiling point of the liquid is reached.

Note: The heating curve of the impure substance has no horizontal portion because impure substances melt over a range of temperatures.

1.4 Paper Chromatography

Chromatography is a technique for separation of components of a solution by passing it through a medium. Paper chromatography is one of the several types of chromatography. It involves use of high quality filter paper as the absorbent material. It helps in analysing components of a substance in a solution.

The components move at different rates. The components separate readily according to how strongly they are absorbed by the medium in comparison to how readily they dissolve in the travelling solution (solvent) i.e. according to their solubility in the solvent. The component that is most soluble moves faster up the paper. An insoluble component remains at the origin. The movement (flow) stops just before the solvent reaches the top of medium also known as **solvent front**. Pure substances form only **one spot** when run in several different solvents. This is the test used for determining purity of a substance.

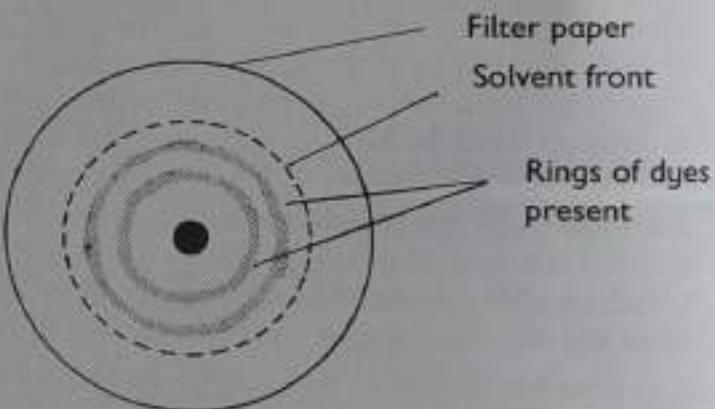


Fig 1.7: A chromatogram of black ink

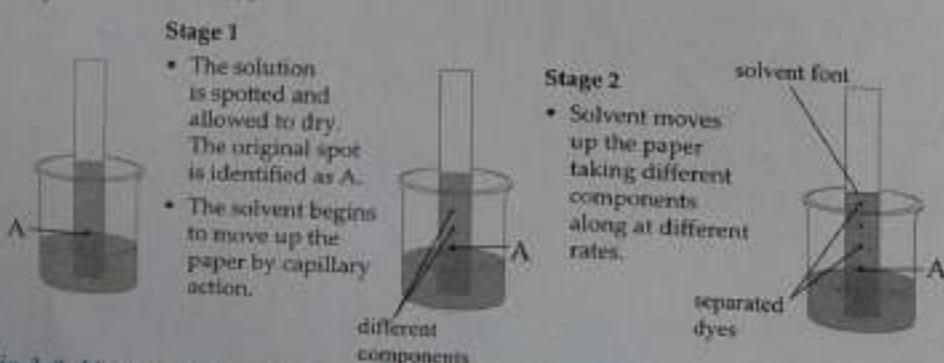


Fig 1.8: Various stages during paper chromatography. The sample is separated as it moves up the paper.

Many different solvents are used in chromatography. Ethanoic acid, ethanol and propanone are examples of organic solvents commonly used since they dissolve many substances which do not dissolve in water.

Relative flow value (R_f)

This is the distance travelled by a particular component (spot) in comparison to the distance travelled by the solvent (i.e. solvent front). The ratio of these two distances is called R_f value.

$$R_f = \frac{\text{Distance moved by the substance}}{\text{Distance moved by the solvent front}}$$

Look at figure 1.9 below. It shows distances moved by pure substance A and pure substance B, A in a mixture and B in a mixture can be described or identified using their relative flow (R_f) value.

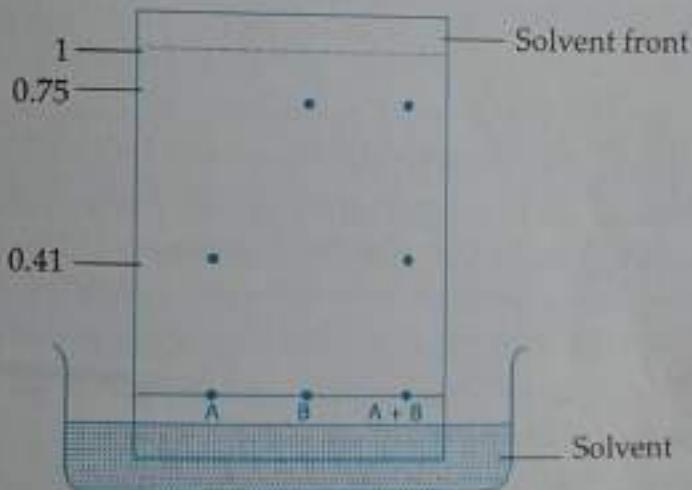


Fig 1.9: Relative flow

R_f ranges from 0 to 1.

R_f value of pure A and A in the mixture is always equal. Therefore R_f can be used to

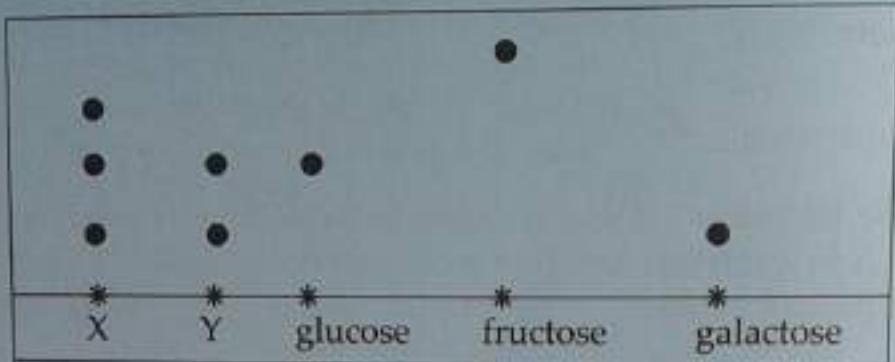
- identify components of mixture.
- determine if a substance is pure.

A pure substance has only one R_f value.

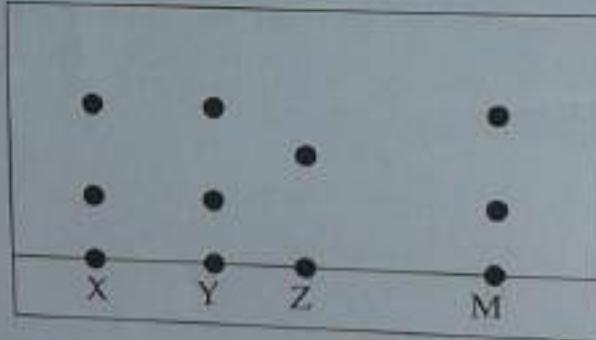
The insoluble component (substance) in a solvent remains on the original spot. A substance flows only and if it is soluble in the solvent used.

Practice exercise 1A

1. A chromatogram of acid enzymes X and Y and three simple sugars are shown below.



- a) Draw the solvent front.
b) Which two simple sugars must be present in X and Y?
2. A chromatogram of ink from different pens used to sign cheques from three suspects (X, Y and Z) and a genuine one are shown below.



A genuine cheque should be signed using ink M. Which suspect has a forged cheque?

1.5 Tests for ions, gases and water

Sometimes we may need to find out the identity of a compound or a gas we are dealing with. Chemists do this by carrying careful systematic tests to identify such substances. The process of carrying out such chemical tests is called **qualitative analysis**. Qualitative analysis involves making careful observations, drawing suitable conclusions and inferences based on the observations made.

Ionic compounds consist of two ions, positively charged ions and negatively charged ions. The positively charged ions are referred to as **cations**. The negatively charged ions are called **anions**.

Identification of cations

The commonly tested cations are: calcium, aluminium, ammonium, zinc, copper, iron(II) and iron (III). These ions show characteristic reactions when reacted with the reagents aqueous sodium hydroxide and aqueous ammonia solutions. Some cations form precipitates of specific colours. Others show interesting behaviours when reacted with the reagents. These reactions or analysis are considered as preliminary tests. Since they may be needed to carry out further tests (analysis) to identify precisely many of the ions.

Measures when carrying out qualitative analysis

When carrying tests for ions, the following must be taken into consideration for successful qualitative analysis.

- Utilise your skills in manipulating correctly the apparatus to make correct observations and logical conclusion.
- Adhere to the procedure strictly. Omissions, shortcuts or alterations of instructions will lead to wrong observations and hence wrong conclusions.
- Do not mix or contaminate substances supplied for qualitative analysis. Contamination of a reagent may spoil an experiment. Droppers once used should be returned to their original reagent bottles or beakers.
- If you feel, during normal practical session, that you can make a logical improvement, on the method suggested, draw it to the attention of the teacher.
- When working in small groups, ensure that you are involved in performing the experiment. Assist other learners with difficulty in handling the apparatus, i.e.
 - (i) Tell the colour observed to students with poor eyesight.
 - (ii) Work on lower benches easily reachable by physically challenged students.
- Do not smell gases directly. Hold the gas source about 15-20 cm away from you and blow the gas towards the nose with your palm, then sniff carefully.



Fig 1.10: Waving gas towards the nose

Test for cations

Dilute sodium hydroxide solution and dilute ammonia solution are often used in conducting preliminary tests for the ions. Further tests are then normally carried out for specific cations.

Experiment 1.4

Aim: To carry out tests for cations using sodium hydroxide solution

Requirements

- 2M sodium hydroxide solution
- Test tube rack
- Droppers
- Test tubes
- Labels
- Salt solution of Fe^{2+} , Cu^{2+} , Ca^{2+} , Zn^{2+} , Al^{3+}

Procedure

1. Place 2 cm³ of each of the cation solutions provided in separate test tubes. Label each test tube correctly.
2. To each solution, add few (3) drops of sodium hydroxide solution and then add more sodium hydroxide until in excess. Do this for all the solution one at time. Record your observations in a table below.

Cation in solution	Observation on addition of 2M NaOH	
	Few (3) drops	In excess
Ca^{2+}		
Al^{3+}		
Zn^{2+}		
Cu^{2+}		
Fe^{2+}		
Fe^{3+}		

Questions

1. a) Which ions formed white precipitates?
b) Which ions did not form precipitates?
2. a) Which ions formed coloured precipitate?
b) Which ions showed no observable change?

Compare your results with those shown in Table 1.3 below.

Results and discussion

When aqueous sodium hydroxide solution is added to the various salts solutions, most form precipitates and some soluble complex ions. The precipitate is as a result of insoluble metal hydroxides. The colour of some of the precipitates and solubility of some metal hydroxides in excess alkali help in identification of the cations.

Table 1.3: Test results for cations using aqueous sodium hydroxide

Cation	Observations on adding aqueous NaOH	
	3 drops	In excess
Ca^{2+}	White precipitate	Insoluble
Al^{3+}	White precipitate	White precipitate dissolves
Zn^{2+}	White precipitate	White precipitate dissolves
Cu^{2+}	Blue precipitate	Insoluble
Fe^{2+}	Pale green precipitate	Insoluble
Fe^{3+}	Reddish brown precipitate	Insoluble

Ca^{2+} , Al^{3+} and Zn^{2+} form white precipitates with sodium hydroxide solution. Their precipitates dissolve in excess alkali as a result of formation of complex ions except that of Ca^{2+} .

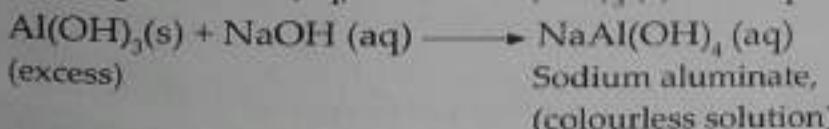
Cu^{2+} , Fe^{2+} and Fe^{3+} form characteristic coloured precipitates which do not dissolve in excess.

Examples of the cations reaction with sodium hydroxide

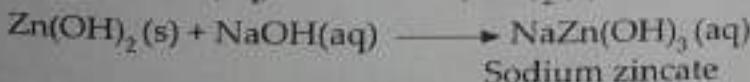
Ca²⁺



AJ54



Zn²⁺



Testing for cations using aqueous ammonia solution

Experiment 15

Aim: To carry out tests for cations using aqueous ammonia solution

Requirements

- Test tubes
 - Droppers
 - 2M ammonia solution
 - Solutions containing Ca^{2+} , Al^{3+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} ions.
 - Test tube racks
 - Labels

Procedure

1. Place 5 cm³ of each of the salt solutions provided into separate test tubes and label them accordingly.
2. To each salt solution, add 3 drops of aqueous ammonia and then add more aqueous ammonia until in excess.
3. Draw the table below in your notebook and record observations made.

Cation solution	Observation on adding aqueous ammonia solution	
	3 (few) drops	In excess
Ca ²⁺		
Al ³⁺		
Zn ²⁺		
Cu ²⁺		
Fe ²⁺		
Fe ³⁺		

Questions

1. a) Which ions formed white precipitates?
b) Which ions did not form precipitates?
2. a) Which ions formed coloured precipitates?
b) Which ions did not form any precipitate?

Results and discussion

Table 1.4: Test results for cations using aqueous ammonia solution.

Cation	3 drops	In excess
Ca ²⁺	White precipitate	Insoluble
Al ³⁺	White precipitate	Insoluble
Zn ²⁺	White precipitate	Precipitates dissolve
Cu ²⁺	Blue precipitate	Dissolves to form deep blue solution
Fe ²⁺	Green precipitate	Insoluble
Fe ³⁺	Red brown precipitate	Insoluble
Pb ²⁺	White precipitate	Insoluble

Ca^{2+} , Al^{3+} and Pb^{2+} form white precipitates with aqueous ammonia solution which do not dissolve in excess.

Zn^{2+} ions form white precipitate in a few drops of aqueous ammonia. In excess of ammonia solution, the white precipitate of zinc ions dissolves forming a colourless solution. Cu^{2+} ions in a few drops of ammonia solution form a blue precipitate that dissolves in excess ammonia to give a deep blue solution due to formation of complex ions. Fe^{2+} and Fe^{3+} form coloured precipitates which do not dissolve in excess of ammonia solution.

Test for anions

Common anions tested are: carbonate (CO_3^{2-}), chloride (Cl^-), iodide (I^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}). There are specific reagents used in identification of each of these anions.

Carbonate (CO_3^{2-})

Add dilute acid (e.g. hydrochloric acid or nitric acid) to the carbonate (CO_3^{2-}). Pass any gas evolved through calcium hydroxide solution (lime water).

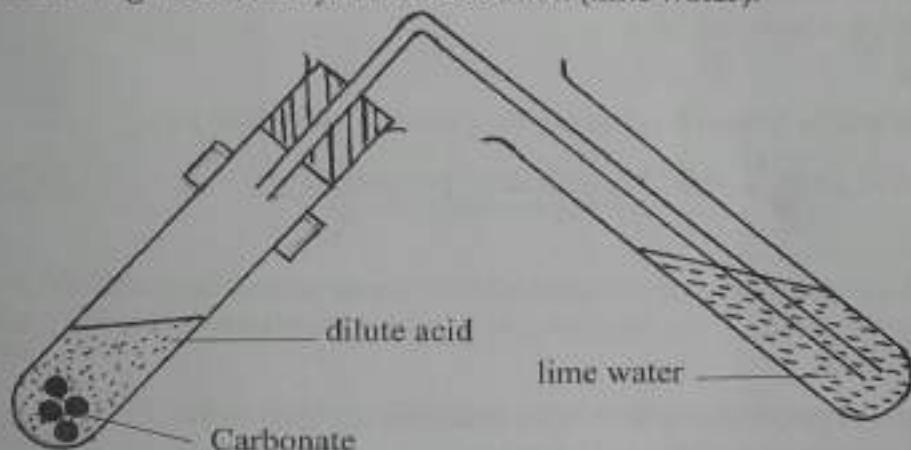
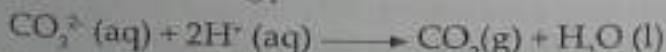


Fig 1.11: Investigating presence of carbonate ions in a substance

Observation

Effervescence occurs and the lime water turns milky. It shows carbon (IV) oxide was produced confirming presence of carbonate ions.



Chloride (Cl^-)

To the aqueous solution, add acidified silver nitrate solution.

Note: Silver nitrate is acidified by adding dilute nitric acid to it.

Observation

A white precipitate forms confirming the presence of chloride ions. Remember silver chloride is an insoluble salt.



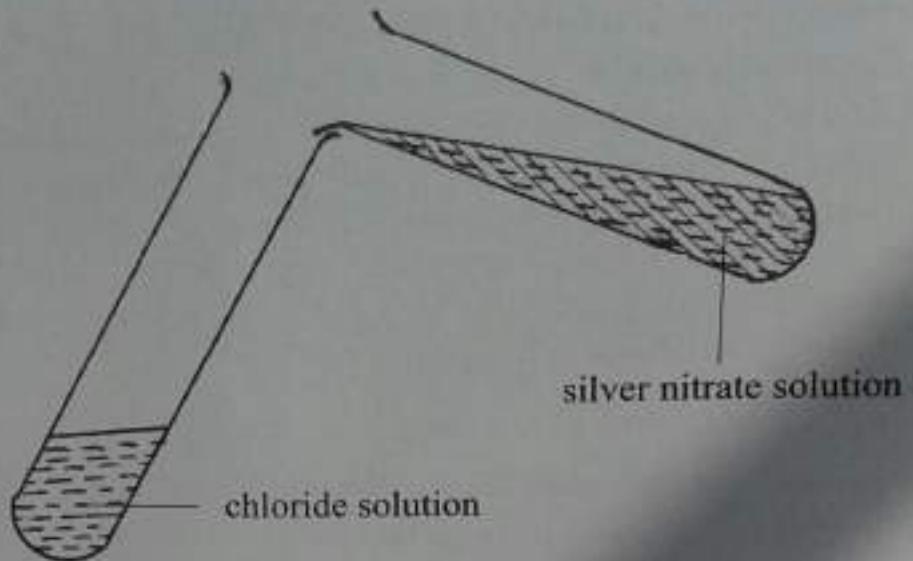


Fig 1.12: Testing for presence of chloride ion

Iodide (I⁻)

Place 5 cm³ of the iodide solution in a test tube. Add 3 drops of nitric acid, followed by aqueous lead (II) nitrate solution.

Observations

A yellow precipitate forms. It confirms the presence of iodide ions.



Nitrate (NO₃⁻)

To a little nitrate solution, add aqueous sodium hydroxide. Drop aluminium foil into the solution and warm gently. Test the gas produced with damp red litmus paper.

Observation

Damp red litmus paper turns blue. This indicates the gas evolved is basic. Hence the gas is ammonia, the only common basic gas.

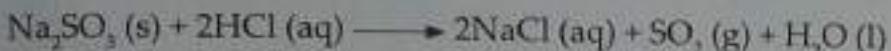


Note: That the nitrate ions are reduced to ammonia, NH₃ (g) which turns damp red litmus paper blue. Addition of hydrogen atoms to NO₃⁻ to give NH₃ is called reduction.

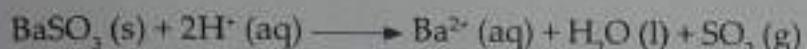
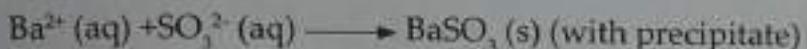
Another test for nitrate is the brown ring experiment. Add equal volume of fresh iron (II) sulphate solution. With the test tube, sloping concentrated sulphuric acid is carefully poured down its side and a "brown ring" forms where the two layers meet. The formula of the brown substance is FeSO₄.NO.

Sulphite (SO₃²⁻)

Add dilute hydrochloric acid to a sulphite solution and heat the mixture. A colourless gas which is sulphur (IV) oxide with a pungent irritating smell is produced. It turns orange potassium dichromate (VI) solution to green. It also decolourises potassium manganate (VII) solution.



Sulphite ion can also be tested with barium nitrate or barium chloride solution. Formation of a white precipitate which is soluble in dilute nitric acid or hydrochloric acid confirms presence of SO_3^{2-} .



Sulphate (SO_4^{2-})

To 2 cm³ of sulphate solution in a test tube, add dilute nitric acid followed by barium nitrate solution.

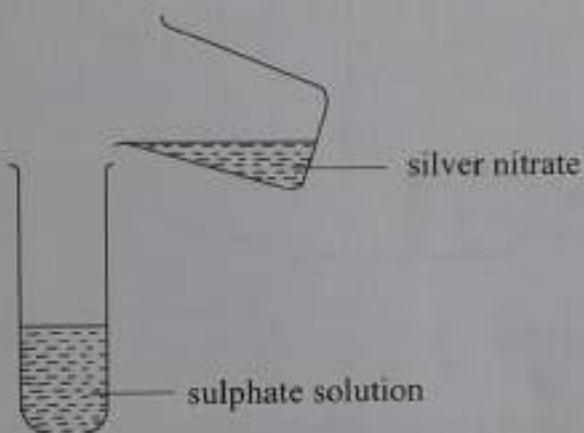
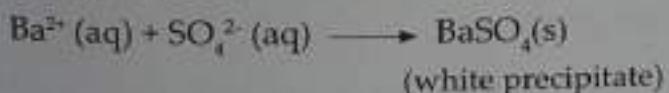


Fig 1.13: Testing for presence of Barium ions

Observation

A white precipitate forms. This confirms presence of sulphate ions.



Sulphide (S^{2-})

Add dilute hydrochloric acid to a sulphide.

Observation

A colourless hydrogen sulphide gas is produced which has characteristics of rotten egg smell. The gas turns filter paper soaked in lead nitrate solution or lead ethanoate solution black.



Identification of gases

There are common tests for gases. The following tests describe the confirmatory tests for some gases.

Ammonia (NH_3)

Introduce damp red litmus paper into a gas jar containing ammonia.

Observation

The damp red litmus paper turns blue. This confirms presence of ammonia gas. Ammonia is the common basic gas.

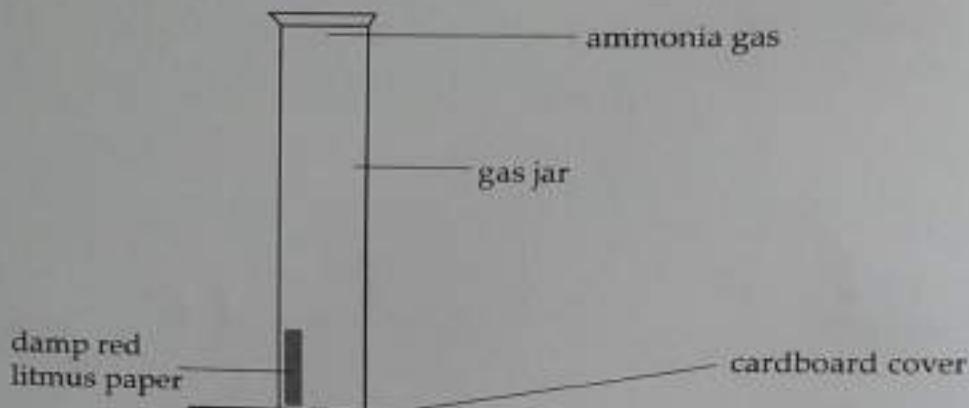


Fig 1.14: Test for ammonia gas

Carbon dioxide

Bubble the gas produced through lime water (calcium hydroxide solution).

Observation

Formation of white precipitate i.e. lime water turning milky confirms the gas is carbon dioxide.

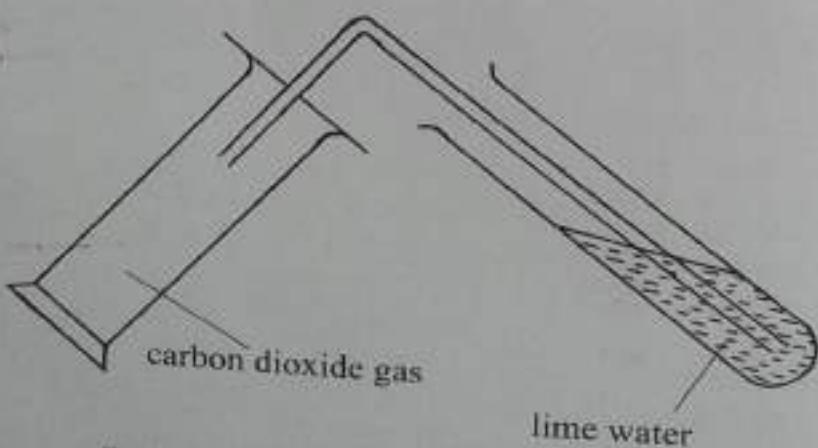
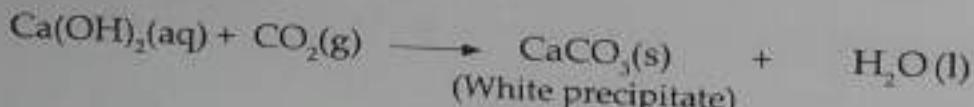


Fig 1.15: Confirmatory test for carbon dioxide

Chlorine

Hold moist blue litmus paper at the mouth of a test tube containing chlorine gas.

Observation

Moist blue litmus paper turns red and then gets bleached. This confirms presence of chlorine gas.

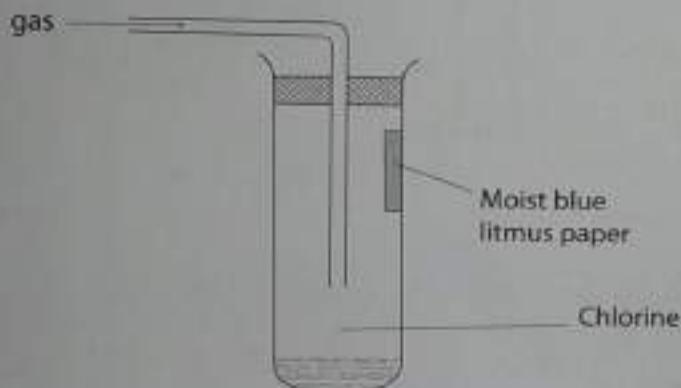


Fig 1.16: Confirmatory test for chlorine gas

Hydrogen chloride gas turns the blue litmus paper red while hypochlorous acid (HClO) is responsible for bleaching Cl_2 the litmus paper.

Hydrogen gas (H_2)

Introduce a burning splint at the mouth of a gas jar containing hydrogen.

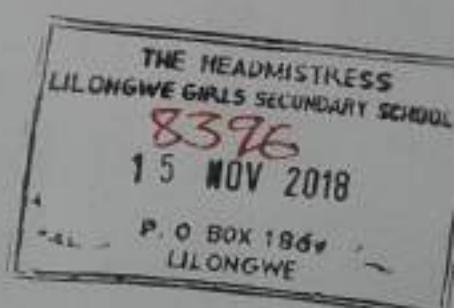
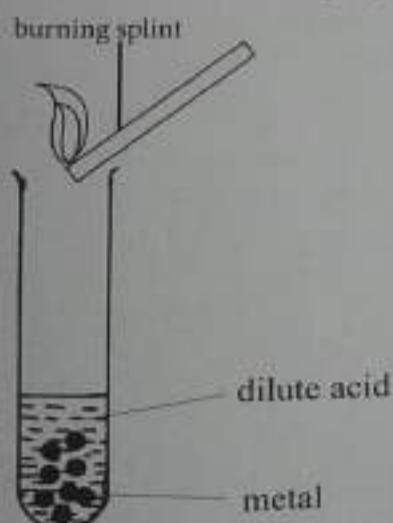


Fig 1.17: Confirmatory test for hydrogen

Observation

If the gas burns with a 'pop' sound, the gas present is hydrogen.

Oxygen gas

Introduce a glowing splint into a gas jar containing oxygen gas.

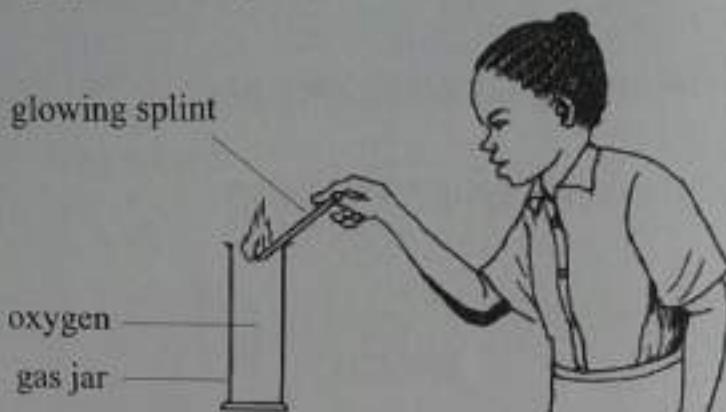


Fig 1.18: Confirmatory test for oxygen gas

Observation

The glowing splint relights (bursts into a flame). This is a confirmatory test for oxygen gas. Oxygen is the only gas that supports burning.

Sulphur dioxide (SO_2)

Dip a filter paper in acidified potassium dichromate (VI) and drop the paper in a gas jar containing sulphur dioxide.

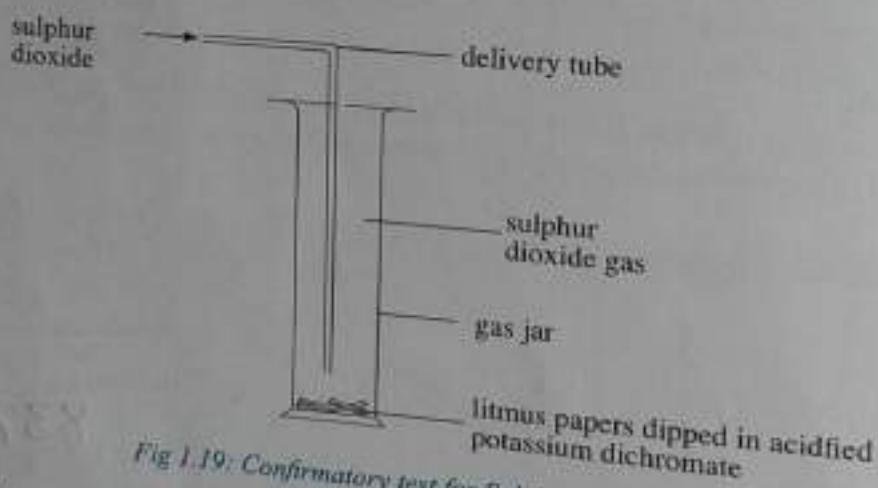


Fig 1.19: Confirmatory test for Sulphur dioxide (SO_2)

Observation

The filter paper turns from orange to green. This confirms the presence of sulphur dioxide.

Alternatively, bubble sulphur dioxide gas through acidified potassium manganate (VII) solution. The acidified potassium manganate (VII) changes from purple to colourless i.e. discolourises. This confirms the gas is sulphur dioxide.

Explanation

- i. Colour change from orange to green.



The oxidation state of chromium changes from +6 in $\text{K}_2\text{Cr}_2\text{O}_7$ to +3 in Cr^{3+} , so the chromium ions are reduced.

- ii. Colour changes from purple to colourless.

This colour changes is possible when using dilute acidified potassium manganate (VII) solution, KMnO_4 .



The manganese ions are reduced from +7 in KMnO_4 (purple) to +2 in Mn^{2+} .

Worked example of qualitative analysis

Example 1

A student carried out the following experiments with solid X. All gases evolved are to be identified. Observations and conclusions were recorded as given in Table 5. Substance X was to be identified.

Table 1.5 shows the results of the qualitative analysis recorded.

Table 1.5: Tests and results for

Procedures	Observations	Conclusions
(a) Put a spatula endful of solid X in a dry test tube. Heat gently and then strongly.	Colourless gas which turns moist blue litmus slightly red is produced. The gas forms a white precipitate with calcium hydroxide solution. Yellow residue when hot. Residue turns white on cooling.	Carbon (IV) oxide produced. Carbonate ions present in X. Zinc oxide formed. Zn^{2+} ions present in X.
(b) Put half spatula endful of X into a clean test tube. Add about 2 cm ³ of dilute hydrochloric acid. Keep the resulting solution.	Effervescence (bubbles). Colourless gas which turns moist blue litmus paper slightly red. Forms a white precipitate with aqueous calcium hydroxide.	Carbon(IV) oxide produced. CO_3^{2-} ions present in X.
(c) To the solution in (b) above add about 5 cm ³ of distilled water. Divide this solution into two portions.	Colourless solution formed.	Coloured ions absent e.g. Cu^{2+} , Fe^{2+} , Fe^{3+} .

(i) To the first portion, add aqueous sodium hydroxide drop by drop until in excess.	White precipitate, soluble in excess to form a colourless solution.	Zn ²⁺ ions present in X.
(ii) To the second portion, add aqueous ammonia solution drop by drop until in excess.	White precipitate soluble in excess to form a colourless solution.	Zn ²⁺ ions in X confirmed.

The student can summarise the results as follows:

The cation present in solid X is Zn²⁺.

The anion present in solid X is CO₃²⁻.

Solid X is zinc carbonate.

Example 2

Carry out the following experiments with substance P which is a mixture of two compounds. You should identify any gas evolved. Record your observations and conclusions in a table like the one shown below.

Table 1.6: Tests and results for analysis of substance P

Procedure	Observations	Conclusions
(a) Put a spatula endful of P into a boiling tube. Add about 15 cm ³ of distilled water, shake well and filter. Keep both the residue and the filtrate.	A green residue and blue filtrate.	One compound of P is insoluble. Cu ²⁺ ions may be present.
(b) Using a narrow spatula put the residue into a clean test tube. Add about 2 cm ³ of dilute nitric acid. Keep the solution.	Effervescence; a colourless gas which turns moist blue litmus paper slightly red. Forms a white precipitate with calcium hydroxide solution	• Carbon(IV) oxide produced. CO ₃ ²⁻ ions present in the insoluble compound of P (residue).
(c) To solution from (b) add aqueous ammonia drop by drop until in excess.	Blue precipitate which dissolves in excess to form a deep blue solution.	Cu ²⁺ ions present in the residue
(d) Divide the filtrate in obtained (a) into three portions	—	

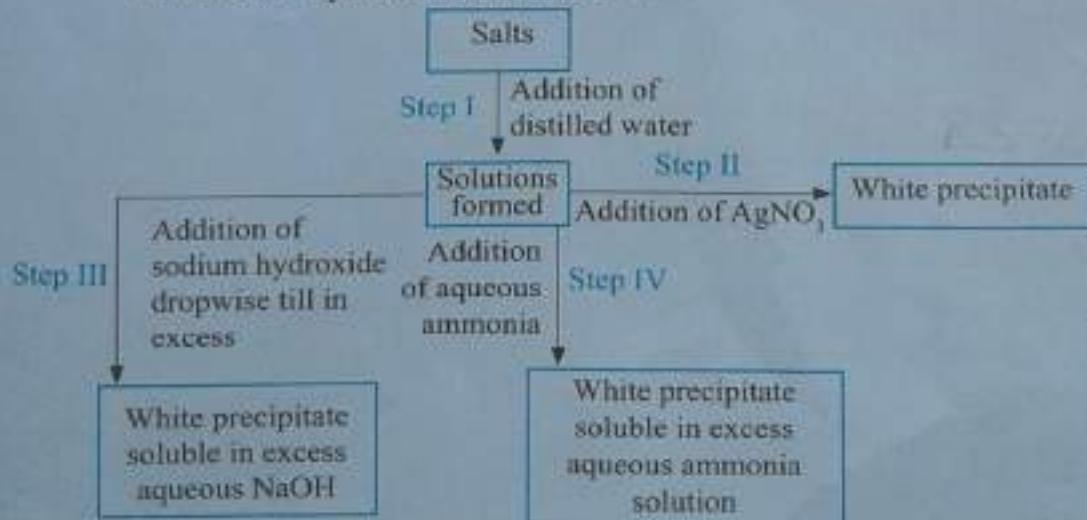
(i) To the first portion add aqueous sodium hydroxide drop by drop until in excess.	<ul style="list-style-type: none"> Blue precipitate insoluble in excess. 	<ul style="list-style-type: none"> Cu^{2+} ions present in the filtrate.
(ii) To the second portion add aqueous ammonia drop by drop until in excess.	<ul style="list-style-type: none"> Blue precipitate soluble in excess to form deep blue solution. 	<ul style="list-style-type: none"> Cu^{2+} ions confirmed in the filtrate.
(iii) Evaporate the third portion to dryness and then heat the remaining solid strongly.	<ul style="list-style-type: none"> A red-brown gas which turns moist blue litmus paper red evolved. A gas which relights a glowing splint also evolved. A black residue formed. 	<ul style="list-style-type: none"> Nitrogen(IV) oxide, NO_3^- ions present in the soluble compound of P. Oxygen evolved. Copper (II) oxide formed.

The ions present in mixture P are copper (II) ions, carbonate ions and nitrate ions. Explain how you can confirm the presence of the anion in the filtrate in part (a).



Practice exercise 1B

- a) Name the reagents used in qualitative analysis.
b) Which anions are identified using the following solutions?
 (i) Silver nitrate.
 (ii) Barium nitrate.
- a) In an experiment to determine the identity of a salt, several tests were done. The flowchart below shows summary of tests done. Study it and answer questions that follow.



- (i) Identify the cation and anion in salt T.
(ii) Name salt T.
- b) A student came across a colourless gas which she suspected to be carbon (IV) oxide. Describe how the student can confirm that the gas is carbon (IV) oxide.
3. a) Aqueous sodium hydroxide was added to various salt solutions as shown in the table. Complete the table correctly by filling the missing information.

Observation on addition of aqueous NaOH		
Cation in solution	3 drops	In excess
Zn ²⁺		
	Green precipitate	
Ca ²⁺		
		Insoluble blue precipitable

- b) State the observation made when aqueous ammonia was added to copper(II) ions solution dropwise until in excess.
4. a) Describe how one would test for the presence of sulphate ions in unknown salt compound.
- b) A glass rod dipped in concentrated hydrochloric acid was placed at the mouth of a test tube containing gas Y. No white fumes were formed. What is the most logical conclusion to make?

Test for presence of water

Experiment 1.6

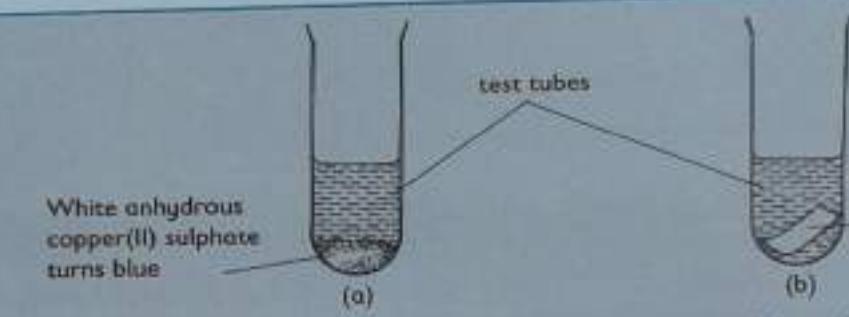
Aim: To test for presence of water

Requirements

- Test tubes
- Anhydrous copper (II) sulphate
- Dry cobalt (II) chloride paper
- Distilled or tap water

Procedure

1. Put about 5 cm³ of distilled or tap water in two separate test tubes.
2. Add anhydrous copper (II) sulphate into one test tube. Record the colour change.
3. Dip dry cobalt (II) chloride paper in the other portion. Record the colour change in table below.



White anhydrous
copper(II) sulphate
turns blue

(a)

Blue cobalt(II)
chloride paper
turns pink

(b)

Fig 1.20: Effects of water on anhydrous copper (II) sulphate and dry cobalt (II) chloride paper

Substance	Observations on addition of water
Anhydrous copper (II) sulphate	
Dry Cobalt (II) chloride paper	

Discussion

The change of colour of white anhydrous copper (II) sulphate to blue and that of blue anhydrous cobalt chloride to pink is a confirmatory test for water.

When anhydrous compounds combine with water, they form hydrated compounds.

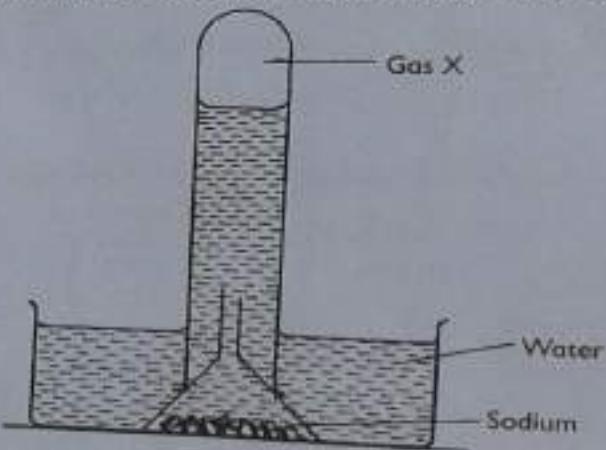


Practice exercise 1C

1. (i) Name two colourless gases with no smell.
(ii) Give two gases with colour and have smell.
2. How can you identify:
 - (i) Ammonia gas.
 - (ii) Chloride salt
 - (iii) Zinc ions
3. Name one salt which is:
 - (i) blue in colour.
 - (ii) green in colour.
 - (iii) pale green in colour.
4. (i) Why do we add nitric acid in the test of chloride when using silver nitrate solution?
(ii) Why do we add nitric acid in the test of sulphate when using barium nitrate solutions?
5. Give the test for:
 - (a) Water?
 - (b) Oxygen
 - (c) Carbon dioxide

Revision Exercise 1





- a. Name gas X

b. Give the test for this gas.

c. What is the name of the resulting solution?

d. Explain why it is not advisable to prepare this gas using potassium instead of sodium using the same set-up.

7. Give reasons for the following observations from experiments.

a. i) When dry cobalt(II) chloride paper is left exposed overnight, its colour turns from blue to pink.

ii) If copper is heated in air its mass increases.

iii) If a clean nail is placed in a test tube containing water, after 2-3 days it rusts, but if a similar clean nail is placed in water which is first boiled, it stays longer before it rusts.

b. Explain briefly why new corrugated iron sheets used for roofing are very shiny but after some time they appear dull.

Topic 2:

Nitrogen, Sulphur and Phosphorus

Success criteria

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



- Describe sources of nitrogen.
- Describe properties of nitrogen.
- Explain uses of nitrogen and its compounds.
- Describe sources of sulphur.
- Describe properties of sulphur.
- Explain uses of sulphur and its compounds.
- Describe the sources of phosphorus.
- Describe properties of phosphorus.
- Explain uses of phosphorus and its compound.

2.1 Nitrogen and its compounds

Nitrogen is a group V element and period 2 of the periodic table as shown in Fig. 2.1 below. It has atomic number 7. Its electronic configuration is 2.5 and it has a valency of 3. It can also exhibit a valency of five. Nitrogen makes up about 78% of the air.

I	II	III	IV	V	VI	VII	VIII
		B	C	¹⁴ ₇ N	O	F	Ne
Li	Be						

Fig. 2.1: Position of Nitrogen in the periodic table

Sources of Nitrogen

Nitrogen is available as free element in the air. It is also found as constituent of certain compounds, for example:

- Fertilizers e.g. ammonium nitrate NH_4NO_3 , Ammonium phosphate $(\text{NH}_4)_3\text{PO}_4$, sodium nitrate NaNO_3 , e.t.c.
- Proteins.
- Amino acids e.g. NH_2COOH in many organic compounds.

Compounds of nitrogen

Nitrogen has a number of compounds. These include:

- (i) Ammonia
- (ii) Acids of nitrogen such as nitric acid, nitrous acid
- (iii) Oxides of nitrogen such as nitrogen (I) oxide, nitrogen (II) oxide and nitrogen (IV) oxide.

Preparation of Nitrogen

Nitrogen can be prepared in the laboratory. It can be also industrially prepared by fractional distillation (isolation) of air.

Laboratory Preparation of Nitrogen

The two common methods of preparing nitrogen in the laboratory are:

1. Isolation of nitrogen from the air.
2. Reaction of sodium nitrite with any ammonium salt.

Experiment 2.1

Aim: To isolate nitrogen from the air.

Requirements

- Combustion tube
- Gas jars
- Stand clamp
- Rubber stoppers
- Beehive shelf
- Copper turnings
- Source of heat
- Wash bottles
- Delivery tubes
- Potassium or sodium hydroxide solution

Procedure

1. Arrange the apparatus as shown in Fig. 2.2 below.
2. Heat the copper turnings strongly.
3. Force air out of the aspirator by passing a stream of tap water slowly into the aspirator.
4. Record your observations.

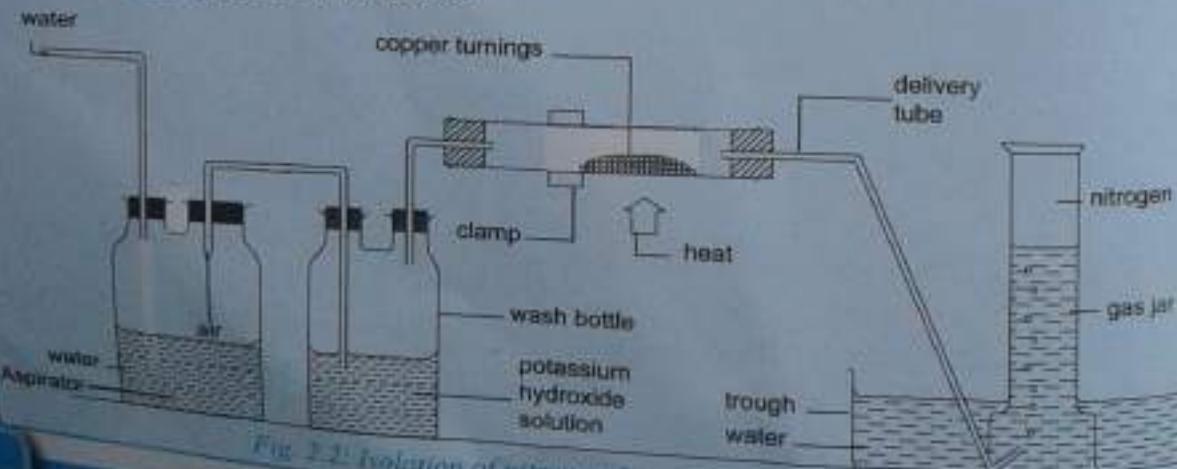


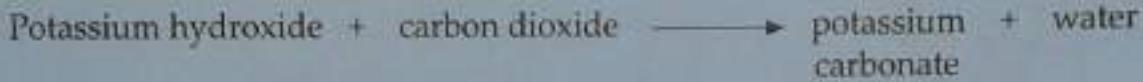
Fig. 2.2: Isolation of nitrogen from the air

Questions

- What do you observe in the wash bottle containing potassium hydroxide solution?
- What is the use of potassium hydroxide solution in this experiment?
- What did you observe inside the combustion tube?
- Why heat the copper turnings?
- What conclusions can you draw from this experiment?

Discussion

When air is forced out of the empty wash bottle it passes through the potassium hydroxide solution which removes carbon dioxide from it. Potassium hydroxide solution reacts with carbon dioxide as follows:



Heated copper turnings combine with oxygen in the air passing over it to form black copper(II) oxide.



The remaining air now largely consists of nitrogen and some impurities. Impurities include noble gases, water vapour and unreacted carbon dioxide and oxygen. Nitrogen being insoluble in water is collected over water or using a syringe.

If the gas is required dry, it is passed through concentrated sulphuric acid or anhydrous calcium chloride. Nitrogen obtained using this method is about 99% pure.

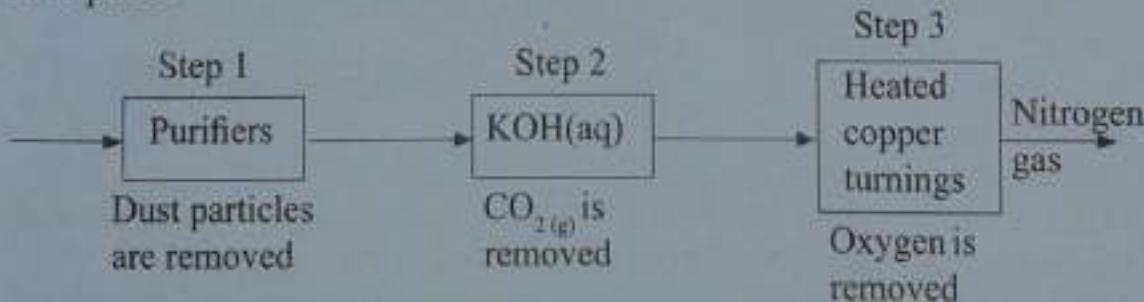


Fig. 2.3: Flowchart showing stages of nitrogen isolation from the air

Question

Explain why it is difficult to remove noble gases from the air?

Experiment 2.2

Aim: To prepare nitrogen by reaction of ammonium chloride and sodium nitrite.

Requirements

- Round-bottomed flask
- Delivery tube
- Bunsen burner or any source of heat
- Trough, beehive shelf, distilled water
- Gas jars, clamp stand, rubber bung
- Sodium nitrite
- Ammonium chloride

Procedure

1. Put some water in a beaker. Add some amount of sodium nitrite and ammonium chloride into the water and stir to dissolve well.
2. Pour the solution into a round-bottomed flask.
3. Arrange the apparatus as shown Fig. 2.4 below.

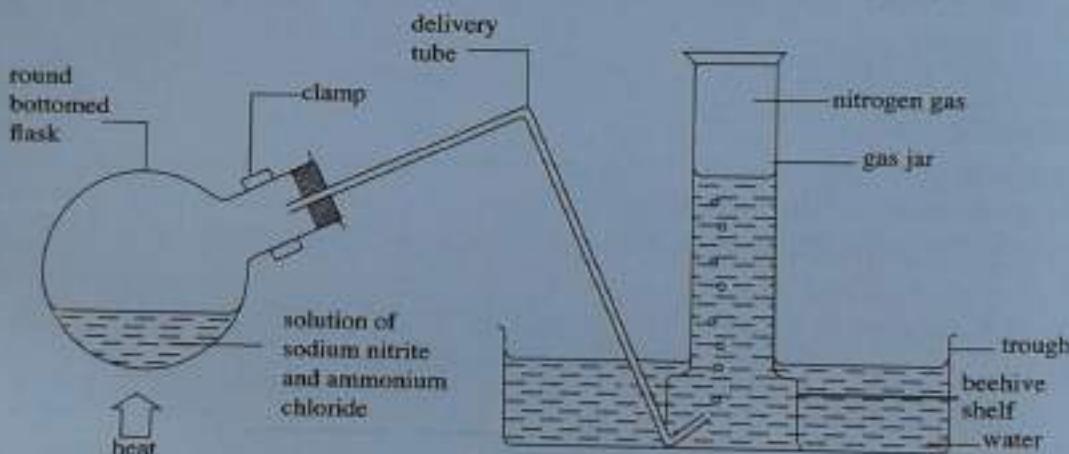


Fig. 2.4: Preparation of nitrogen

4. Warm the flask lightly and then remove the heat. What do you observe in the flask and gas jar? Record your observations in your note book.
5. Collect five gas jars of nitrogen and keep them for the next experiment.

When a solution of sodium nitrite and ammonium chloride is warmed in the flask, effervescence occurs. The reaction increases rapidly even without further heating. Bubbles are seen in the gas jar as a colourless gas is collected over the water.

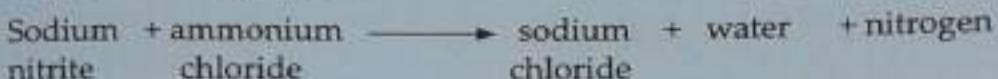
Sodium nitrite reacts with ammonium chloride to first form ammonium nitrite.



The ammonium nitrite then decomposes to produce nitrogen.



Overall reaction equation:



If nitrogen gas is required dry, it is passed through concentrated sulphuric acid or anhydrous calcium chloride to remove water vapour.

Note: Solid ammonium nitrite can be heated to produce nitrogen. However, the ammonium nitrite explodes on heating. Therefore the method is not recommended for use in the laboratory.

Properties of nitrogen

Experiment 2.3

Aim: To determine some of the properties of nitrogen

Requirements

- Wooden splint
- Blue and red litmus papers
- Aqueous calcium hydroxide
- Magnesium ribbon
- Sulphur powder
- Five gas jars full of dry nitrogen collected from experiment 2.2
- A pair of tong

Procedure

Perform the following tests in Table 2.1. Draw and record your conclusions.

Table 2.1: Investigating the properties of nitrogen

Experiment	Observations	Conclusions
1. Observe the colour and smell of nitrogen in the 1 st gas jar.		
2. Introduce a glowing splint into the 1 st gas jar.		
3. Introduce a burning splint into the mouth of the 1 st gas jar.		
4. Drop wet, blue and red litmus papers into the second gas jar.		

- | | | |
|--|--|--|
| 5. Add a few drops of aqueous calcium hydroxide into the third gas jar. Shake gently. | | |
| 6. Lower a burning magnesium ribbon into the fourth gas jar. Add water to the products formed. | | |
| 7. Lower burning sulphur on a deflagrating spoon into the fifth gas jar. | | |

Physical properties of nitrogen

- Has no colour.
- Has no smell (odourless).
- It is insoluble in water.
- It is less dense than air.

Chemical properties of nitrogen

(i) Combustion

Nitrogen does not burn or support combustion. This is why a glowing splint stop glowing or burning splint goes off when introduced into gas jar containing nitrogen gas.

(ii) Effect on litmus indicator

Nitrogen is neutral gas. Litmus papers show no colour change.

(iii) Effect on aqueous calcium hydroxide

Nitrogen has no effect on calcium hydroxide solution.

(iv) Reaction with magnesium and sulphur

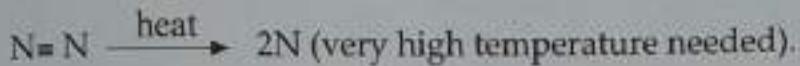
Nitrogen reacts with a burning magnesium metal to form magnesium nitride.



Magnesium nitride reacts with water to form magnesium hydroxide solution and ammonia gas.



However, nitrogen does not react with burning sulphur. This is because the heat produced from burning sulphur is not sufficient to break the strong triple covalent bonds ($N=N$) between the nitrogen atoms. In general nitrogen is **inert** gas at room temperature. It does not react with most substances at room temperature. The reaction with burning magnesium metal is made possible due to the high temperatures and a lot of heat energy produced by the burning magnesium capable of breaking the strong covalent bonds of the nitrogen atoms. The single nitrogen atoms formed now can react with magnesium.



(v) Inert character of Nitrogen

Inertness refers to the reluctance of an element to participate in reactions. A number of elements particularly group O elements were initially thought not to react and were called **inert** gases. Nitrogen is also largely considered as an inert element.

Nitrogen is a diatomic gas that have strong triple covalent bonds($N=N$) between the atoms of its molecules. These bonds require a lot of energy to break. Since the bonds must first be broken before nitrogen can react, at room temperatures or not very hot temperatures, nitrogen does not react. Under these conditions nitrogen is described as inert. However under very high temperatures conditions as we have seen; it can react e.g. with burning magnesium.

Industrial isolation of nitrogen from air

Large scale production of nitrogen is carried out industrially through a process called **fractional distillation or liquefaction** of air.

The first step in this process is the removal of impurities such as water vapour, dust particles and carbon dioxide. Carbon dioxide and water vapour which solidify easily would block the pipes if not removed at this stage.

The air is then compressed to about 200 atmospheres making it very hot. It is then allowed to expand through a jet causing it to become very cold. Some of it turns into liquid (liquefy). The compression and expansion process is repeated several times and each time the air gets much colder. By the time it reaches -200°C , most of the gases, that is, nitrogen, oxygen and argon have become liquid except neon and helium. The two noble gases are thus removed.

Nitrogen and oxygen have different boiling points. This makes it easy to separate them during the liquefaction process. Liquid nitrogen having a lower boiling point (-196°C) distils first. The nitrogen is collected and stored under pressure in steel cylinders. The remaining liquid containing mainly oxygen and argon is further heated. Argon whose boiling point is -186°C distils leaving oxygen with a higher boiling point of -183°C . These two gases are also collected and stored.

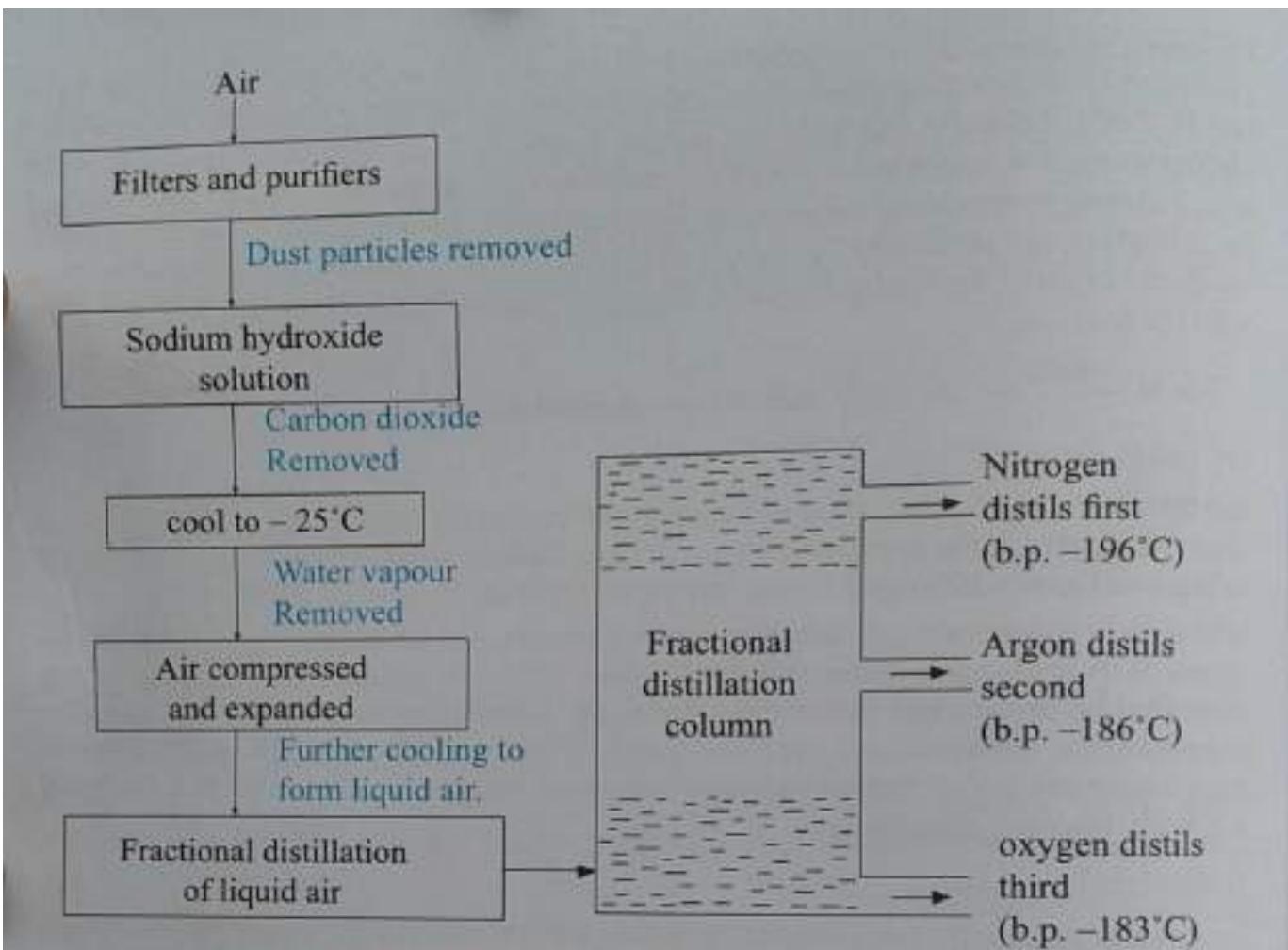


Fig. 2.5: Flowchart showing stages in fractional distillation of liquid air

Uses of nitrogen

- It is used in the Haber process to manufacture ammonia gas.
- The boiling point of liquid nitrogen which is -196°C makes it suitable to be used as a coolant to quickly freeze substances. For example it is used for long period of storage of body tissues and bull's semen for future use.
- It can also be used in the mending of pipes. When liquid nitrogen is poured on the pipe it freezes the liquid inside allowing repair work to be conveniently carried out.
- It is used in food processing and packaging to keep off oxygen. This provides an inert atmosphere preventing oxidation of the food since most bacteria cannot survive in absence of oxygen. Therefore the food can stay fresh for a long period of time.
- Because of its inert nature at low temperatures, it is pumped in the ships' tanks transporting crude oil to remove any oxygen. This prevents any possible dangerous explosion that can occur from crude oil vapours mixing with oxygen.

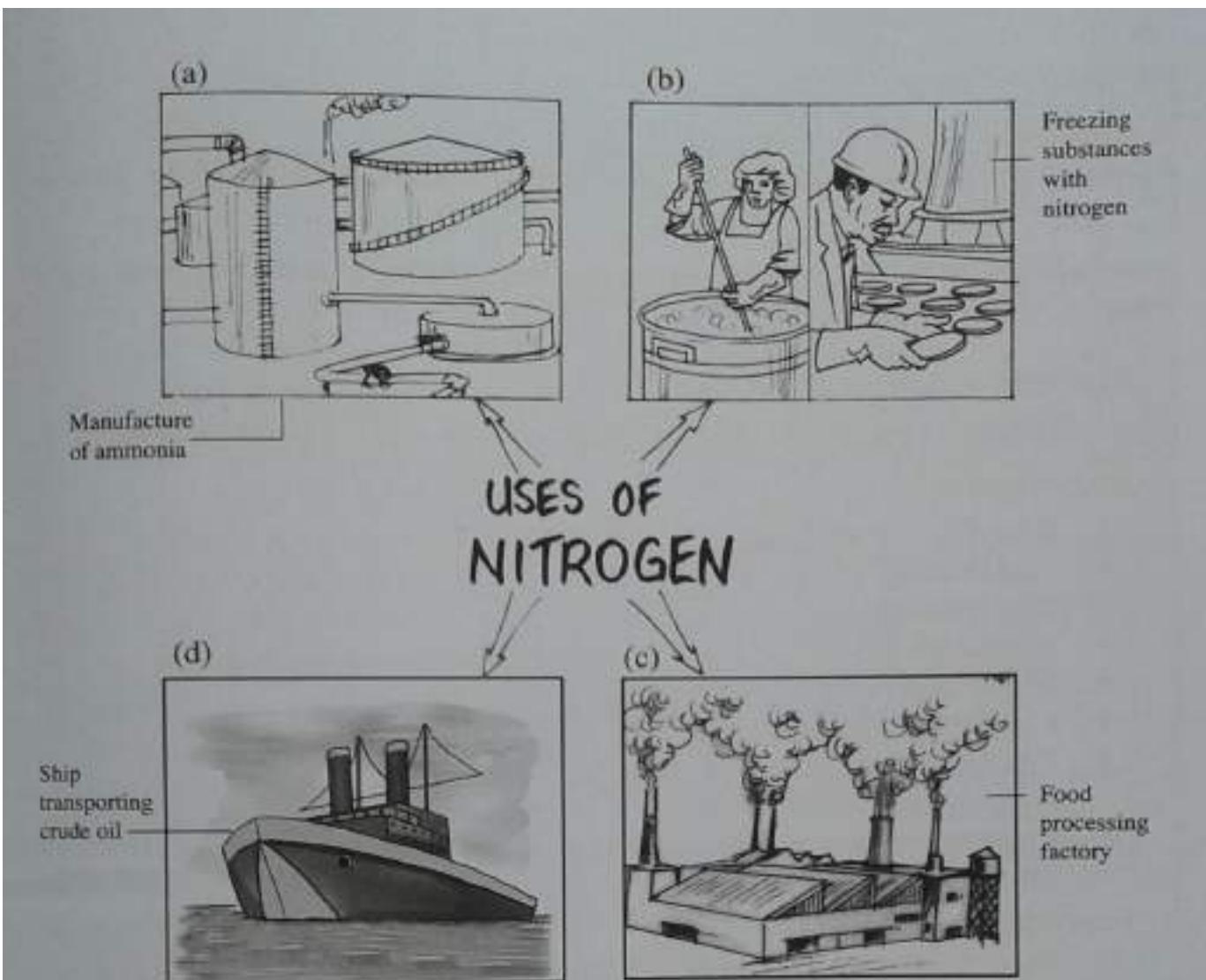


Fig. 2.6: Uses of nitrogen



Practice exercise 2A

1. Write the overall equation for the reaction of sodium nitrite and ammonium chloride.
2. Nitrogen can be obtained from the air by fractional distillation of air.
 - (a) Name the substances that are removed before air is compressed.
 - (b) What factor makes it possible for nitrogen to be removed from air by the named process?
3. (a) Write an equation for the reaction of nitrogen with magnesium. Name the product formed.
 (b) Name three uses of nitrogen.

Nitrogen compounds

Ammonia gas

Ammonia gas can be prepared in the laboratory or industrially by the **Haber process**.

Laboratory preparation of ammonia gas

Ammonia gas is usually prepared in the laboratory using an ammonium salt and a base.

Experiment 2.4

Aim: To prepare ammonia using ammonium chloride and calcium hydroxide

Requirements

- Round-bottomed flask
- Glass tubing
- Drying tower
- Several gas jars
- Mortar and pestle
- Cardboard cover
- Calcium hydroxide
- Ammonium chloride
- Calcium oxide
- Litmus papers

Procedure

1. Place small amounts of calcium hydroxide and ammonium chloride in a mortar.
2. Grind the mixture well using the mortar and pestle and put the mixture in a round-bottomed flask.
3. Arrange the apparatus as shown in Fig. 2.7 below.

Caution: Make sure that the flask is sloping before the experiment starts.

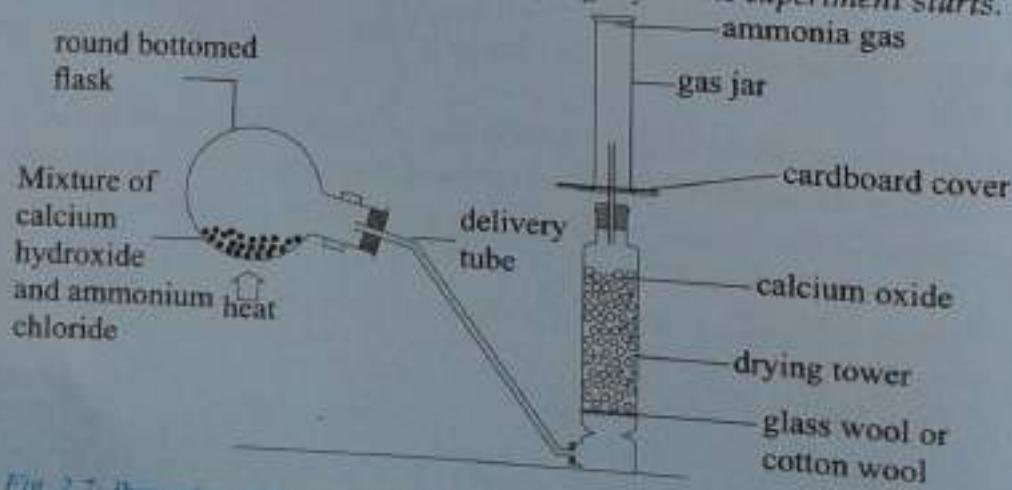


Fig. 2.7: Preparing ammonia gas using ammonium chloride and calcium hydroxide

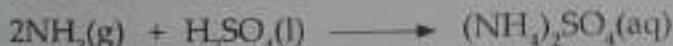
4. Heat the mixture.
 - What do you observe on the cool part of the flask and the delivery tube?
 - Record your observations in your notebook.
 5. Check whether the gas jar is full, by putting a moist red litmus paper at the mouth of the jar. The litmus paper will turn blue if the jar is full.
 6. Collect four jars of this gas and keep it for the next experiment.
 - (i) What is special about the drying of ammonia gas?
 - (ii) What property of gas is indicated by the method of the gas collection?

Discussion

When a mixture of calcium hydroxide and ammonium chloride is heated, ammonia gas is given off. The gas is dried using calcium oxide.



Calcium oxide is used in drying of ammonia gas since the gas reacts with the other usual drying agents such as anhydrous calcium chloride or concentrated sulphuric acid. With anhydrous calcium chloride it forms a complex solid compound ($\text{CaCl}_2 \cdot 4\text{NH}_3$). Ammonia reacts with concentrated sulphuric acid to form ammonium sulphate.



Water vapour is formed during the reaction. Some of it condenses on the cooler part of the flask and delivery tube. Therefore if the flask is not kept in sloping position, the water can run back into the hot part making it crack. Ammonia is collected by upward delivery because it is less dense than air.

Physical properties of ammonia gas

- It has a pungent choking smell.
 - It is colourless.
 - It is very soluble in water. Water rises rapidly in a gas jar full of this gas and fills or almost fills it if inverted in a trough containing water. This is demonstrated in fountain experiment.

Chemical properties of ammonia gas

1. Combustion

Ammonia does not burn in air nor support combustion.

2. Effect on litmus paper

Ammonia turns moist red litmus paper blue. It is the common alkaline gas known.

3. Reaction with hydrogen chloride

It reacts with hydrogen chloride gas to form white fumes of ammonium chloride.

Industrial manufacture of ammonia by Haber Process

Raw materials

The raw materials needed for the Haber process are **nitrogen** and **hydrogen**. Nitrogen is obtained from air by **fractional distillation of liquid air**. Hydrogen is usually obtained from the **natural gas** (methane) or crude oil. Hydrogen can also be obtained by electrolysis of acidified water or brine where electricity is cheap and readily available.

Optimum conditions necessary for the Haber process

- A mixture of nitrogen and hydrogen in the ratio of 1:3 by volume.
- A pressure of about 200 – 250 atmospheres.
- A temperature of about 400°C – 500°C.
- Finely divided iron catalyst impregnated with aluminium oxide as a promoter of the catalyst.

Process

A mixture of nitrogen and hydrogen in the ratio of 1:3 by volume is purified, dried and introduced into the reaction chamber where they are reacted.

High pressure and low temperatures give high yield, but the higher the pressure, the greater the cost of equipment to produce and maintain the pressure. At low temperatures, the rate of reaction is slow. Therefore a compromise has to be reached between a reasonable rate of reaction and a reasonable yield of ammonia. Most industries use temperatures of 400°C – 500°C and pressure of 500 atmospheres. However finely divided iron catalyst is used to increase the rate of reaction. The catalyst is mixed with aluminium oxide to increase its efficiency. A substance such as aluminium oxide which increases the efficiency of a catalyst is called a **promoter**.

Reactions taking place

When nitrogen and hydrogen react under the conditions mentioned, only about 10% of ammonia is formed. The reaction is **exothermic**.



The heat produced during the reaction is channelled to the heat exchanger together with the unreacted nitrogen, hydrogen and the 10% ammonia formed. This helps to maintain the temperatures at 500°C needed for the reaction. The ammonia produced and the unreacted hydrogen and nitrogen are then taken to the liquefier (condenser) where ammonia is liquefied or dissolved in water. The unreacted nitrogen and hydrogen are re-circulated back to the compressor. Fig. 2.5 shows stages and processes in the industrial manufacture of ammonia.

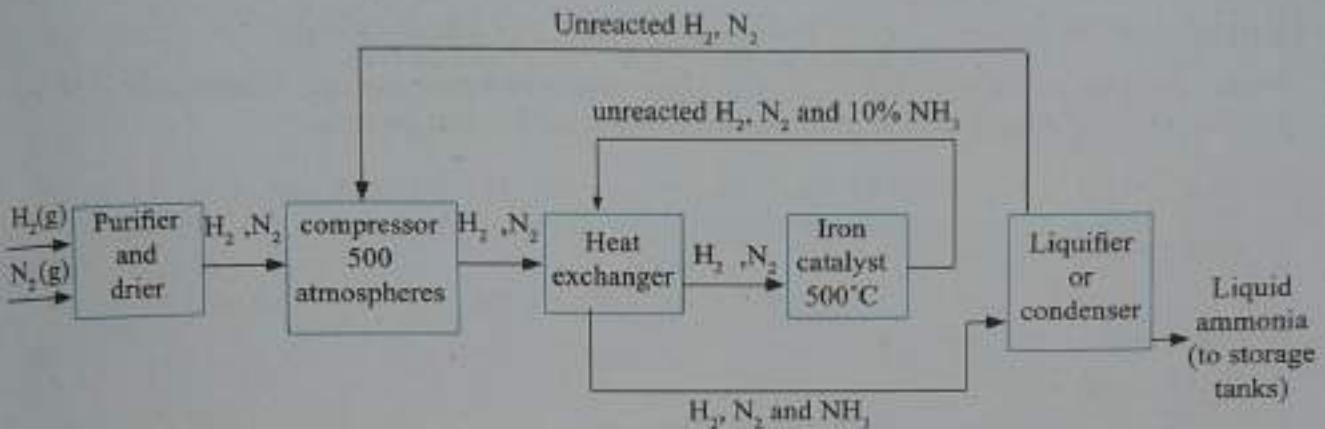


Fig. 2.8: Manufacture of ammonia by Haber process

Note: Nitrogen and hydrogen must be dried and purified first to remove dust particles, which may poison the catalyst. Argon which enters the plant with the nitrogen is also removed.

Uses of ammonia

1. Large quantities of ammonia gas are used to make fertilizers.
2. Ammonia gas is used in the manufacture of nitric acid.
3. Liquid ammonia is used as a refrigerant in large scale refrigerating plants and factories.
4. Ammonia solution is used as a solvent in cleaning agents e.g. in laundries.
5. Ammonia is used in the manufacture of ammonium salts such as **ammonium chloride** which is used in dry cells and **ammonium carbonate** used in smelling salts. Smelling salts produce ammonia gas slowly at room temperature acting on the heart to prevent fainting and dizziness.
6. Ammonia is used in the manufacture of dyes, wood pulp, plastics and fibres such as nylon.

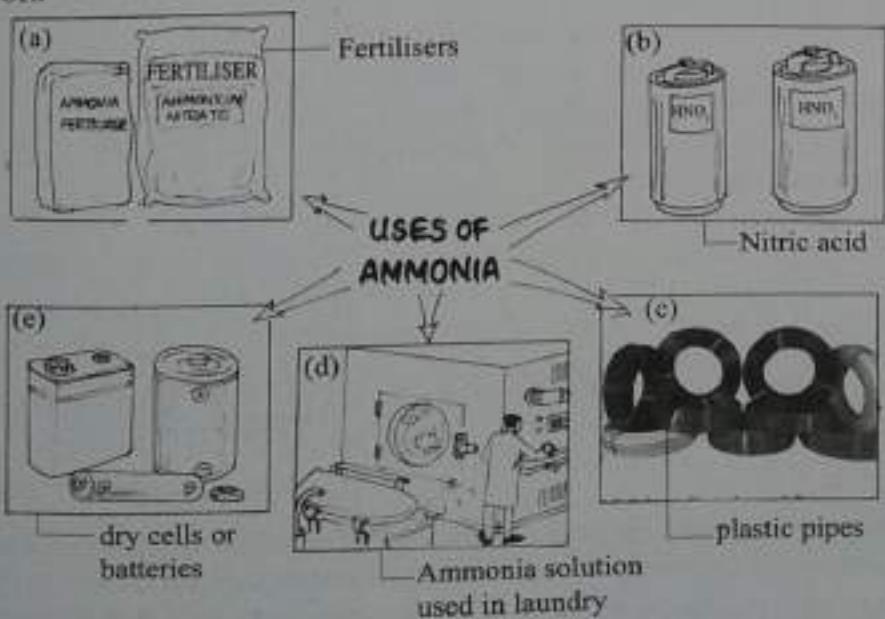


Fig. 2.9: Some uses of ammonia

Nitric acid

Nitric acid is a mineral acid. It is a powerful oxidizing agent. Nitric acid can be prepared in laboratory as well as industrially by Ostwald process.

Laboratory preparation of nitric acid

Experiment 2.5

Aim: To prepare nitric acid using potassium nitrate and concentrated sulphuric acid.

Requirements

- Retort flask
- Concentrated sulphuric acid
- Clamp stand
- Round or flat-bottomed flask
- Potassium nitrate

Procedure

1. Arrange the apparatus as shown in Fig. 2.10 below.

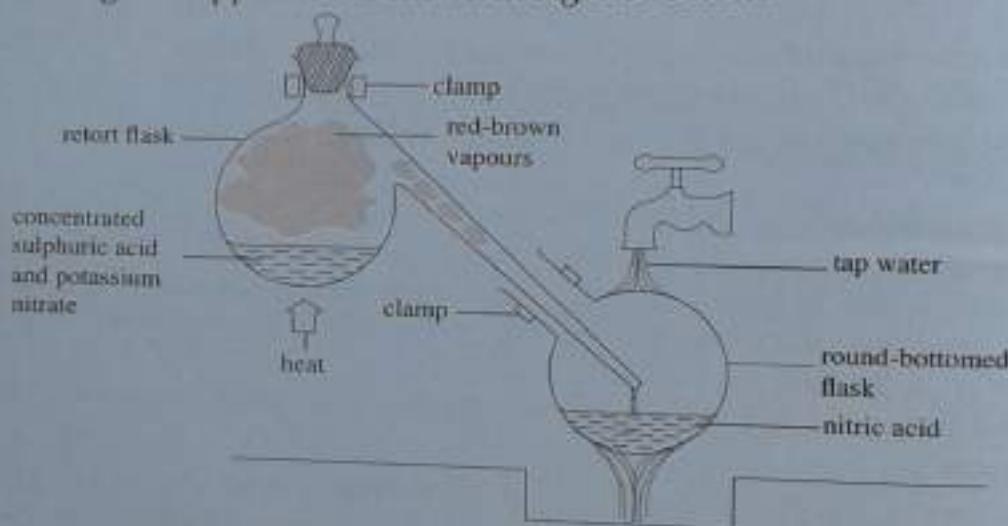
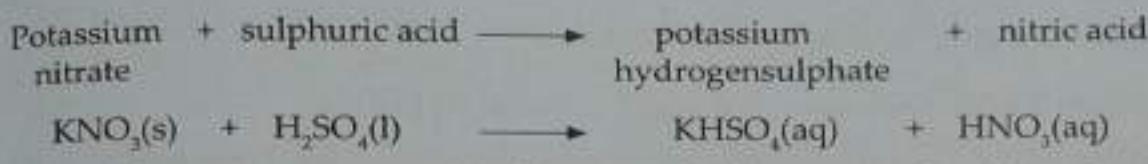


Fig. 2.10: preparing nitric acid

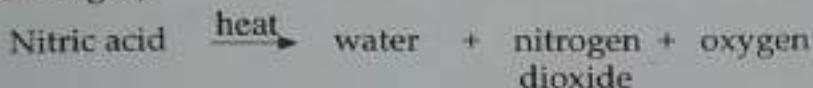
2. Put some potassium nitrate in the retort flask. Add concentrated sulphuric acid to cover the nitrate.
3. Run the tap water to cool the apparatus.
4. Heat the retort flask gently. What do you observe in the retort flask and the rounded bottomed flask? Record your observations.
5. Keep the acid formed for the next experiment.
 - a) Why are all the apparatus used in this preparation made of glass?
 - b) What can you conclude from this experiment?

Discussion

When concentrated sulphuric acid is added to potassium nitrate and heated, the potassium nitrate dissolves gradually and effervescence occurs. Nitric acid forms and distils because it is more volatile than concentrated sulphuric acid. Its vapours condense to form a yellow liquid.



The red-brown vapours seen in the retort flask is as a result of the decomposition of some of the nitric acid by heat, forming red-brown nitrogen(IV) oxide (nitrogen dioxide gas).



The nitric acid collected is yellow because it contains some dissolved nitrogen(IV) oxide, otherwise, pure nitric acid is colourless. The yellow colour can be removed by bubbling air through the acid.

A retort flask is used in the preparation of nitric acid because it is made entirely of glass. Hot nitric acid vapours attack cork or rubber stoppers and tubings.

Generally, heating all nitrates with concentrated sulphuric acid produces nitric acid. However potassium nitrate is preferred in laboratory preparation of nitric acid because it has no water of crystallisation which can dilute the acid produced. Sodium nitrate can also be used but it is hygroscopic.



Note: Nitric acid is kept in dark bottles. This is because light decomposes the acid into water, nitrogen(IV) oxide and oxygen.

Manufacture of nitric acid by Ostwald Process

Nitric acid is manufactured by the **catalytic oxidation of ammonia**. Ammonia is obtained through the Haber process. The catalyst used is platinum - rhodium gauze. The raw materials required are **ammonia**, air and water.

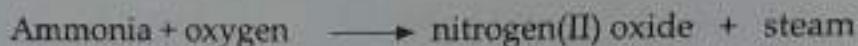
Optimum conditions needed

- Excess air
- Ammonia
- A temperature of $850^{\circ}\text{C} - 900^{\circ}\text{C}$
- Platinum - rhodium catalyst

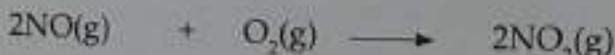
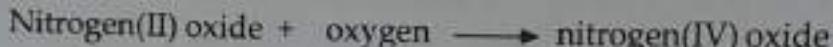
The air and ammonia must be free of dust and other impurities to avoid poisoning the catalyst.

Reactions taking place

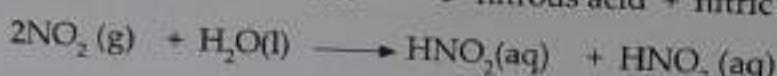
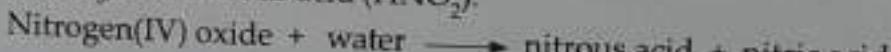
The first reaction in this process produces nitrogen(II) oxide (nitrous oxide) and water. The heat produced in this step maintains the suitable temperature and therefore no further heating is required.



Nitrogen(II) oxide and steam are cooled by air from the compressor. Nitrogen(II) oxide is further oxidised by the air to produce nitrogen(IV) oxide.



Nitrogen(IV) oxide is then passed through water where it dissolves to form nitrous acid (HNO_2) and nitric acid (HNO_3).



Excess air is passed to oxidise nitrous acid to nitric acid.

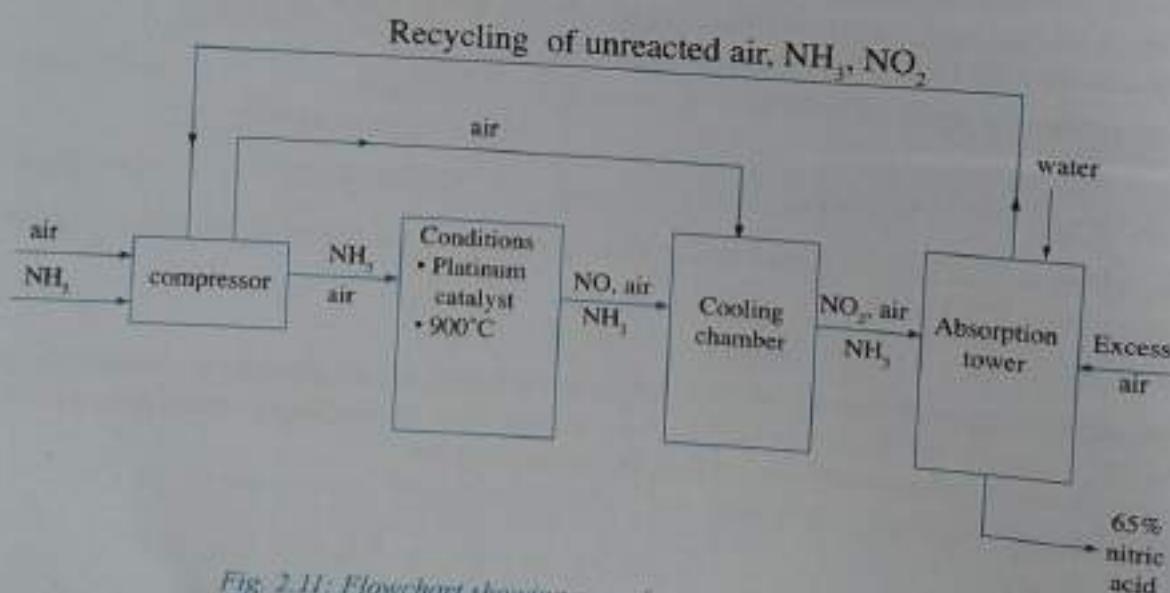
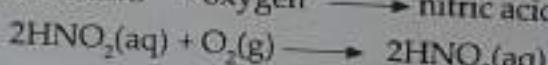
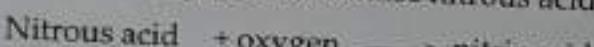


Fig. 2.11: Flowchart showing manufacturing stages of nitric acid

About 65 per cent nitric acid and 35 per cent water are produced from a single conversion. The unreacted air, ammonia and nitrogen(IV) oxide are re-circulated back to the compressor. The concentration of the nitric acid produced can be increased by distillation.

Uses of nitric acid

- Manufacture of nitrate fertilisers.
- Manufacture of explosives e.g. TNT and dynamite.
- Manufacture of dyes and drugs.
- Manufacture of plastics.

- (v) It is used as an oxidising agent in textile industries.
- (vi) It is used in the refining of gemstones.
- (vii) It is used in the identification of gold. Copper, bronze and copper iron disulphide (CuFeS_2) react with concentrated nitric acid. The acid does not react with gold, hence it can be used to distinguish gold from those other substances which have similar appearance.



Practice exercise 2B

1. Why are all the apparatus for preparation of nitric acid made of glass?
2. Give three oxides of nitrogen.
3. Name three uses of nitric acid

Manufacture of ammonium nitrate fertiliser

Plants need nitrogen to form essential protein molecules. They obtain this in a suitable form, nitrates. Nitrate can be added to soil in the form of fertilizers such as ammonium nitrate. Ammonium nitrate is the most important of the nitrogenous fertilizers.

Ammonium nitrate is manufactured by reacting nitric acid and ammonia.

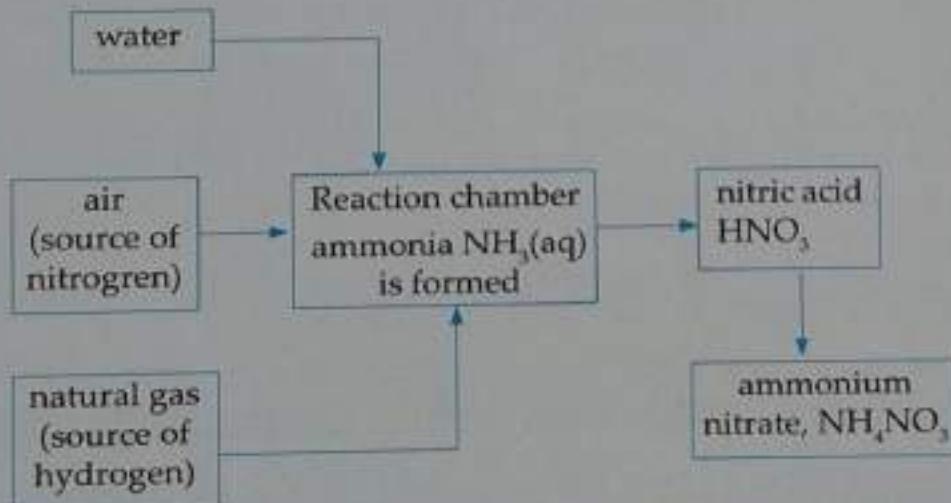
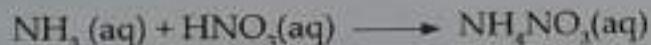


Fig. 2.12: Flowchart showing production of ammonium nitrate fertiliser

The ammonium nitrate is crystallized into granules which can be easily spread on the land. When ammonium nitrate dissolves in water, it forms two ions, ammonium ions, NH_4^+ and nitrate ions NO_3^- . The plants can absorb these ions through their roots or leaves. In this way plants are able to get the nitrogen to make the essential proteins.

Ammonium nitrate is hygroscopic. Because of this, it is packed with a drying agent to prevent the granules from sticking together. Ammonium salts tend to make the soil slightly acidic. When necessary the ammonium fertilizers may be mixed with calcium carbonate (chalk) which helps to neutralize the acidic effect.

Determining Percentage of nitrogen in ammonium nitrate

We can calculate the actual amount of nitrogen in a given fertilizer. This is usually expressed as a percentage. From the formulae of various fertilizers we first add the relative atomic masses of each element in the compound then calculate the percentage.

Example 1

Calculate the percentage of nitrogen in ammonium nitrate.

Solution

The formulae of ammonium nitrate is NH_4NO_3

$$\begin{aligned}\text{R.F.M of } \text{NH}_4\text{NO}_3 &= (2 \times 14) + (1 \times 4) + (3 \times 16) \\ &= 80\end{aligned}$$

$$\text{Fraction of N} = \frac{28}{80}$$

$$\begin{aligned}\% \text{ of N} &= \frac{28}{80} \times 100 \\ &= 35\%\end{aligned}$$

Example 2

Calculate the percentage of nitrogen in ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$.

Solution

R.F.M of $(\text{NH}_4)_2\text{SO}_4$

$$\begin{aligned}&= (2 \times 14) + (2 \times 1 \times 4) + 32 + (16 \times 4) \\ &= (28 + 8 + 32 + 64) \\ &= 132\end{aligned}$$

$$\text{Fraction of nitrogen is } \frac{28}{132} \times 100\%$$

$$\begin{aligned}\text{Percent of nitrogen} &= \frac{28}{132} \times 100\% \\ &= 21.2\%\end{aligned}$$

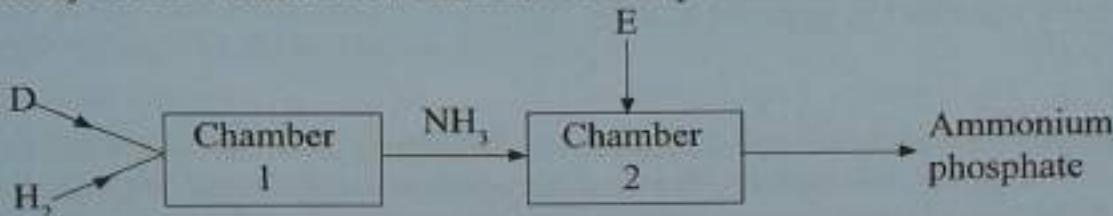
Practice exercise 2C

1. Calculate the percentage of nitrogen in the following fertilisers.
 - (a) Urea, $\text{CO}(\text{NH}_2)_2$
 - (b) Diammonium phosphate, $(\text{NH}_4)_2\text{HP}$
2. Calculate the number of grams of nitrogen in the 100 g of $(\text{NH}_4)_2\text{CO}_3$.

3. State the optimum conditions required for large scale production of ammonia.
4. Aqueous ammonia can be used to test cations. Write ionic equations to show the reactions of aqueous ammonia with the following salts solutions.

- (a) Zinc nitrate
- (b) Iron(III)chloride
- (c) Aluminium sulphate

5. Study the flowchart below and answer the questions that follow.



- (a) Identify substances D and E.
- (b) Give the optimum conditions necessary for the reaction in chamber 1.
- (c) Write an equation for the reaction in chamber 2.
6. Ammonia gas can be reacted with a certain reagent to produce ammonium sulphate which is an important fertiliser.
- (a) Write an equation to show how this fertiliser is formed.
 - (b) Calculate the percentage by mass of nitrogen in the fertiliser. ($N = 14$, $O = 16$, $H = 1$, $S = 32$).
 - (c) Both ammonium sulphate and sodium nitrate are used as fertilisers. Which of the two is fast-acting? Explain your answer.

2.2 Sulphur and its compounds

Sulphur is a group VI element and period 3 element of the periodic table as shown in Fig. 2.13 below. It has an atomic number of 16. Its electronic configuration is 2.8.6.

	I	II	III	IV	V	VI	VII	VIII
1								
2								
3	Na	Mg		Al	Si	P	$\frac{32}{16}$ S	Cl
4								

Fig 2.13: Position of sulphur in the periodic table

Sulphur is a yellow solid substance. It is a non-metal elements. It exhibits crystalline and non-crystalline allotropes. The crystalline forms are the **rhombic sulphur** and **monoclinic sulphur**.

Sources of sulphur

Sulphur occurs naturally in volcanic regions or regions where volcanoes were formerly active. It is found in its elementary form in several countries such as Italy, Mexico, Japan and the USA. Sulphur can occur as a "free" element or combined in compounds such as:

- hydrogen sulphide found in petroleum, coal deposit and natural gas.
- metal sulphides e.g. zinc blende (ZnS), iron pyrites (FeS_2), copper pyrites (CuS_2), galena (PbS) etc.
- metal sulphates e.g. gypsum ($CaSO_4 \cdot 2H_2O$).

Extraction of sulphur by Frasch process

The sulphur beds in Texas and Louisiana in USA are as much as 30 metres thick and occur at a depth of 160 metres. Between the surface sulphur and deposit, there is a layer of quicksand which makes it difficult to use common methods mining.

Hermen Frasch (1852–1914) an American chemist devised a method of mining sulphur, hence the process is named after him.

The basic principle of Frasch process is that sulphur is melted underground and pumped up to the surface of the earth. A borehole is drilled up to the deposit layers of sulphur and three concentric pipes are sunk into the bore as illustrated in Fig 2.14.

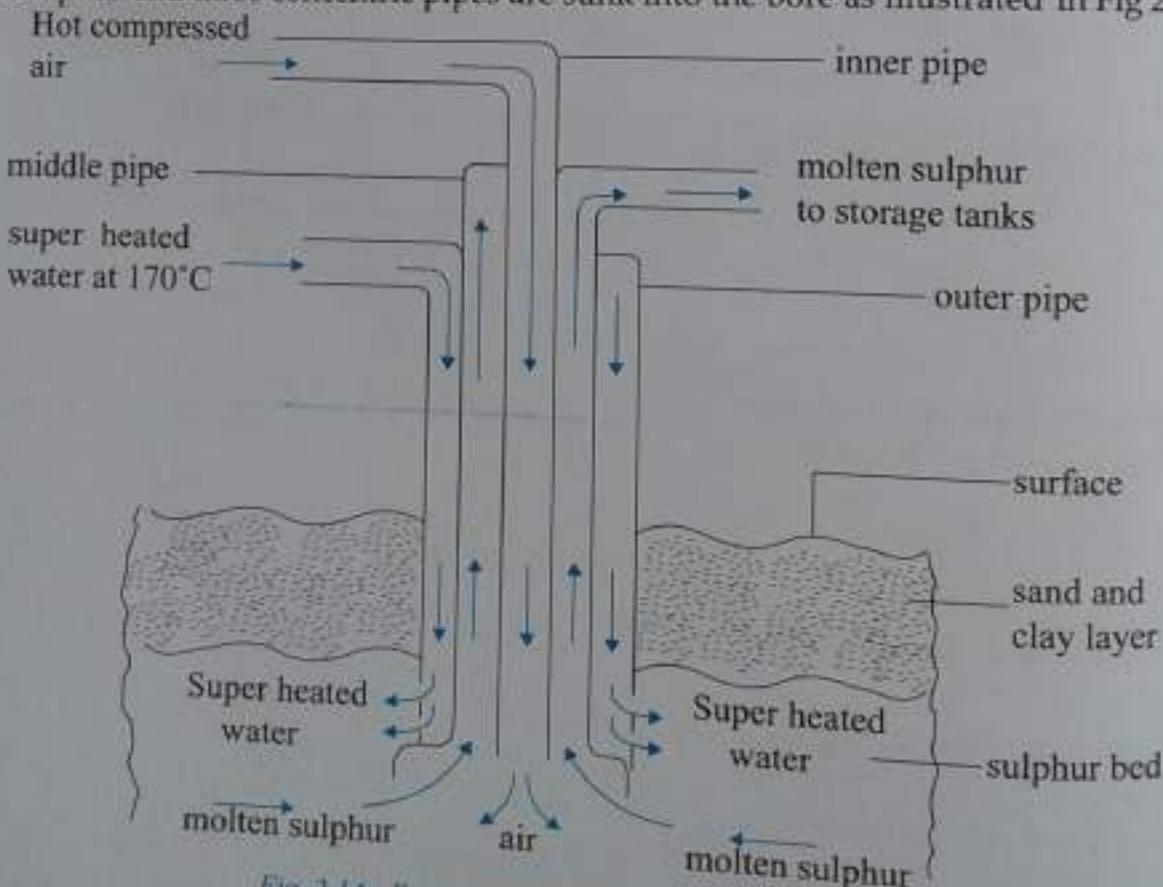


Fig. 2.14: Extraction of sulphur by Frasch process

Remember: Sulphur combines with water, it forms sulphur acid which is the major component of acidic rain, which corrodes materials and paints. Therefore mining of sulphur should be done in small quantity.

Functions of the three pipes during the extraction of sulphur

The outermost pipe which has the widest diameter of the three pipes is sunk to the sulphur bed. This pipe delivers **superheated** water. The second pipe is held a little above the surface of sulphur deposits. This pipe is the outlet for molten sulphur. The inner pipe brings **hot compressed air** into the sulphur deposits to force molten sulphur up the middle pipe to the storage tanks.

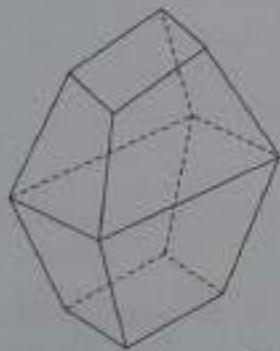
The extraction process

Superheated water at 170°C (under 10 atmospheres pressure) is pumped down the outermost pipe. The purpose of the superheated water is to melt sulphur at 113°C . Hot compressed air at about 15 atmospheres pressure is pumped down the innermost pipe to force up the froth of molten sulphur. This molten sulphur rises through the annular space between the inner most pipe and the second pipe. The molten sulphur is collected and stored in tanks. Sulphur cools and solidifies into solid blocks. The sulphur that is obtained from this process is over 99% pure.

Allotropes of sulphur

Rhombic sulphur or alpha sulphur (α -sulphur)

Rhombic sulphur is also known as **alpha** (α) sulphur. It is a yellow crystalline solid with an octahedral shape. Rhombic sulphur is stable below 96°C . Above this temperature, needle-shaped long prism crystals of monoclinic sulphur are slowly formed.



(a): Octahedrally shaped
rhombic sulphur



(b): Monoclinic sulphur

Fig. 2.15: Allotropes of sulphur

Monoclinic sulphur or beta-sulphur (β -sulphur)

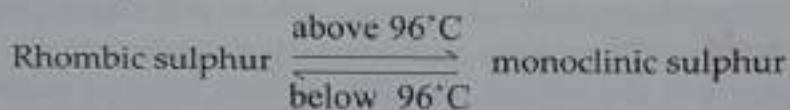
Monoclinic sulphur also known as beta-sulphur (β), is a yellow crystalline solid. It is obtained by allowing molten sulphur to solidify. Long prism shaped needle like sulphur as shown in Fig 2.15(b) form on the walls of the container. They can be easily separated from the molten sulphur by pouring off the latter. If monoclinic sulphur is

kept at room temperature for a few days, it gradually changes back to rhombic sulphur.

Table 2.2: Characteristics of rhombic and monoclinic sulphur

	Characteristics	Rhombic sulphur	Monoclinic sulphur
1.	Shape of the crystals	Octahedral	Long prism needle like
2.	Colour of the crystal	Yellow	Yellow
3.	Stability	Below 96°C	Above 96°C or 96°C to 119°C
4.	Density/m.p	2.07 g/cm ³ ; 113°C	1.96 g/cm ³ ; 119°C

Transition temperature of the two allotropes is 96°C.



The other two non-crystalline forms of sulphur are known as **amorphous sulphur** and **plastic sulphur**.

Plastic sulphur is a brown rubber-like liquid substance. It forms when the liquid is supercooled (suddenly cooled). The liquid gradually changes to a hard yellow opaque substance (rhombic sulphur).

Action of heat on sulphur

Experiment 2.6

Aim: To investigate the action of heat on sulphur

Requirements

- Boiling tube
- Source of heat
- Pair of tongs
- Sulphur
- Water

Caution: This experiment must be done in a fume chamber or an open space. The brown vapour of sulphur formed is poisonous.

Procedure

1. Transfer about a spatulaful powdered sulphur into a boiling tube.
2. Heat the powdered sulphur gradually as you move it in and out of the flame.
3. Observe any changes and record your observations as you heat. Continue the heating process until a dark brown vapour is formed.
4. Pour the boiling sulphur into a beaker of cold water. What do you observe?
 - Describe all the changes observed while the sulphur was being heated.
 - Describe the appearance of sulphur after it had been cooled in water.

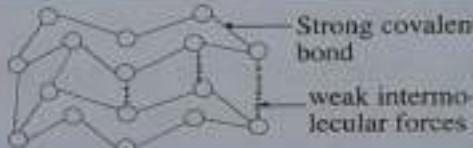
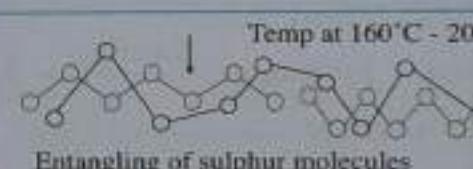
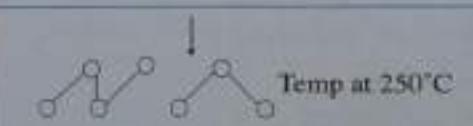
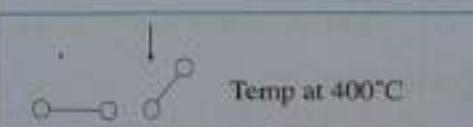
Discussion

Sulphur when heated undergoes a series of changes as you must have observed during the experiment. Table 2.3 shows changes that occur on heating of sulphur.

Table 2.3: Changes that occur on heating sulphur

Temperature	Observation
113°C	Sulphur melts to give a mobile amber liquid. As the temperature rises further; the liquid darkens.
180°C	The liquid becomes very thick or viscous. The colour changes gradually from red to black.
250°C	The liquid is so thick and viscous that it cannot flow.
Above 250°C	The colour becomes brighter and the liquid once more becomes mobile.

Table 2.4: Explanation about what happens when sulphur is heated

Explanation	Structure
1. Sulphur exists as S ₈ molecules at room temperature. The crown-shaped molecules are packed neatly together to form crystals.	
2. Melts at 113°C. Intermolecular forces are broken.	
3. The rings of 8 atoms open up as the molten sulphur is heated more strongly. The long chains entangle and make liquid sulphur viscous.	
4. Long chains start to break up to form smaller units. Liquid sulphur becomes less viscous (mobile).	
5. Short units escape from liquid as sulphur vapour.	

Physical properties of sulphur

- Sulphur is a yellow, non-metallic solid.
- It has low melting point.
- It is insoluble in water.
- Sulphur is soluble in organic solvents like methylbenzene and carbon disulphide among others.

Chemical properties of sulphur

Reaction of sulphur with oxygen

Experiment 2.7

Aim: To investigate reaction of sulphur with oxygen

Requirements

- Deflagrating spoon
- Source of heat
- Sulphur powder
- Gas jar full of oxygen

Procedure

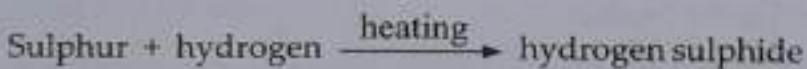
1. Place a small amount of sulphur in a deflagrating spoon and heat it.
2. Introduce the burning sulphur into gas jar of oxygen. What do you observe?
3. Record your observation.

Discussion

Sulphur burns in air or oxygen with a bright blue flame to form white fumes. The fumes are sulphur dioxide.



It can also combine directly with other non-metals like hydrogen.



Reaction of sulphur with metals

Experiment 2.8

Aim: To investigate the reaction of sulphur with metals

Requirements

- Spatula
- Source of heat
- Ignition tube
- Test tube holder
- Iron powder, copper turnings
- Sulphur powder

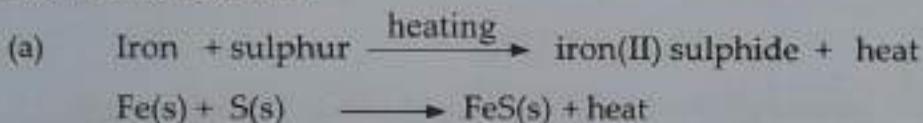
Procedure

1. Place spatulaful sulphur powder and spatulaful powdered iron in an ignition tube.
2. Heat the mixture. What do you observe?
3. Examine the residue when it has cooled down.
4. Repeat the experiment using copper turnings and sulphur powder.
 - What did you observe in each case? Record your observation in your notebook.
 - Suggest other metals that can combine with sulphur.
 - What do we call the above method of preparing salts?
 - What do you conclude?
 - Write balanced equations for the reactions.

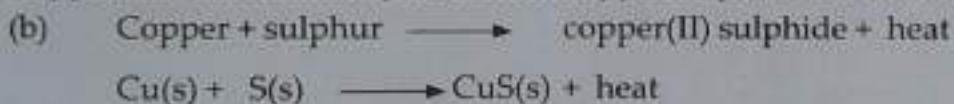
Discussion

Sulphur reacts with most metals to form metal sulphides.

A mixture of iron powder and sulphur reacts to form iron(II) sulphide. It is an exothermic reaction.



Copper also reacts with sulphur to form copper sulphide and the reaction is exothermic.



Other metals such as zinc and lead combine with sulphur when heated to form respective metal sulphides.

Reaction of sulphur with dilute and concentrated acids

Experiment 2.9

Requirements

- Sulphur powder
- Test tubes
- Test tube holders
- Dilute sulphuric, nitric and hydrochloric acids
- Concentrated sulphuric, nitric and hydrochloric acids
- Source of heat

Caution: Reaction of hot concentrated sulphuric acid with sulphur should be done in fume chamber or open space.

Procedure

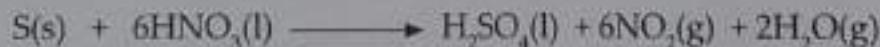
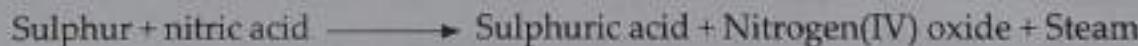
1. Place about 1 cm³ of dilute sulphuric acid in a test tube and add a small amount of sulphur powder to it. What do you observe?
2. Repeat step 1 using dilute nitric acid and hydrochloric acid instead of sulphuric acid.
3. Place a small amount of sulphur in a clean test tube. Add one to two drops of concentrated sulphuric acid and warm. What do you observe?
4. Repeat step 3 using concentrated nitric and hydrochloric acids.
 - Do dilute acids react with sulphur?
 - Which concentrated acids react with sulphur?

Discussion

Sulphur does not react with dilute acids. However, it is oxidised by hot concentrated oxidizing acids such as sulphuric acid and nitric acid. With concentrated sulphuric acid, sulphur is oxidised to sulphur (IV) oxide (sulphur dioxide).



Concentrated nitric acid oxidises sulphur to sulphuric acid, while the acid is reduced to red-brown nitrogen(IV) oxide.



Uses of sulphur

Sulphur is used in many ways. Some of the uses include:

1. In the manufacture of sulphuric acid (H_2SO_4). Sulphuric acid is used in the manufacture of detergents, plastics among many other household and industrial products.
2. For making gun powder and matches.
3. For manufacture of fire works.
4. In the vulcanization (hardening) of rubber.
5. For manufacturing germicides and fungicides.
6. In the manufacture of medicines.
7. In photographic development.
8. For making bleaching agents.
9. In making artificial hair colours or dyes.

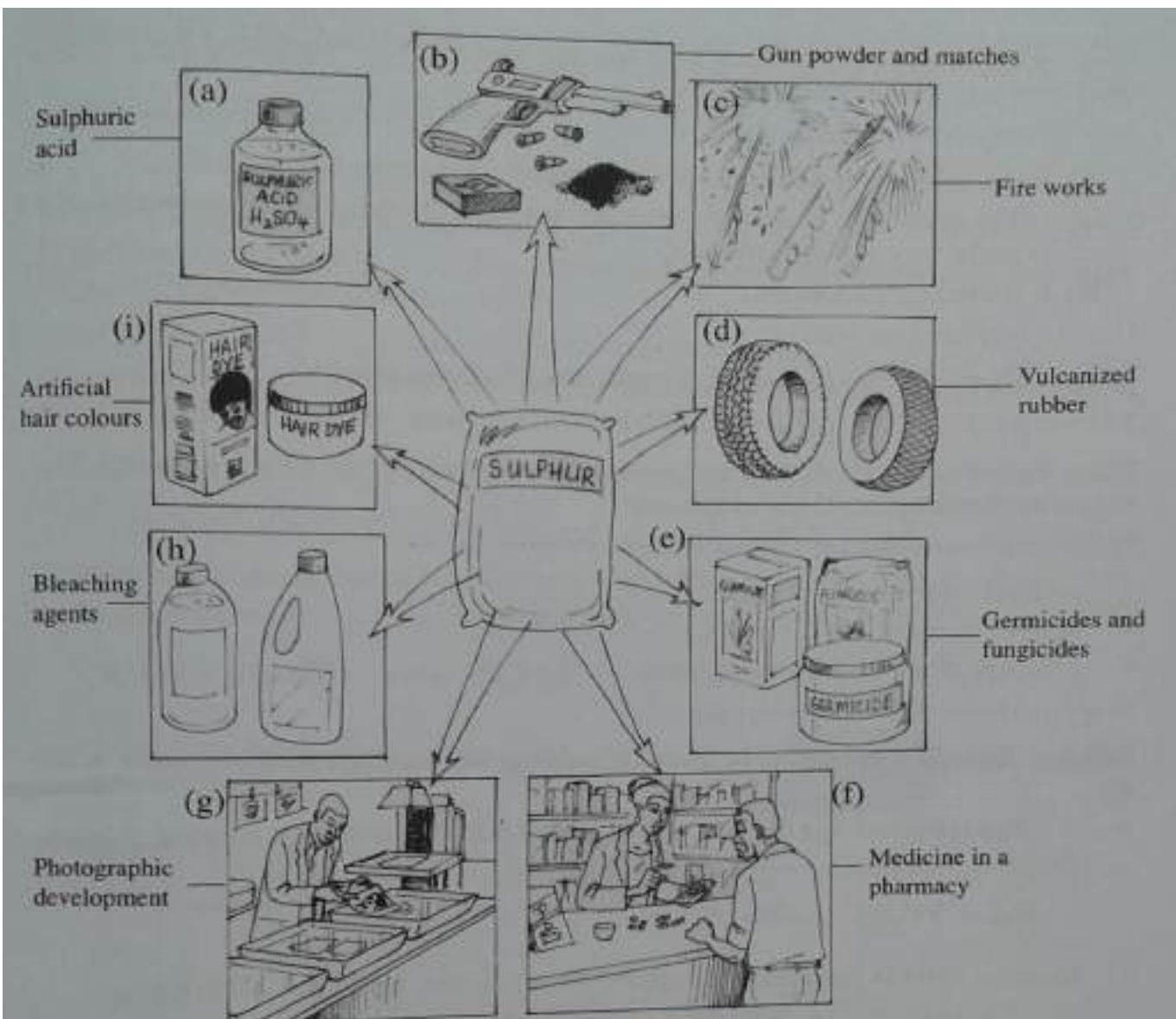


Fig 2.16. Uses of sulphur



Practice exercise 2D

1. Describe the two crystalline forms of allotropes of sulphur.
2. List four uses of sulphur.
3. Give the physical properties of sulphur.

Compounds of sulphur

Sulphur has a number of important compounds. These include:

- (i) Fluorides of sulphur e.g. sulphur difluoride.
- (ii) Oxides of sulphur such as sulphur dioxide, sulphur trioxide and disulphur oxide.
- (iii) Hydrides of sulphur.
- (iv) Metal sulphides e.g. zinc blende (ZnS) and iron pyrites.

Some of the sulphur compounds such sulphur dioxide SO_2 and sulphur trioxide SO_3 have very important industrial uses.

Uses of sulphur dioxide

- It is used for bleaching, as fumigant and in food preservatives.
- Large quantities of sulphur dioxide are used in the contact process for the manufacture of sulphuric acid.
- It is used as disinfectant.

Uses of sulphur trioxide

It is mainly used in the industrial manufacture of sulphuric acid.

Manufacture of sulphuric acid by Contact process

Many tonnes of sulphuric acid are produced every year by the **Contact process**. The stages in Contact process are as follows:

Optimum conditions for contact process

- catalyst – vanadium(V) oxide.
- temperatures of $450^\circ\text{C} - 500^\circ\text{C}$.
- pressure of about 2-3 atmospheres.

Stage 1: Production of sulphur dioxide

Sulphur dioxide is produced by burning sulphur or roasting metal sulphides in the air.

- Sulphur is burned in a furnace in presence of purified air to form sulphur dioxide.
 $\text{S(s)} + \text{O}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g})$

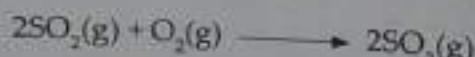
- Sulphur dioxide can also be produced from roasting metal sulphides e.g.



Stage 2: Conversion of sulphur dioxide to sulphur trioxide

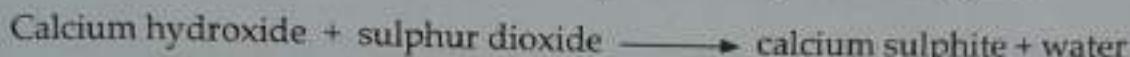
Sulphur dioxide is dried in a drying tower and cooled to an optimum temperature of $450 - 500^\circ\text{C}$ and a pressure of about 2 - 3 atmospheres.

More air is passed through the reactor packed with vanadium oxide (V_2O_5) catalyst. The reaction is exothermic and no external heating is required. Sulphur dioxide is converted to sulphur trioxide.



This is a **reversible** reaction. A reversible reaction is a reaction that can go in either direction.

The unreacted sulphur dioxide, SO_2 , is reacted with calcium hydroxide in the chimneys forming salt and water. This prevents air pollution by the waste gases.

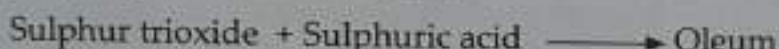


This process is called **scrubbing** the gas.

Note: Vanadium(V) oxide is used as a catalyst because it is cheaper and less easily poisoned by impurities than platinum.

Stage 3 : Conversion of sulphur trioxide to sulphuric acid

Finally the sulphur trioxide is absorbed in concentrated sulphuric acid forming an oily liquid product called **oleum**.



Sulphuric acid is obtained by diluting oleum with water.

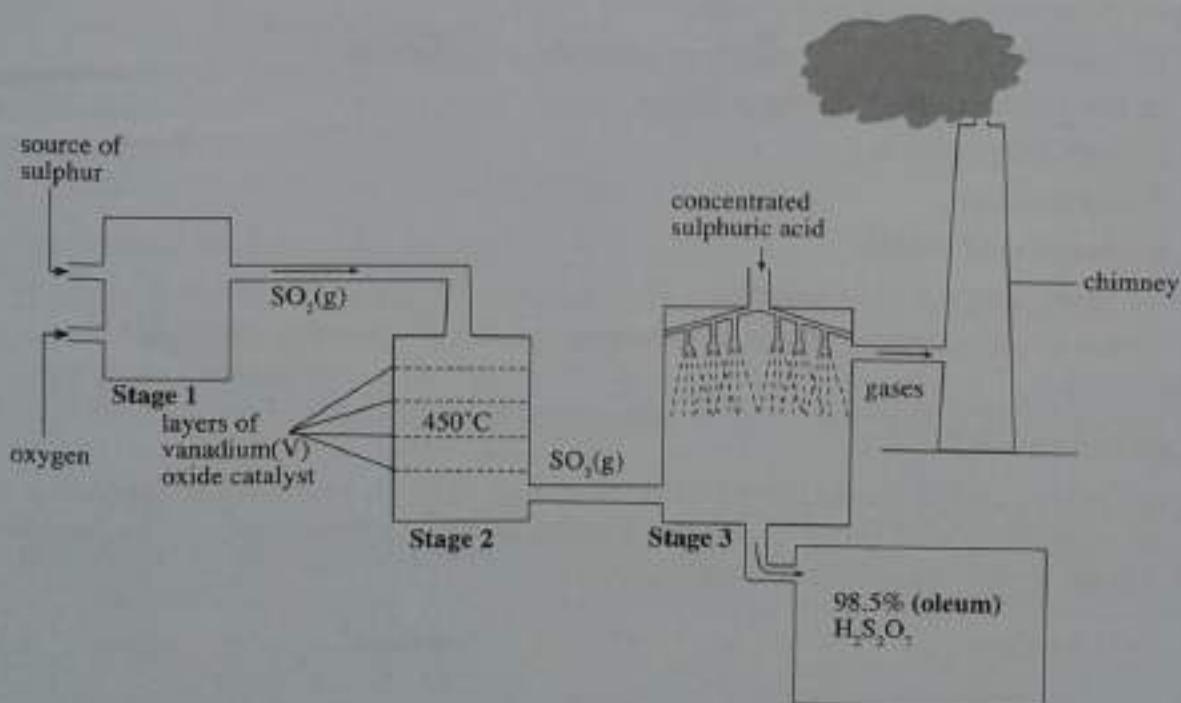
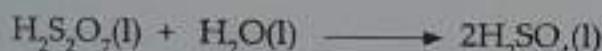


Fig. 2.17: Contact process of manufacturing sulphuric acid

Note: Sulphur trioxide is not directly dissolved in water because the reaction produces a lot of heat that acid sprays (fumes) are formed instead of liquid acid.

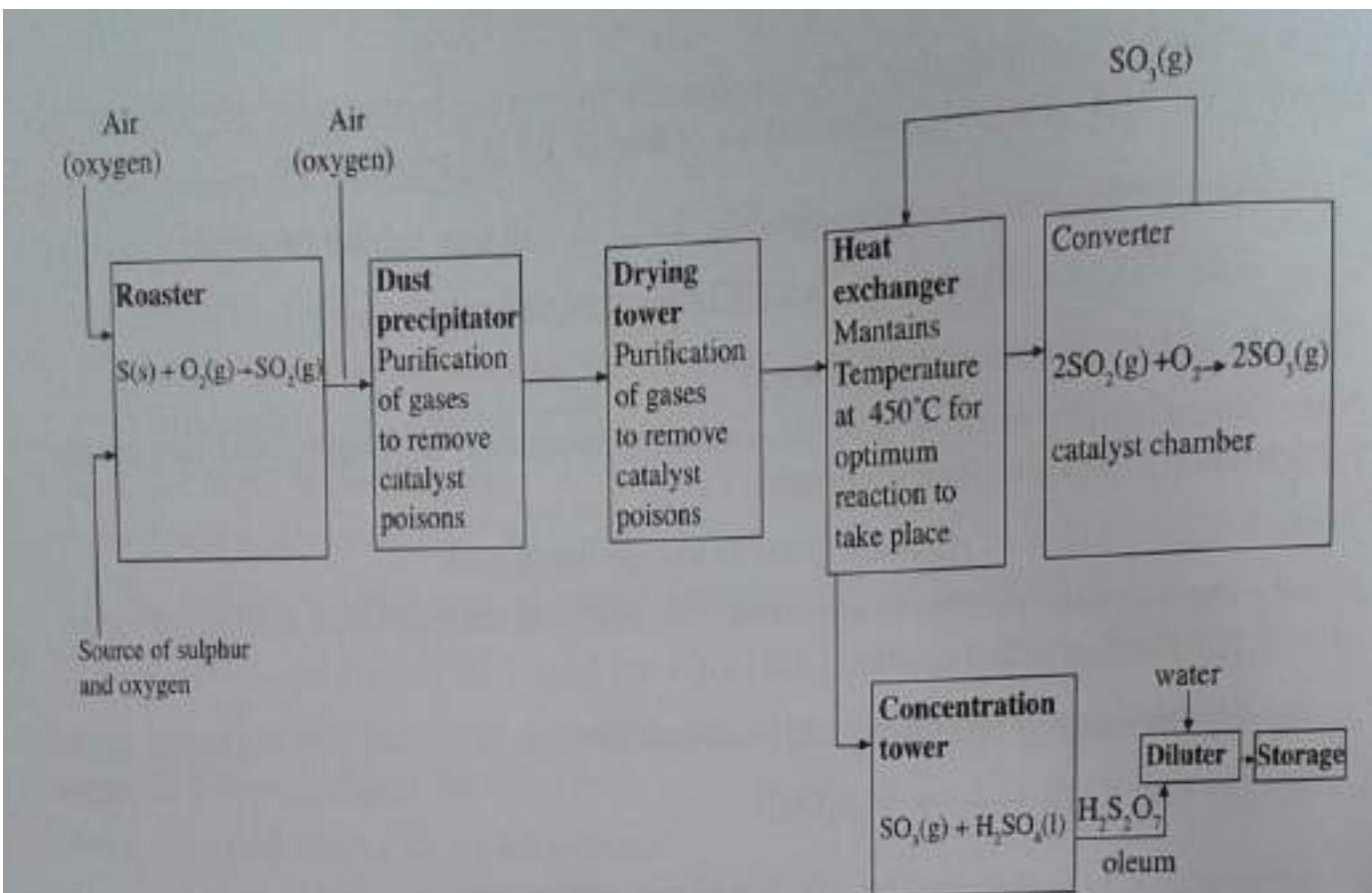


Fig. 2.18: Flowchart for Contact process

Uses of sulphuric acid

Sulphuric acid is used in many ways.

1. To manufacture fertilisers such as ammonium sulphate.
2. In the production of synthetic fibres.
3. In petroleum refining
4. In car batteries.
5. In cleaning of metals.
6. To make soaps and detergents.
7. To make dyes, drugs, paints, explosives and many other compounds.

Remember!

Sulphuric acid is highly corrosive chemical that is potentially explosive in concentrated form. It can cause severe skin burns, therefore should be handled with care while in the laboratory.

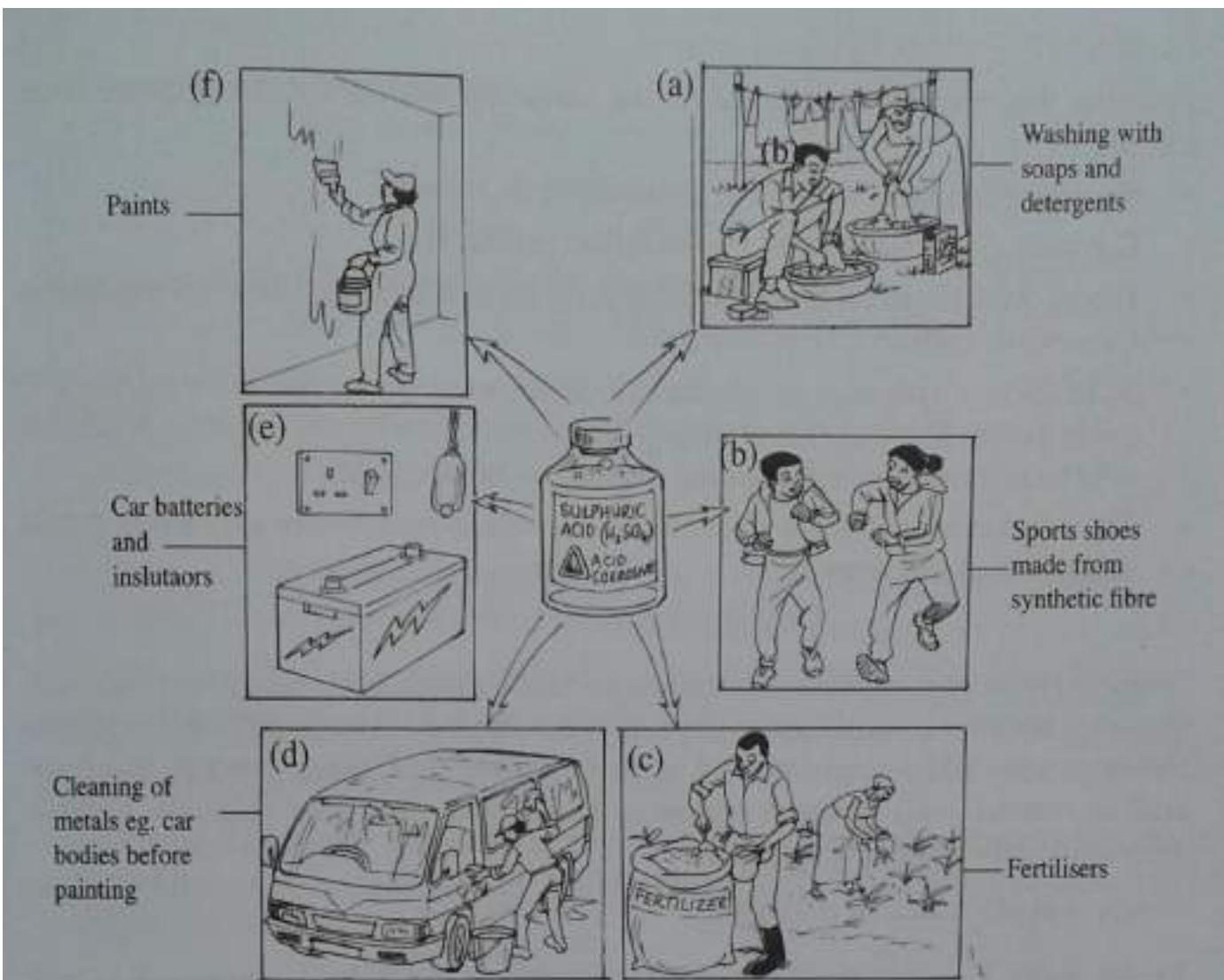


Fig 2.19: Uses of sulphuric acid

Pollution control in Contact process

Environmental aspects in Contact process

1. In stage 2, 99.5% of the sulphur dioxide gets converted into sulphur trioxide. The unreacted sulphur dioxide and any leak of sulphur trioxide if they get into the atmosphere causes serious air pollution besides other side effects. It leads to acid rain which damages building, car bodies due to corrosion and alter acidity of the soil.
2. Residents where such manufacturing plants are situated have complained about:
 - plants not doing well in the region.
 - dying of fish in rivers.
 - respiratory complications.

Control of Pollution in Contact process

To avoid this, controls are needed on the waste gas during Contact process. These include:

- Recycling sulphur(IV) oxide to the catalytic chambers.
- Converting the toxic wastes into harmless products.
- People working in these industries should be well protected and not exposed to these toxic wastes.
- Solid calcium hydroxide or calcium carbonate can be used to neutralise sulphur(IV) oxide before it leaves the chimney. In the process calcium sulphate is formed which can be used in the building industry to make plaster.
- The reaction in each stage gives out heat. As much heat energy as possible should be conserved and reused.

Manufacture of ammonium sulphate

One of the most important use of sulphuric acid is the production of inorganic fertilisers. One such fertiliser is manufacture of ammonium sulphate. Ammonia is obtained from **Haber** process while sulphuric acid is manufactured by **Contact** process. Sulphuric acid is reacted with aqueous ammonia to produce ammonia sulphate fertiliser according to the following equation.



Excess water is evaporated from aqueous ammonium sulphate solution. It is then cooled to crystallise. The wet ammonium sulphate crystals is conveyed (by conveyor belt) to the drier where it is dried by hot air. It is then conveyed to the storage area, cooled and packaged.

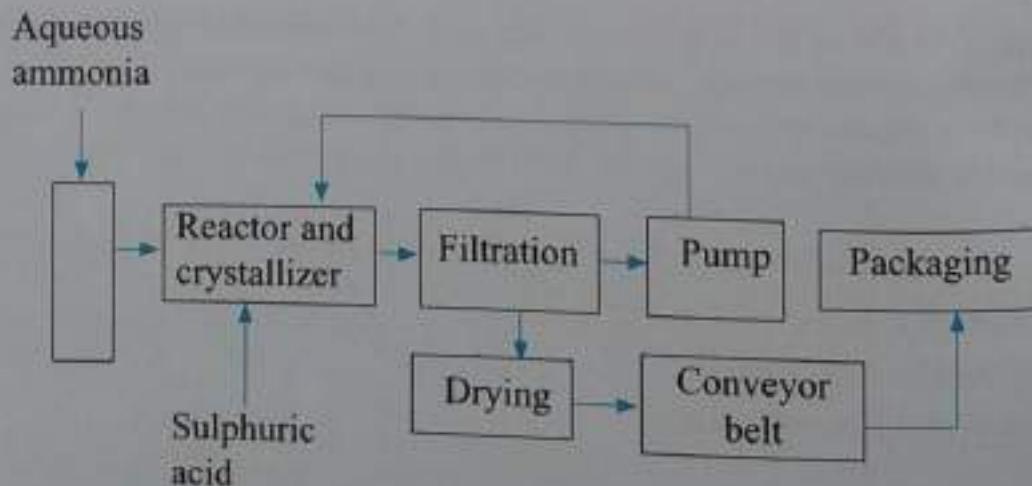


Fig. 2.20: Flowchart for manufacturing ammonium sulphate



Practice exercise 2E

1. Sulphuric acid is manufactured by Contact process.
 - a) Give the raw materials for the process?
 - b) Draw a flow diagram showing the steps in making sulphuric acid. Include equations.
 - c) Name the catalyst used in the contact process?
 - d) In the last step, sulphur(VI) oxide is not dissolved in water. Explain.
 - e) List four uses of sulphuric acid.
2. Oleum ($H_2S_2O_7$) is an intermediate in the industrial manufacture of sulphuric acid. How is oleum converted into sulphuric acid?
3. Name one fertiliser manufactured using sulphuric acid. Briefly describe how the named fertiliser is manufactured.

2.3 Phosphorous and its Compounds

Phosphorus is a group V and period 3 element of the periodic table. Its atomic number is 15 and the electron configuration is 2.8.5. Phosphorus has a valency of three, but it can also exhibit a valency of five.

	V	VI	VII	VIII
	N	O	F	He
	31 P 15	S	Cl	Ar
	As	Se	Br	Kr
	Sb	Te	I	Xe
	Bi	Po	Ar	Rn

Fig 2.21 Position of phosphorus in the periodic table

Sources of phosphorous

Phosphorus is not found as a free element in nature. It occurs in many mineral rocks mainly phosphates. Its chief ore is calcium phosphate $Ca_3(PO_4)_2$. Phosphorus is also a major constituent of bones.

Extraction of Phosphorus

Phosphorus is obtained as white phosphorus by reduction of its ore, mainly calcium phosphate. Sand and coke are continuously fed into the electric furnace. The electric current supplies high temperatures of about $1450^\circ C$, to promote the reaction between calcium phosphate and silicon dioxide producing phosphorus pentoxide.

Tricalcium phosphate + Silicon dioxide \longrightarrow Calcium silicate + phosphorus pentoxide



Phosphorus pentoxide then reacts with coke (carbon) which reduces it to the element phosphorus and carbon monoxide.

Phosphorus pentoxide + carbon \longrightarrow phosphorus + carbon monoxide



Calcium silicate slag is tapped off from the bottom of the furnace.

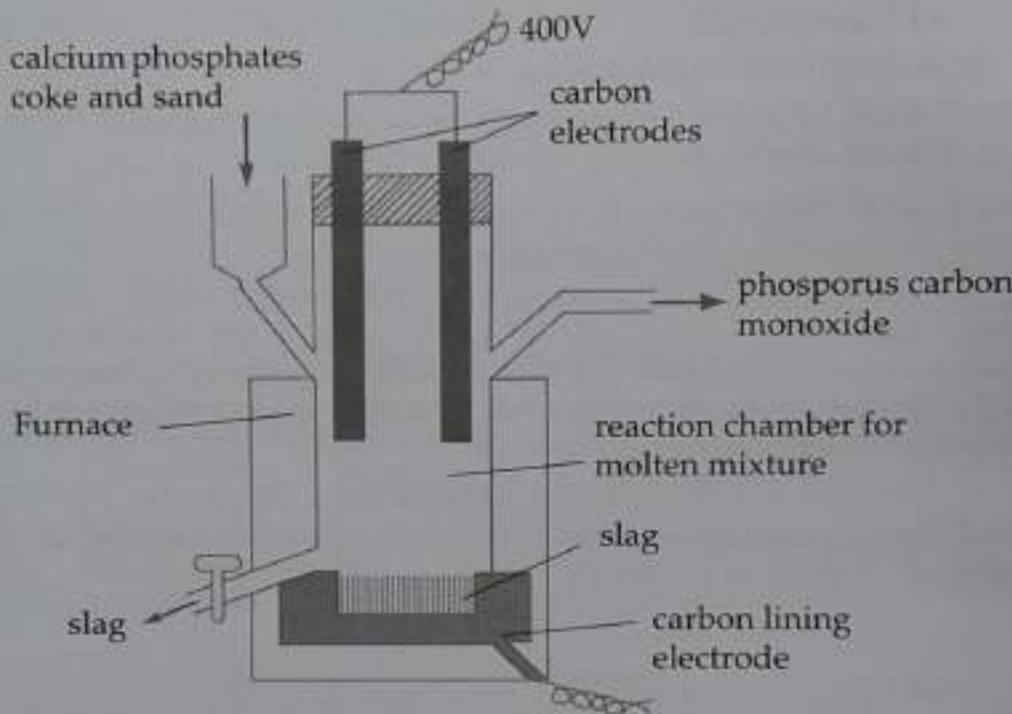


Fig. 2.22: Extraction of phosphorus

White phosphorus can be converted to the more stable allotrope of red phosphorus by heating it in absence of air at 270°C for several days. Above this temperature, the reaction can be explosive.

Allotropes of Phosphorus

Phosphorus exhibits two common allotropes.

White phosphorus - It turns pale yellow on exposure to light. It is self igniting and can catch fire very easily when exposed to air or oxygen. Therefore, it is usually kept under water. It gives off a very poisonous vapour. It is very unstable, most reactive and highly toxic of the two allotropes.

Red phosphorus - It is the stable form at all temperatures. It does not catch fire easily unlike the white phosphorus. It may be formed by heating the white phosphorus to 250°C or by exposing white phosphorus to sunlight.

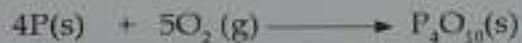
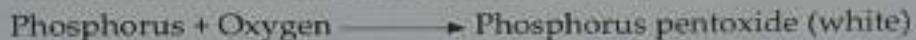
Physical properties

- Phosphorous is a yellow solid at room temperature.
- Melting point is 44°C.
- Boiling point is 280°C.
- Density 1.8 g/cm³.
- Does not conduct heat or electricity.

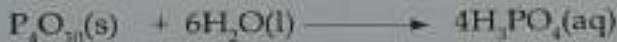
Chemical properties

1. Yellow phosphorus burns in oxygen to form two oxides: **phosphorus pentoxide** and **phosphorus trioxide**.

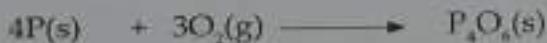
- (a) Yellow phosphorus burns in plenty of air (oxygen) with brilliant flame to form white fumes. The white fumes solidify as white solids.



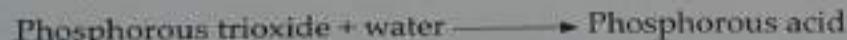
Phosphorus pentoxide when shaken with water dissolves to form phosphoric acid.



- (b) When yellow phosphorus burns in a limited supply of oxygen, a white solid of phosphorus trioxide is formed.



Phosphorus trioxide dissolves readily in water to produce phosphorous acid.

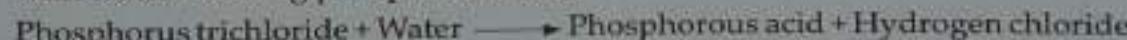


2. When warm white phosphorus is put in a gas jar full of dry chlorine gas, it catches fire. It reacts with chlorine to form a mixture of two chloride compounds: **phosphorus trichloride** and **phosphorus pentachloride**.

- (a) Phosphorus + Chlorine \longrightarrow Phosphorus trichloride

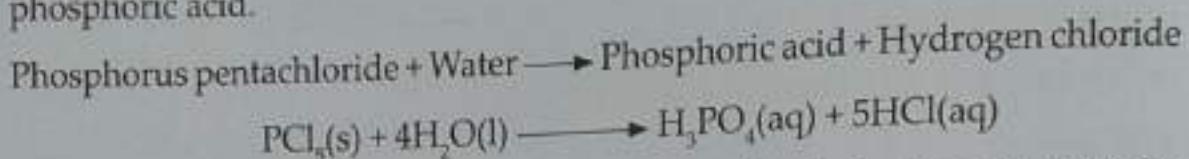


Phosphorus trichloride is a liquid with a boiling point, 76°C. It produces fumes in the air because of its reaction with moisture. The liquid is attacked with water forming phosphorous acid.





Phosphorus pentachloride reacts vigorously with water to produce phosphoric acid.



The most common compounds of phosphorus are the derivatives of phosphate (PO_4^{3-}) from phosphoric acid. Phosphorus is an essential plant nutrient hence finds its major use as a constituent of fertilizers in the form of phosphates.

Uses of phosphorus

1. The red phosphorus is used in the making of "safety" matches. The striking surface of the match stick is made of a mixture of red phosphorous, glue and ground glass. The glass powder is used to increase friction. The match head contains an oxidizing agent. (White phosphorous and an oxidizing agent were used in matches earlier days but due to its poisoning which caused bones of the jaw and face to rot, it was outlawed. Matches nowadays consist of compounds of phosphorus e.g phosphorus sulphide.
2. Detergents, toothpaste and baking powder contain compounds of phosphorus e.g. tooth paste contains calcium pyrophosphate $\text{Ca}_4(\text{P}_2\text{O}_7)_2$ and sodium monofluorophosphate among other compounds. Phosphoric acid is also used in foods such as soft drink.

Table 2.5 Other compounds of phosphorous and their uses

Phosphorus compounds	Use
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ Monocalcium phosphate	Baking powder
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ Dicalcium phosphate	Animal food additive
H_3PO_4 (phosphoric acid)	Manufacture of phosphate fertilizer
$\text{Na}_5\text{P}_3\text{O}_{10}$ (sodium tripolyphosphate)	Detergents

3. Phosphoric acid is used in the manufacture of inorganic fertilizers which is sold as "superphosphate" e.g. ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ and diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$.



Practice exercise 2F

1. Which allotrope of phosphorus is used in the manufacture of matches?
2. Name the chief one of phosphorus.
3. Write a balanced equation for reduction of phosphorus pentoxide with carbon.
4. Name the commercial uses of phosphorus and its compounds.



Revision Exercise 2

1. Soils which lack sulphur cannot sustain crop farming. How can you add sulphur in such soil.
2. Explain how concentrated sulphuric acid dry the grass.
3. (a) Describe briefly what happens when ammonium nitrite is heated in a boiling tube. Use a chemical equation.
(b) Explain why a brightly glowing splint relights in nitrogen (I) oxide. Use a chemical equation.
4. (a) Name two raw materials needed in the manufacture of ammonia.
(b) Give three optimum conditions required in the Haber process.
5. Powdered sulphur was placed in deflagrating spoon and heated in a Bunsen flame until the sulphur starts to burn.
 - (a) What is seen when the sulphur burns?
(b) Write an equation for the reaction above.
(c) When the gas in (b) is dissolved in water, name the solution that is formed and write the equation for the reaction.
(d) If a few drops of litmus solution was added to (c) above, what would be the colour of the solution.
(e) Write an equation for the reaction that will occur between the solution formed in (c) above and sodium hydroxide solution.
6. (a) Name the compound of phosphorus used in matches?
(b) Give the compounds formed when phosphorus burns in limited air and in plenty of air. Use chemical equations.

Topic 3: Chemical bonding and properties of matter



Success criteria

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

- a) Describe properties of ionic and covalent compounds.
- b) Explain structural differences between ionic and covalent compounds.
- c) Differentiate between polar and non-polar covalent bonds.
- d) Relate intermolecular forces to properties of covalent compounds.
- e) Define the term allotropy.
- f) Relate the properties of allotropes of carbon to their uses.
- g) Explain similarities between diamond and silicon dioxide.
- h) Describe the uses of metals in relation to their properties.
- i) Explain the physical properties of alloys.
- j) State the uses of alloys.

Introduction

In Form 2, we learnt about the different types of bonding: **ionic bonding**, **covalent bonding** and **metallic bonding**. We defined a chemical bond as an attraction between two particles. In this unit we shall study about properties of ionic and covalent bonds, allotropies of elements, uses of metal and their alloys in relation to their properties.

The type of bonding in a compound determines its properties. Ionic compounds have ions while covalent bonds consist largely of molecules. Ionic bonds are very strong while the molecules of covalent compounds are bonded by relatively weak intermolecular forces i.e. **van der Waal forces** and **hydrogen bonding**.

3.1 Properties of ionic and covalent compounds

Properties of ionic compounds

Ionic compounds exhibit ionic bonding in them. General properties of ionic compounds include:

- i) Ionic compounds are electrolytes. They conduct electricity in solution or molten state.
- ii) They have high melting and boiling points. See Table 3.1.

Table 3.1: Melting and boiling points of some ionic compounds

Element	NaCl	KBr	NaI	MgCl ₂
Melting point(°C)	808	735	662	714
Boiling point(°C)	1465	1435	1304	1418

- iii) They are generally soluble in water.
- iv) Ionic compounds are insoluble in organic solvents like benzene or propanone.
- v) They are usually crystalline solids. Ionic crystals are brittle.

Properties of covalent compounds

Covalent compounds have covalent bonding. Examples of covalent compounds include sulphur, sugar, carbon and organic solvents such as propane and ethanol. General properties of covalent compounds include:

- i) They do not conduct electricity.
- ii) They have low melting and boiling points. See Table 3.2.

Table 3.2: Melting points of some covalent compounds

Element	Hydrogen	Oxygen (O_2)	Methane (CH_4)	Sulphur	Water (H_2O)
Melting point($^{\circ}C$)	-259	-219	-182	120	0
Boiling point($^{\circ}C$)	-253	-183	-161	444	100

- iii) Most are insoluble in water.
- iv) They are soluble in organic solvents like benzene and propanone.
- v) Most of them are gaseous or volatile liquids at room temperature and pressure.
- vi) Most of them have scent.

However, some covalent compounds for example diamond and graphite have unusually high melting and boiling points. Diamond melts at $3\ 550\ ^{\circ}C$ while graphite melts at $3\ 730\ ^{\circ}C$. Others like large molecules plastics and carbohydrates decompose before their melting points are reached.

Let us carry out some experiments to demonstrate the physical properties of ionic and covalent compounds.

Experiment 3.1

Aim: To investigate the melting points of covalent compounds and ionic compounds.

Requirements

- Boiling tubes, test tube holders
- Clock or stop watch
- Sugar, sodium chloride (table salt)
- Source of heat

Procedure

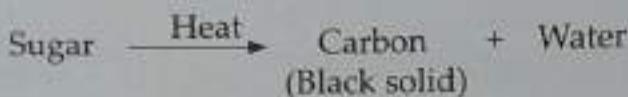
1. Put two spatulaful of sugar in a dry boiling tube. To another dry boiling tube, add two spatulaful of table salt.
2. Heat the boiling tubes with their contents each in turn.
3. Note and record the time when:
 - i) Sugar starts to melt and completely decompose.
 - ii) Salt starts to melt.

4. Compare the time recorded and explain your observation.

Substance	Time taken to start melting	Ionic/covalent compound
Sugar		
Salt		

Discussion

When sugar is heated it quickly melts and get decomposed. A black solid remains, the solid is carbon.



Sodium chloride makes a cracking sound on heating. It does not melt or decompose. The heat supplied by this kind of heating is not sufficient to melt the sodium chloride (i.e. break the ionic bonds). Sodium chloride being an ionic compound has strong electrostatic forces which form very strong ionic bonds. Therefore ionic compounds have high melting points. Sugar being a covalent compound has weak covalent bonds which require little heat energy to break. Hence sugar has low melting point just like most covalent compounds.

Electrostatic forces in covalent and ionic compounds

In experiment 3.1, when sugar and sodium chloride were heated, sugar quickly melted and decomposed. Sodium chloride did not melt. This occurrence is due to the different strengths of the electrostatic forces between these two substances.

Covalent bonds too exhibit ionic bonding character to some extent. This phenomenon is due to unequal sharing of covalent bond electrons. The more electronegative atom tends to pull the shared electrons toward itself creating partial negative charge on it. The less electronegative atom becomes partially positively charged. This is what we referred to **ionic bonding character** in covalent. This kind of ionic bonding is weak and does not cause much increase in the strength of the bonds in covalent compounds.

Solubility and volatility of ionic and covalent compounds

Substances that can dissolve in a particular solvent such as water is said to be soluble. Different substances may dissolve in a range of solvents or specifically in one. Some compounds do not solve at all.

Experiment 3.2

Aim: To investigate solubility and volatility of ionic and covalent compounds.

Requirements

- Watch glasses
- Test tubes
- Distilled water, acetone, paraffin
- Sodium chloride

Procedure

1. Pour equal amounts of acetone, paraffin and water in separate watch glasses. Record the time these liquids take to disappear from the watch glass.
2. Label three test tubes A, B and C.
3. Put some cooking fat in test tube A, add acetone and shake. Record your observation.
4. In test tube B and C, place little amount of grounded sodium chloride. Add some amount of water into test tube B. In test tube C add equal amount of paraffin. Insert a stopper or cork into each test tube and shake vigorously. Record your observation.

Discussion

When acetone was put in a watch glass, it did not take long before disappearing completely from the watch glass. Water and paraffin being less volatile remained in the watch glass. A substance which evaporates readily at normal temperature and atmosphere pressure is said to be **volatile**. Some organic solvents are highly volatile while others are less volatile.

Sodium chloride, an ionic compound, dissolves in water but does not dissolve in paraffin. Water being a polar liquid was able to break down the ionic bond of sodium chloride hence dissolving it. Ionic compound, readily dissolves in water and other polar solvents but do not dissolve in organic solvents such as paraffin.

Covalent compounds, being non-polar, readily dissolve in organic solvents. This is why cooking fat dissolved in acetone but would not dissolve in water.

Electrical conductivity of covalent and ionic compounds

(a) Conduction of electricity by substances in solutions

Experiment 3.3

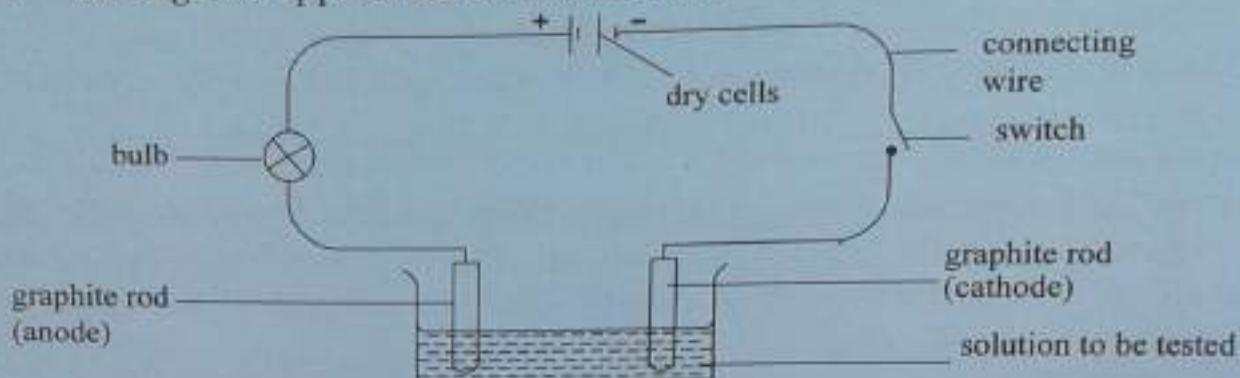
Aim: To investigate the electrical conductivity of covalent and ionic compounds in solutions.

Requirements

- Battery/dry cells, bulb
- Connecting wires fitted with crocodile clips
- Sugar, urea, copper (II) chloride, sodium chloride, mineral acids (hydrochloric, nitric and sulphuric acids), paraffin wax, graphite rods, sulphur, lead (II) bromide.
- Tripod stand, crucible
- Distilled water
- Organic solvents such as ethanol, propanone (acetone), methylated spirit.

Procedure

- Arrange the apparatus as shown below.



- Switch on the current.
- Before dipping the graphite rods into the solutions, bring the electrodes into contact with one another and observe if the bulb lights up.
- Place the graphite rods apart in the beaker.
- Switch off the current.
- Pour pure water into the beaker.
- Switch on the current. Does the bulb glow?
- Switch off the current. Add a few drops of concentrated sulphuric acid to the water in the beaker.
- Switch on the current. Does the bulb now light up?
- What do you observe on the graphite rods? What does this indicate?
- Repeat the above experiment using same graphite rods and the solutions of the following compounds: sugar, urea, copper (II) chloride, sodium chloride, mineral acids and organic solvents.
- Note the changes (if any) occurring around the graphite rods and in the contents of the beaker. Rinse the beaker and the rods thoroughly with distilled water before each new solution is used.
- Copy Table 3.3 and fill in your results, include all the other substances being investigated.

Table 3.3: Electrolytes and non-electrolytes

Solutions	Does the bulb light		Any observation made on the	
	Yes	No	anode (+ve)	cathode (-ve)
Copper(II) chloride				
Sugar				
Sodium chloride				
Mineral acids				
Sodium chloride				
Copper(II) chloride				
Pure water				
Acidified water				

Discussion

Different results are obtained in this experiment when different solutions are used. Liquids such as acidified water, sodium chloride solution, mineral acids and copper(II) chloride solution conduct electricity. Aqueous solutions which conduct electric current are called **electrolytes**. These solutions have free ions which transfer (conduct) the electric current.

The current decomposes the electrolyte as it passes through it. Aqueous solutions such as sugar and urea do not conduct electricity. These are known as **non-electrolytes**. They exist as discrete molecules, that is the covalent bond does not dissociate. This explains why the organic solvents such as ethanol and propanone are non-conductors of electricity.

Experiment 3.4

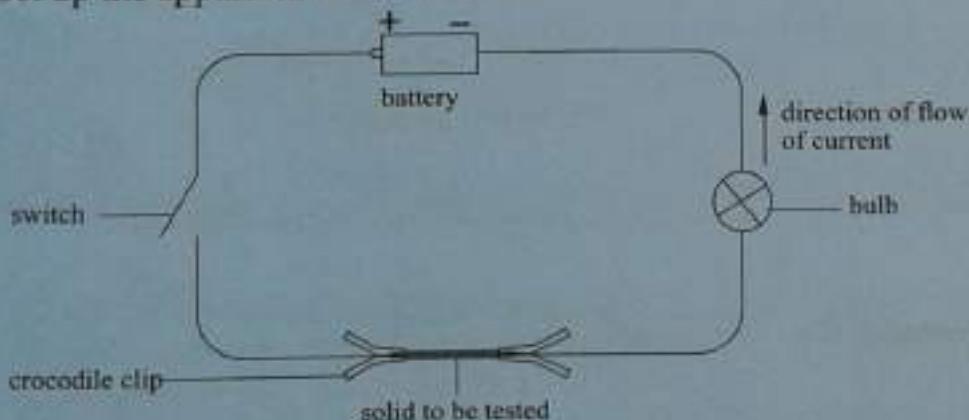
Aim: To investigate electrical conductivity of ionic and covalent compounds in solid state

Requirements

- Torch cells or battery (a source of D.C)
- Crocodile clips
- Bulb (6V)
- Charcoal
- Sulphur
- Rubber
- Paper
- Metals – copper, zinc, aluminium, tin, lead, iron
- Compounds of sodium chloride, sugar, lead (II) bromide
- Iodine crystals
- Connecting wires
- Graphite
- Wood
- Glass
- Plastic

Procedure

1. Set up the apparatus as shown below.



2. Bring the crocodile clips close together without letting them come into contact. Observe the bulb.
3. Let the crocodile clips touch each other and observe the bulb. What happens?
4. Now clip a graphite (carbon) rod and observe the bulb.

- Clip a piece of metal e.g. copper or iron and observe the bulb.
- Record your observations in a table similar to Table 3.4 below.
- Repeat the experiment using the other materials listed and each time record your observations.

Table 3.4: Conductors and Non-conductors

Name of substance	Observation on the bulb
Graphite	
Copper	
Sugar	
Sulphur	
Urea	
Copper (II) chloride	
Lead (II) bromide	
Aqueous mineral acids	

Discussion

When all metals were used, the bulb lit up. Metals are good conductors of electricity. The only non-metal that conducted electricity is graphite. Graphite and all metals have free mobile electrons that flow allowing transfer of electric current. All other solid materials such as paper, plastic and glass do not conduct electricity. Ionic compounds such as sodium chloride and lead (II) bromide in their solid states as well sugar do not conduct electricity.

A full battery or torch cells are usually drawn as indicated in the circuit diagram shown in Fig. 3.1. The long vertical strokes represent the +ve terminal while the short ones represent the -ve terminal.

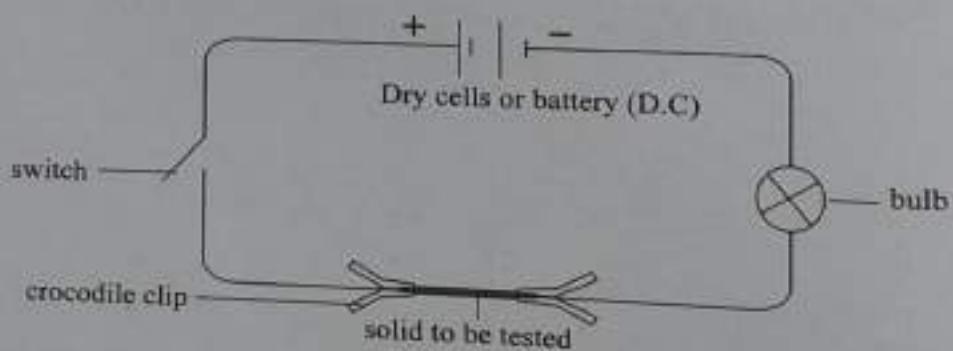


Fig. 3.1: How a direct current source is represented in a circuit

(b) Conduction of electricity by substances in molten state

We have seen in the Experiment 3.3 and 3.4 that some compounds conduct electricity in solution or solid state. Other substances do not conduct electricity irrespective of their state. In the next experiment we will investigate electrical conductivity of some compounds and elements in their molten state.

Experiment 3.5

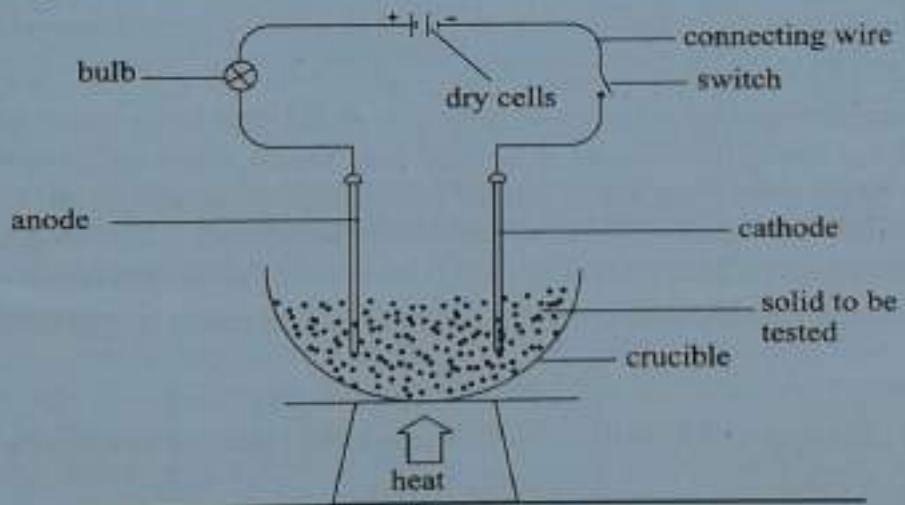
Aim: To investigate electrical conductivity of ionic and covalent compounds in molten state

Requirement

- Crucible
- Graphite rods
- Connecting wire fitted with crocodile clips
- Battery/dry cells with cell holder
- Bunsen burner
- Tripod stand
- Pipe-clay triangle
- Lead(II) bromide or lead(II) iodide
- Sulphur
- Paraffin wax

Procedure

Note: Lead(II) bromide or lead(II) iodide produce poisonous fumes. The experiment should be performed in a fume cupboard or in an open space like a field.



1. Set up the apparatus as shown above.
2. Fill the crucible with either lead(II) bromide or lead(II) iodide to approximately two thirds of the container.
3. Place the crucible and its contents on a pipe clay triangle supported by a tripod stand.
4. Insert the graphite electrodes into lead(II) bromide and close the switch. Does the bulb light?
5. Open the switch.
6. Gently heat the crucible until lead(II) bromide melts.

- Adjust the burner so that the substance remains in molten state as the experiment progresses. Close the switch. Does the bulb light?
- Observe whether there is any chemical reaction around the electrodes.
- Record your observations as shown in Table 3.5.
- Repeat the experiment using other substances such as paraffin wax, naphthalene, calcium chloride, sugar. Use a clean crucible for each substance and clean the electrodes thoroughly before using it with the next substance.

Table 3.5: Results for electrical conductivity of molten substances

Substance	Does bulb light?		Observation at the electrodes	
	Solid	Molten	Anode	Cathode
Lead (II) bromide	No	Yes	Red brown fumes of bromine	Grey bead of lead metal
Sulphur				
Wax				
Lead (II) iodide etc				

Discussion

When we insert the electrodes in lead(II) bromide solid, the bulb does not light. But the bulb lights when lead(II) bromide is heated and melts. This indicates that molten lead(II) bromide conducts electricity. Metal (ionic) compounds in molten state are electrical conductors. It is also observed that other substances like sulphur, paraffin wax and sugar do not conduct electricity when in solid or molten form.

Other examples of substances that conduct electricity are given in Table 3.6.

Table 3.6 Electrical conductors and non conductors

Substances that conduct electricity	Substances that do not conduct electricity
Sodium chloride solution	Pure water
Copper(II) chloride solution	Sugar solution
Sodium hydroxide solution	Paraffin wax
Molten lead(II) bromide	Molten sulphur
Molten lead(II) iodide	Solid lead(II) bromide
Hydrochloric acid	Solid sodium chloride
Sulphuric acid	Ethanol (alcohol)
Ethanoic acid	Urea
Most salts in molten or aqueous form	

Structures of ionic and covalent compounds

Structure of Ionic compounds

The ions are arranged in a regular pattern forming a **crystalline** structure. The crystal lattice consists of the opposite charged ions with strong electronic attraction between them. There is alternating arrangement of cations and anions forming a **giant ionic structure**. For example, in solid sodium chloride, the sodium and chloride ions are not combined or attached to any particular chloride ion, i.e. there is not sodium chloride molecule but each sodium ion has 6 equidistant chloride ions around it octahedrally arranged. Each chloride also has 6 equidistant sodium ions around it octahedrally arranged. This forms each giant crystal.

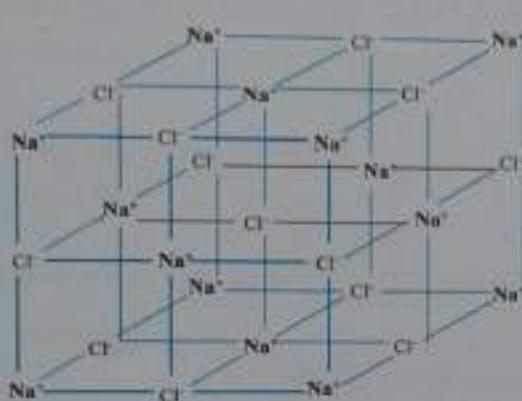


Fig. 3.2: (a) Part of a sodium chloride ions



(b) Octahedral arrangement of 6 around a chloride ion

Effects of structures of ionic compounds on their properties

- i) The strong electrostatic attraction between the ions in the structure requires large amount of heat to break down. This causes the high melting and boiling points of ionic compounds see Table 3.1.
- ii) They are soluble in water but not in organic solvents. They are slightly soluble in some organic solvents such as ethanol, ether and benzene. Water molecules being polar (i.e. atoms in the water molecule, H_2O) have partial positive charge δ^+ and partial negative charge δ^- . When ionic substance is placed in water, there is strong attraction between the ions of the solute and polar ends of the water molecules. This causes the break up of the crystal lattice structure and the ions are then surrounded by water molecules, a process called **hydration**. Hydration process is usually accompanied by evolution of sufficient energy which is used in breaking the ionic bonds.
- iii) They conduct electricity in molten or aqueous state. In solid state, ionic compounds do not conduct electricity. This is because the ions are locked in fixed positions in the crystal lattice (structure) and not able to move freely. In molten state when the crystalline structure is broken down, the ions are now free to move and carry with them electric charges thereby conducting electricity.
- iv) The regular octahedral arrangement pattern of alternating anions and cations gives them the rigid crystalline structure.

Structures of covalent compounds

Covalent bonds exist in both elements (non-metallic) and molecular compounds. Examples of covalent elements are: sulphur, phosphorus, carbon and bromine.

Covalent compounds include: ethanol, ethanoic acid, oils, ammonia and carbon dioxide. These usually form separate molecules.

Types of structures in covalent compounds

i) Simple molecular structures

In simple molecular structures, the atoms forming the molecules are held together with strong covalent bonds while the molecules themselves are attracted to one another by weak intermolecular forces called **van der Waal's forces or hydrogen bonds**.

Examples of substances with simple molecular structure are carbon dioxide, oxygen, sulphur, water and iodine molecules.

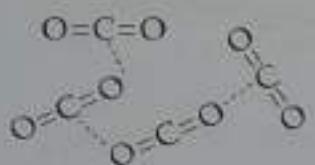
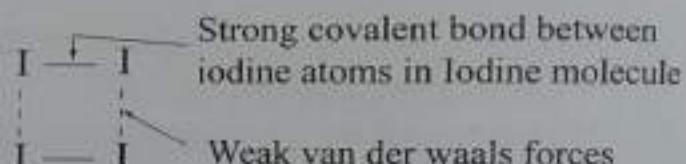


Fig. 3.3. (a) Structure of Carbon dioxide



(b) Structure of iodine

Effects of simple molecular structure

Due to the presence of weak intermolecular forces, covalent compounds with simple molecular structure exhibit the following properties.

- Low melting and boiling points. Little heat energy is required to break these weak intermolecular forces, hence their low melting and boiling points. When heated, they quickly melt or vapourise (sublime). For example iodine with weak van der Waals forces between its molecules will quickly sublime on heating.
- They are non polar and generally insoluble in water. But they dissolve in most organic solvents.
- Since they exist as discrete molecules, they do not conduct electricity except graphite.
- The solids are soft due to the weak intermolecular force of attraction between the molecules.

ii) Giant atomic structure

It is possible for many atoms to link up together forming chains of covalent bonds. When this occurs, **giant molecules** are formed. Giant covalent structure (also known as giant atomic structure) is attained when such linking happens. Commonly known substances with giant atomic structure are diamond, silicon dioxide and graphite. The atoms linking up in the chain form very strong three dimensional structures except for graphite.

a) Graphite

This is a form of carbon element. Its crystal consists of layers of carbon atoms. Each

layer is a giant atomic molecule in two dimensions only. The atoms in a layer are joined by strong covalent bond. However, the layers are joined by weak intermolecular forces, and the layers can easily slide over each other. This makes graphite a soft and slippery substance. During the formation of the strong covalent bonds, only three of the outermost electrons are involved, the fourth electron is often delocalized. These delocalized electrons are mobile in the structure making graphite a good conductor of electricity.

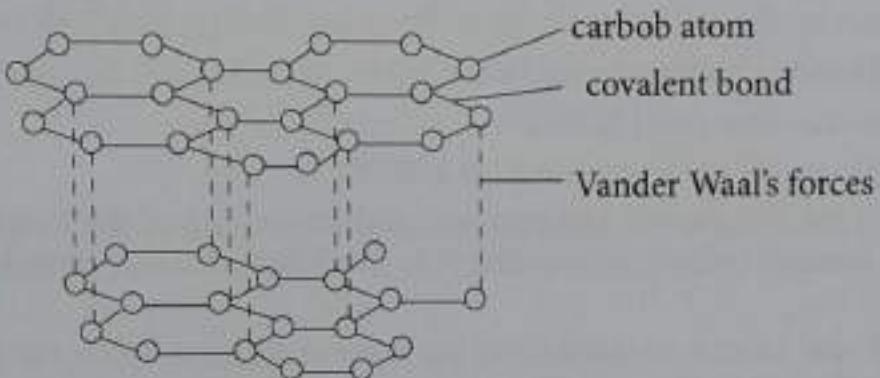


Fig. 3.4: Structure of graphite

b) Diamond and silicon dioxide

In diamond, all the outermost (valence) electrons are involved in the covalent bonding. A diamond crystal is a giant molecule in three dimensions. Each carbon is joined by covalent bonds to four other carbon atoms. The four carbon atoms are tetrahedrally arranged and the covalent bonds interlace forming a tetrahedron structure. This makes the structure very strong and rigid.

- Diamond has no free mobile electrons. Therefore, it is poor conductor of electricity. The strong covalent bonds between the carbon atoms in its structure about are responsible for its very high melting and boiling points. Diamond sublimes at about 3550°C .
- The tetrahedral arrangement and interlacing of the bonds in all directions throughout the structure is believed to make diamond a very hard element. Diamond is the **hardest** known element.

c) Silicon dioxide

This is a compound formed from silicon and oxygen. It has strong covalent bonds equivalent to those in diamond. Therefore silicon dioxide has high melting and boiling points. The melting point is 1610°C and boiling point is 2230°C . It is insoluble in water but soluble in organic solvents. Since all its electrons are held in fixed positions in the structure, it is a very poor conductor of electricity.

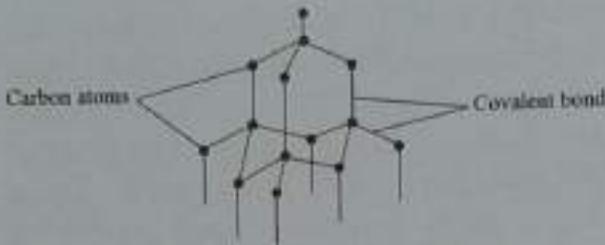


Fig. 3.5: Tetrahedral structure of diamond

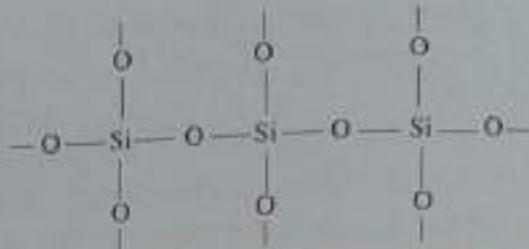


Fig. 3.6: Structure of silicon dioxide

Effects of giant atomic structure on the properties of the substance

- The substances generally have high melting and boiling points, for example;
 - Silicon dioxide - melting point 1610°C , boiling point 2230°C .
 - Graphite - melting point 3730°C .
 - Diamond - melting point (sublimes) 3550°C
- Because of the tetrahedral arrangement and interlacing of the bond, diamond is the most hardest known substances. It is used in making of drilling and cutting tools.
- Diamond and silicon dioxide have all their outermost electrons held in fixed positions. Therefore, they are very poor conductors of electricity.

3.2 Covalent bonds and dative bonds

When a bond is formed by sharing of a pair electrons, a covalent bond is formed. The shared pair of electrons can be equally contributed by the atoms involved or donated by one of the atoms. In the case, where the shared pair of electrons are equally donated by the atoms involved, the bonding is referred to as **normal or pure covalent bond**.

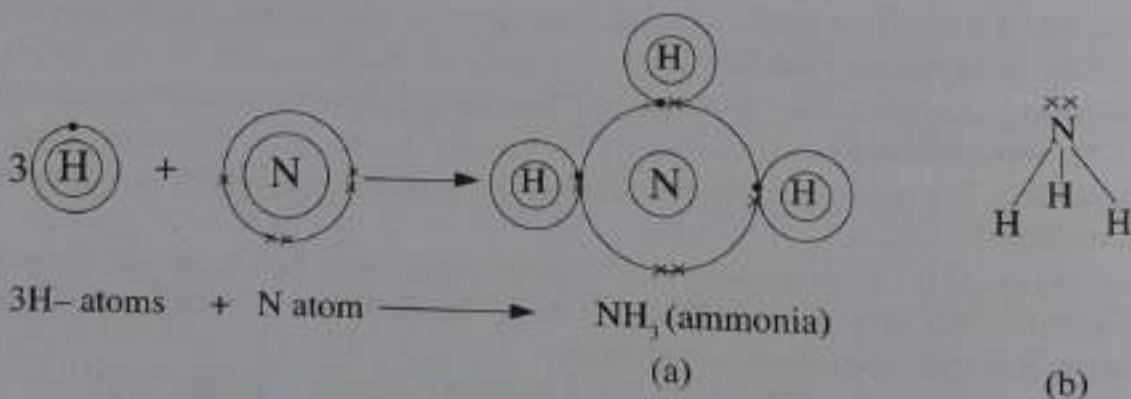


Fig. 3.7: Formation of dative bonds in ammonium ion

In some instances, when covalent bonding occurs, only one of the atoms involved contributes all the shared pair of electrons. When this happens, the bond formed is called **dative covalent bond** or simply as **dative bond**. Example of dative bonding occurs in the formation of ammonium ion. Nitrogen atom in the molecule of ammonia having a lone pair of electrons donates to hydrogen (H^+) ion as illustrated in Fig. 3.8.

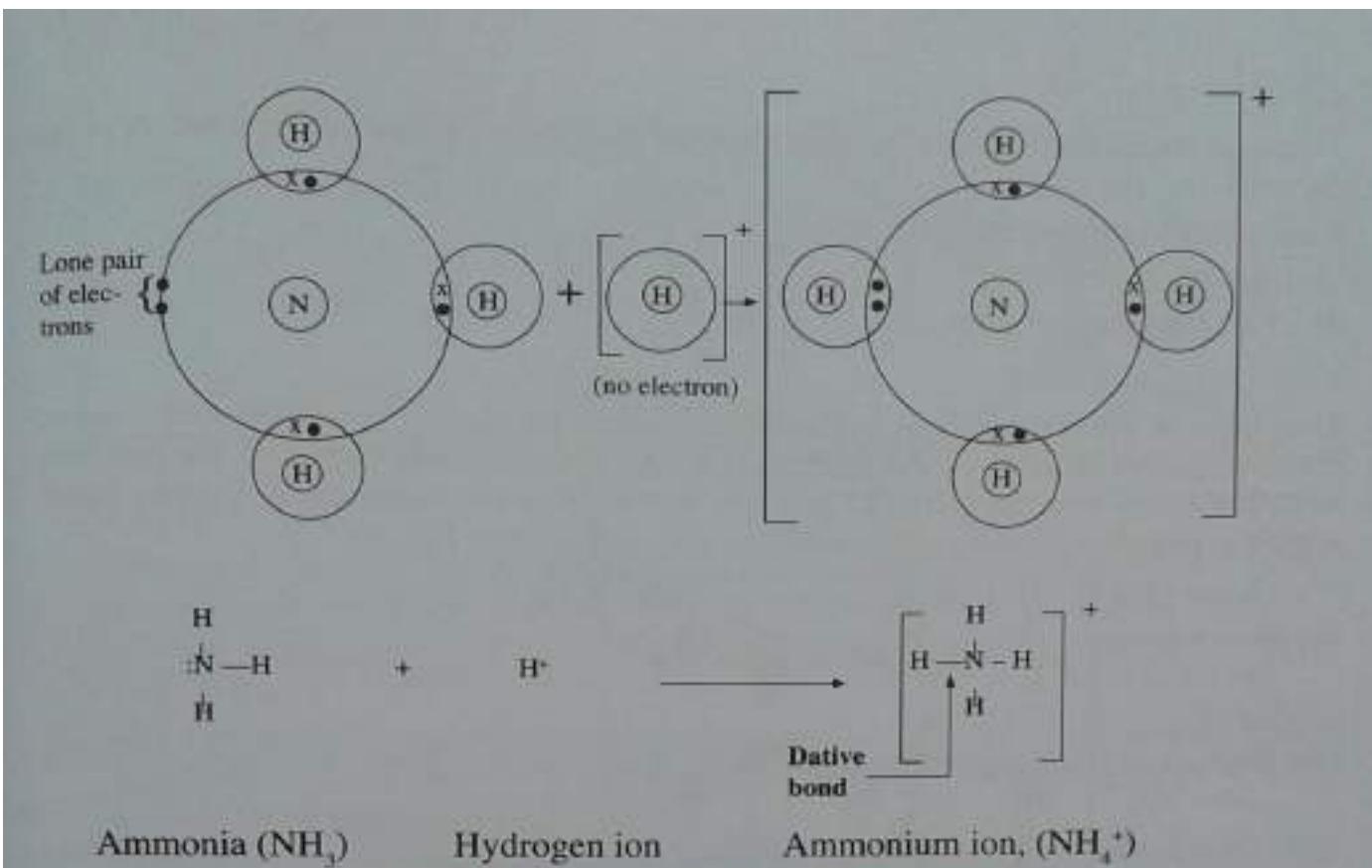


Fig. 3.8: Formation of dative bond in ammonium ion

Polar and non-polar covalent bonds

When the covalent bond is formed between two identical atoms e.g. H-H or Cl-Cl, the electrons are shared equally and the bond is 100 per cent covalent. If the atoms are not the same e.g. H – Cl, H – O or N – H, the electrons contributed are usually not shared equally. There is an electron displacement towards the more electronegative atom. The affinity or attracting power of atom to attract an electron to form ion is called **electronegativity**.

When the shared electrons tend to be attracted more on one side of the bonding atoms, the side to which the electrons are pulled more becomes partially **negative** while the other end becomes partially **positive**. If this happens, in a molecule, such as water, it is said to be **polar**. This unequal sharing of covalent bond electrons is responsible for the ionic character in some covalent compounds as mentioned earlier. The ionic character varies in the covalent compounds. For example, the ionic character in the $\text{H}^+\text{-Cl}^-$ bond is about 17 percent while that in $\text{H}^+\text{-O}^-$ bonds of water is about 30 per cent.

The following are electronegativity values of some elements.

F	4.0	
O	3.5	Increase
N	3.0	
C	2.5	
H	2.1	in electronegativity

The most electronegative element is fluorine.

3.3 Intermolecular forces

These are forces of attraction holding together molecules of substances. The forces are generally weak.

Examples of intermolecular forces

- i) Hydrogen bonding
- ii) Van der Waals forces

i) Hydrogen bonding

This type of bonding occurs between molecules containing hydrogen and a more electronegative atom than the hydrogen atom. The attraction between the partially negative atom and the partially positive hydrogen constitutes the **hydrogen bond** which is usually represented by a dotted line as shown in Fig. 3.9.

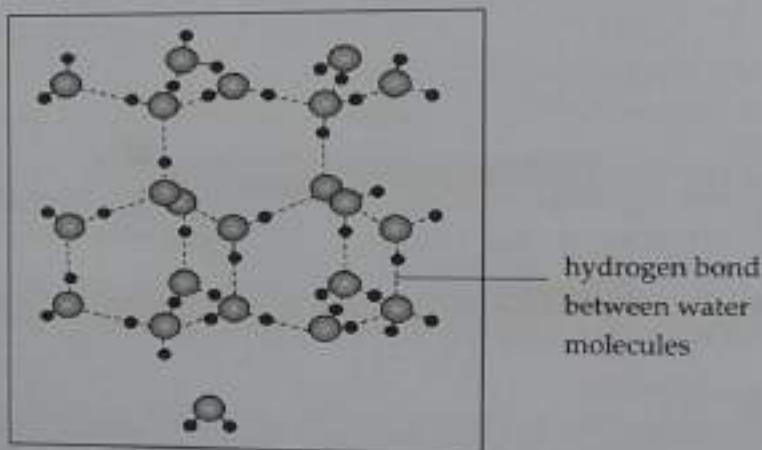


Fig. 3.9: Examples of hydrogen bonding

The partially positive hydrogen in one molecule somehow attracts the partially negative atom, i.e. oxygen, in another molecule. This weak attraction is what is known as **hydrogen bonding**. Hydrogen bonding can also occur between different molecules e.g. ammonia and water.

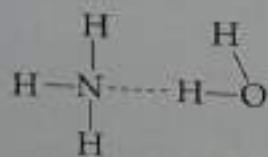


Fig. 3.10: Hydrogen bonding between ammonia and water molecules

i) Van der Waals forces

These forces were discovered by Johannes van der Waals, whom they are named after. The forces are present in most molecules but their significance is evident when the molecules are close to each other. Van der Waals forces are for example found among the halogens, and between different layers of the graphite. Their effect increase with the mass of the molecules, but between two molecules their effect is negligible. Their cumulative effects significantly influence some physical properties of covalent compounds e.g. organic compounds.

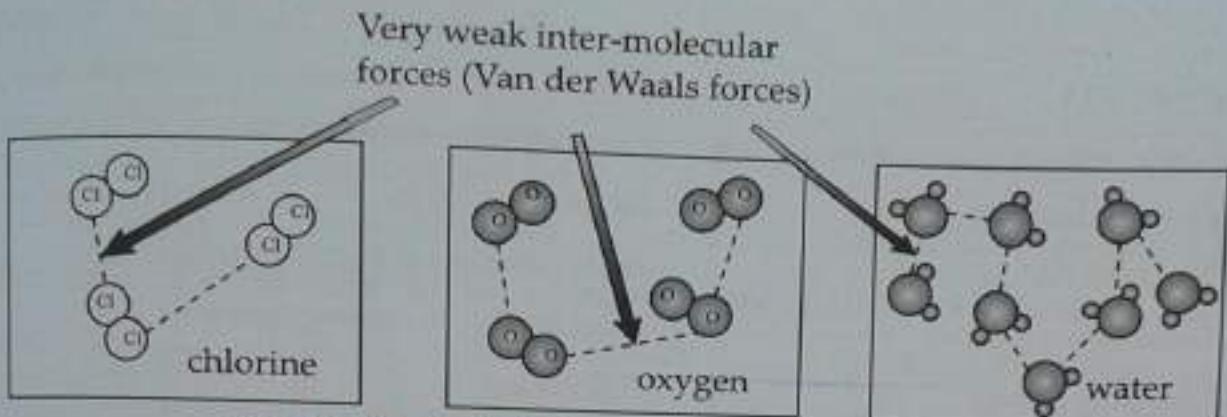


Fig. 3.11: Van der Waals forces in chloride, oxygen and water

Effects of intermolecular forces on physical properties

- Because hydrogen bonds should be overcome during boiling, water has higher boiling point compared to many other covalent compounds of similar mass.
- Surface tension of water is great due to hydrogen bonding among the water molecules.
- Van der Waal's forces significantly contributes to the higher boiling and melting points for some elements. For example the halogens with increasing melting and boiling point moving down the group.
- The presence of hydrogen bond between water molecules gives it the liquid state. Without these bonds, water would exist in gaseous state at room temperature and pressure.

3.4 Allotropy

Allotropy is the existence of an element in more than one form without change of state. The various forms are called **allotropes**. Oxygen, carbon and sulphur are some of the elements with allotropic property.

The allotropes exhibit different physical properties and sometimes even varying chemical properties.

Allotropes of Oxygen

Oxygen and ozone are allotropes. Ozone has a triatomic molecule and oxygen is a diatomic molecule. Ozone can be made from Oxygen. It can also be converted back to oxygen by heat.

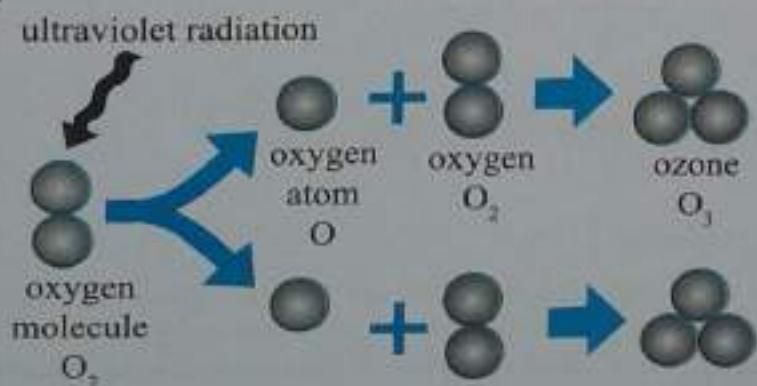


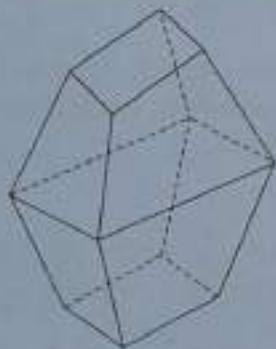
Fig. 3.12: Formation of ozone

Table 3.8: Comparison between oxygen and ozone

Oxygen (O_2)	Ozone (O_3)
1. Gas at room temperature.	Gas at room temperature.
2. Density 16(H=1).	Density 24(H=1).
3. Not attacked by heat.	Heat converts it to oxygen.
4. Oxidizing agent	Very strong oxidizing agent.
5. Not poisonous .	Poisonous.
6. Does not react with potassium iodide solution.	Liberates iodine from potassium iodide solution..

Practice exercise 3A

1. The following are the crystalline allotropes of sulphur.



i. _____



ii. _____

- (a) Identify the above allotropes of sulphur.
 (b) Name the two non-crystalline allotropes of sulphur.

2. Explain why molten sulphur form viscous liquid when heated at temperatures between 160°C - 200°C but when continued to be heated upto 250°C it becomes less viscous.
 3. State the transition temperature between the two crystalline allotropes of sulphur. Which one is the more stable form?

Allotropes of carbon

Carbon exists as diamond, graphite and amorphous carbon. Diamond and graphite are **crystalline**. The amorphous carbon is largely non-crystalline. Amorphous carbon are in the form of charcoal, soot or coke. When we talk of allotropes of carbon, often diamond and graphite are the ones considered.

Table 3.7: composition between diamond and graphite

Characteristics	Diamond	Graphite
Appearance	Colourless, transparent crystals that sparkle in light.	Dark-grey, opaque and shining.
Density	Highest (3.5 g/cm^3).	Moderate (2.3 g/cm^3).
Hardness	Hardest natural substance known.	Soft and silvery.
Electrical Conductivity	Does not conduct electricity.	Conducts electricity.

Uses of diamond

- It is used for making jewellery e.g. necklace, rings and earrings. This is because of its highly attractive sparkling appearance. It is a very precious gemstone.
- Diamond being a very hard metal due to the giant atomic structure and tetrahedra arrangement of bonded electrons in the structure in all direction. This makes diamond find important uses in making of drilling equipment, boring and cutting tools which require high tensile strength, toughness, hardness and non-brittle properties.

Uses of graphite

- The sliding property of the layers of graphite due to weak intermolecular forces between the layers enables graphite use as lubricant and making of pencils.
- It is used to reinforce metals and broken bones.
- Graphite being a good conductor of electricity is used as the positive terminals in dry cells and as electrodes in industry. The delocalised electrons in the structure of graphite is responsible for its electrical conductivity. Remember during the formation of covalent bonds in graphite, only three electrons are involved in the bond formation, the fourth electron is left free and able to move freely.

Practice exercise 3B

1. Mention the two allotropes of oxygen.
2. Why is co-ordinate bonding (dative) bonding a special covalent bonding?
3. Mention two characteristics of rhombic sulphur.
4. Explain why graphite conducts electricity and diamond cannot yet both are allotropes of carbon.

Properties of metals and their uses

There are many types of metals available on earth. They are largely extracted from their ores in the earth's crust. Metals exhibit metallic bonding as you learnt in Form 2. In experiment 3.4, we saw that all metals conduct electricity. Examples of these metals include: copper, aluminium, zinc and iron. Fig 3.13 shows metallic bonding in metals.

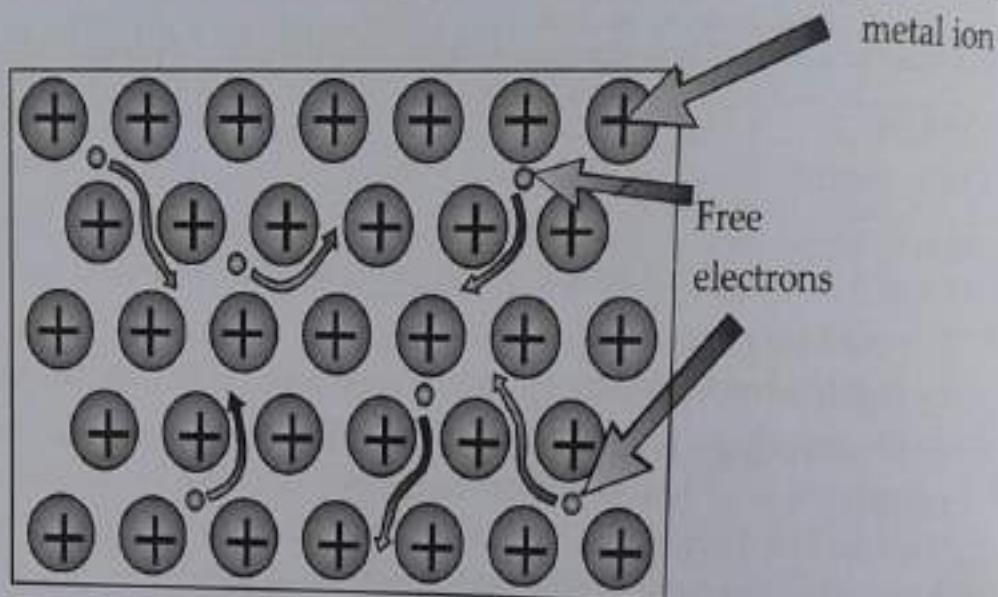


Fig 3.13: Metallic bonding

Research activity

1. Collect some metals such as magnesium, aluminium, iron and zinc.
 - (a) Which metals are shiny in appearance?
 - (b) Which metals are dull in appearance?
2. Try bending these metals into different shapes.
 - (a) Which metals were easily bent?
 - (b) Which metals were very difficult to bend? Suggest a reason for this observation.
3. Holding the metals using a pair of tongs or suitable materials, heat each metal using a bunsen burner.
 - (a) Which metals easily burn?
 - (b) Which metals glowed?
 - (c) Which metals took so long to get red hot?
 - (d) Explain the difference in the observations made.

Table 3.9: shows the general physical properties of some common metals.

Table 3.9 Physical properties of some metals

Metal	Melting Point(°C)	Boiling Point(°C)	Density g/cm³	Thermal Conductivity	Electrical Conductivity	Malleability	Ductility
Sodium	98	883	0.97	good	good	malleable	ductile
Aluminium	660	2467	2.70	good	good	malleable	ductile
Zinc	420	907	7.14	good	good	malleable	ductile
Iron	1535	2750	7.86	good	good	malleable	ductile
Copper	1085	2572	8.96	good	good	malleable	ductile

Melting and boiling points

Metals generally have high melting and boiling points. This is due to the strong metallic bonds between the fixed positive ions embedded in the 'sea' of delocalised electrons.

However, sodium is an exception with a low melting point of 98°C. This is because of the few delocalised electrons available for bonding decreasing the strength of the metallic bonds in its structure. Recall that sodium has a valency of one. So, only one electron is released per atom to the delocalised 'sea' of electrons. This explains the relative softness of sodium and the other metals of group I elements. They are collectively called soft metals.

Density

Metals have high densities because of their giant metallic structures except for sodium and group I metals. The atoms of metals are packed together very closely. The observed different densities in metals is due to different arrangements of atoms in their structures. Again, density increases with increasing atomic number. This is because the mass of an atom increases as the atomic number increases.

Thermal and electrical conductivity

Metals are the best conductors of heat. The delocalised electrons forming a sea or cloud of electrons are free and not part of any particular atoms. The easy movement of these electrons explains the great conducting power of solid or liquid metals for heat and electricity. When one end of the metal is heated, the heat is quickly felt on the other end because the kinetic energy of the delocalised electrons is increased, they vibrate much faster, move and hit the nearby electrons resulting in the transfer of heat. This process will continue until the free electrons transfer the heat to the colder end.

Electrical conductivity uses similar principle of heat conductivity. However the electrons move along the wire instead of just vibrating. A flow of electrons in a metal atom pushes the electrons nearest to it so that the entry of one electron pushes out another electron to the opposite end of the metal. This leads to conduction of electrical current.

Ductility and malleability

- Most metals are **ductile** i.e. they are capable of being drawn out into wires. The atoms within a metal are arranged in layers. Ductility involves slipping of these layers of atoms over each other when the metal is pulled or hit. This results in the formation of wires as shown in Fig. 3.14.

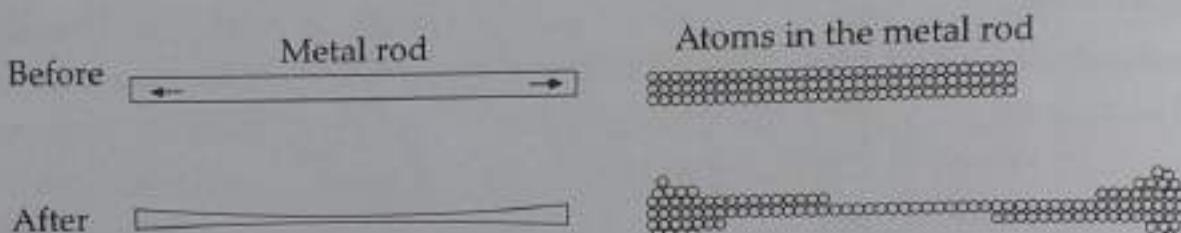


Fig. 3.14: Ductility in metals

- Most metals are also **malleable** i.e. they are capable of being hammered into thin sheets. The hammer exerts strong forces on the layers of atoms in the structure of the metal. Because of this property, metals can be bent and moulded into different shapes. This is illustrated in Fig. 3.15 below.

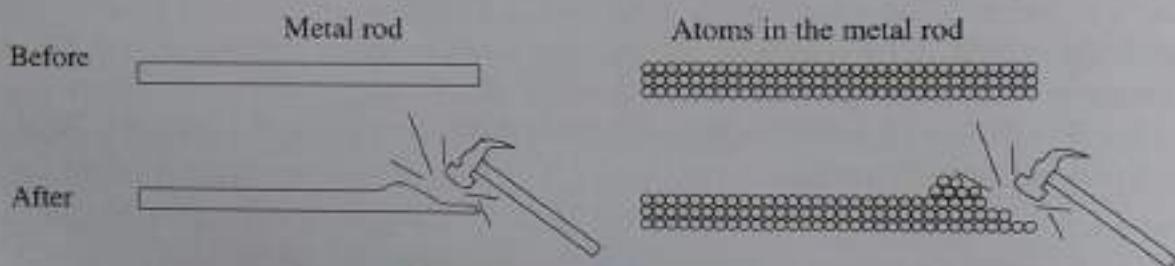


Fig. 3.15: Malleability in metals

Uses of metals

The following are some of the uses of metals based on their properties.

Copper

- It is a very ductile metal thus it can be very easily drawn into copper wires and pipes.
- It is an excellent heat conductor finding use in soldering or brazing work.
- Because of its toughness, it is used in arrow heads and other tools which are required not to shatter.
- The attractive golden lustre find heavy use in jewellery and ornaments making.

Aluminium

- It is used in overhead powerlines because it is a good electrical conductor and lighter than copper.
- It is also used in making bodies and other parts of automobile that require light weight.

- Because of its shiny metallic lustre, it is widely used in jewellery and as food wrapping material. Its shiny surface reflects heat well keeping the food hot for a long time.
- Because of its light weight and good heat conductivity, aluminium is used in making most cooking utensils.

Zinc

- It is used in batteries because of its good electrical conductivity.
- Many electrical appliances contain zinc.

Iron

- Because of its malleability, it is beaten into thin sheet in the making of roofing sheets, cutting tools such as pangas and hoes.
- Its good heat and electrical conductivity finds useful application in heating appliances such as iron box and cooking pans.

Alloys and their uses

Metals show robust properties such as high density and good tensile strength, good heat and electrical conductivity and excellent ability to be beaten into different shapes. In many applications these properties are not all needed at the same time. At times, some of these properties may be required to be enhanced to achieve desired standard quality or combination of properties.

In order to obtain such a combination of characteristic properties, metallurgists (experts in the science of metals) developed alloys. An alloy is a mixture of two or more elements one of which is a metal. An alloy is obtained by mixing the base metal with a given element or elements to confer the desired quality of strength, malleability, weight or hardness among others.

Some of the important uses of alloys

- i) Copper alloys are very tough. Hence they are used in tools, weapons and military wares that require not to shatter. Copper alloys attractive golden colour finds good use in jewellery and ornament making.
- ii) Duralumin, an alloy of aluminium with copper and smaller quantities of magnesium, silicon and iron is very strong, has lower density and much lighter. This makes it heavily used in the manufacture of aircraft parts.
- iii) Alloys of iron such as steel improve its tensile strength, lowering its brittleness, makes it tough and hard. These qualities are desirable in making machinery, cutting tools and iron forgery works.

Table 3.10 shows some of their alloys, properties and their uses.

Table 3.10: Some alloys and their uses

Alloy	Composition	Properties	Used to make
Brass	70% Copper 30% Zinc	• Harder than pure copper • 'Gold' coloured	• Utensils • Screw • Radiators
Bronze	90% Copper 10% Tin	• Harder than pure copper	• Machinery • Decoration work
Steel	Stainless steel 74% Iron 18% Chromium 8% Nickel	• Tough • Does not corrode	• Cutlery • Surgical instruments • Kitchen sinks
	Tungsten steel 95% Iron 5% Tungsten	• Tough • Hard even at high temperatures	• Edges of high-speed cutting tools
	Manganese steel 87% Iron 13% Manganese	• Tough • Springy	• Drill bits • Springs
	Mild steel 0.3% Carbon 99.7% Iron	• Stronger and harder than pure iron • It is not brittle	• Car bodies • Axles • Bridges
	Medium steel 99.55% Iron 0.45% Carbon	• Tougher than mild steel	• Car springs • Chains
	Cast iron 95.5% Iron 4.5% Carbon	• Easily molded	• Gear boxes • Engine blocks • Brake discs
Duralumin	95% Aluminium 4% Copper smaller amounts of other elements	• Strong • Light weight	• Parts of airplanes • Rockets • Cans • Foils • Kitchen utensils

Revision Exercise 3



1. What is the difference between ionic bonding and covalent bonding?
2. Sugar solution is a non-electrolyte while sodium chloride solution is an electrolyte. Explain.
3. What is co-ordinate bonding?
4. State two allotropes of:
 - a) Carbon
 - b) Oxygen
 - c) Sulphur
5. State two uses of each of the following
 - a) Diamond
 - b) Graphite
6. State two uses of
 - a) Copper
 - b) Zinc
 - c) Aluminium
7. Suppose you are a member of Area Development committee (ADC) in your community. The committee seeks proposal on construction of a bridge across a river in your area. Suggest three alloys that you would recommend to the committee to choose as part of the materials for the bridge construction. Give reasons why the committee should accept your proposal.

Topic 4: Stoichiometry

Success criteria

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

- a) Write balanced chemical equations.
- b) Work out relative formula mass of a compound.
- c) Define the mole of a substance.
- d) Convert moles into other units of measurement.
- e) Determine the percentage of water in molecular and hydrated ionic compounds.
- f) Deduce empirical and molecular formulae from relevant data.
- g) Calculate concentration of solutions.
- h) Prepare standard solutions.
- i) Determine the concentration of a solution using filtration.
- j) Determine the yield in a chemical reaction.



4.0 Introduction

Chemists use **chemical equations** to conveniently express the different reactions they investigate. Even though the reactions vary, in every reaction there are **reactants** and **product(s)**. The chemical equations show precisely the reactants, products and their combining mole ratios (amount of each substance).

Chemical equations must be balanced as we learnt in Form one. Unbalanced equations are unacceptable in chemistry. Stoichiometry of chemical reactions refers to an overall balanced equation. We must remember that the formula of elements and compounds in an equation must also be correctly written. This demands the knowledge of valencies of the elements and radicals.

4.1 Chemical formulae of compounds

In writing balanced equations, correct chemical formulae must be used. Therefore lets remind ourselves how to write chemical formulae of compounds.

When elements react to form compounds, they do so by bonding. The capacity or strength of the atom to form the bonds is known as the **valency** or **combining power** of the element. The valency of an element is determined by the number of electrons in the outermost energy level. These electrons are also referred to as **valence electrons**. Knowledge of the valencies of elements or radicals is also important in writing chemical formulae of compounds and balancing of equations. Table 4.1 shows valencies for elements in different groups of the periodic table.

Table 4.1: Valency and charges of ions of the group elements

Group	I	II	III	IV	V	VI	VII	VIII
Valency	1	2	3	4	3	2	1	0
Charge on the ion	1+	2+	3+		3-	2-	1-	0

Most elements have one valency. However there are some elements that display more than one valency in different reactions. Table 4.2 gives examples of elements with varying valencies.

Table 4.2: Elements with multiple valencies

Element	Symbol	Valencies
Carbon	C	2 and 4
Lead	Pb	2 and 4
Iron	Fe	2 and 3
Copper	Cu	1 and 2
Sulphur	S	2,4 and 6
Cobalt	Co	1, 2 and 3
Manganese	Mn	2 and 7
Chromium	Cr	3 and 6

Radicals and their valencies

Radicals are groups of atoms that are covalently bonded together to form complex ions. They cannot exist in their own and participate in reactions as a unit. They have either positive or negative charges. Table 4.3 gives examples of some radicals and their valencies.

Table 4.3: Radicals and their valencies

Radical	Charge on ion	Valency
Ammonium	NH_4^+	1
Hydrogen sulphate	HSO_4^-	1
Hydrogencarbonate	HCO_3^-	1
Hydroxide	OH^-	1
Nitrate	NO_3^-	1
Carbonate	CO_3^{2-}	2
Sulphate	SO_4^{2-}	2
Phosphate	PO_4^{3-}	3

Writing chemical formulae

The following are general steps in writing chemical formulae.

Step 1: Write the correct symbol of the element or radical.

Step 2: Write the valency of each element or radical.

Step 3: Exchange the valencies of the elements. Write the exchanged valencies as subscripts.

Step 4: Write the symbols close together.

Note: Always remember to write correct symbols and valency for each element or radical.

Example 1

Write the formula for sodium sulphate.

Solution

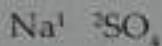
Step 1

Write the symbols of the elements and radical.



Step 2

Write the valency of the element and radical as superscripts.



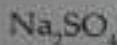
Step 3

Exchange the valencies by writing them below the symbols as shown by the arrows.



Step 4

Write the symbols close together.



Example 2

Write the formulae of the following compounds.

- | | |
|-----------------------|----------------------|
| (a) Sodium carbonate | (c) Iron hydroxide |
| (b) Potassium nitrate | (d) Calcium chloride |

Solution

- (a) Sodium carbonate

Symbol	Na	CO ₃
Valency	1	2



- (b) Potassium nitrate

Symbol	K	NO ₃
Valency	1	1



- (c) Iron hydroxide

Symbol	Fe	OH
Valency	2	1

Formula	$\text{Fe}^2 \cancel{\text{OH}} \rightarrow \text{Fe(OH)}_2$
(d) Calcium chloride	
Symbol	Ca Cl
Valency	2 1
Formula	$\text{Ca}^2 \cancel{\text{Cl}} \rightarrow \text{CaCl}_2$

Note: For (c) we write brackets because the radical consists of two different elements. For (d) it is wrong to put brackets e.g. $\text{Ca}(\text{Cl})_2$, since C and I do not represent different elements.

Example 3

Write the formula of lead (IV) oxide.

Solution

- (a) Lead (IV) oxide

Symbol	Pb	O
Valency	4	2
Formula	$\text{Pb}^4 \cancel{\text{O}} \rightarrow \text{PbO}_2$	

Note: Before we bring the valencies down, we must divide the valencies by a common factor. In this case it is 2. Thus the formulae PbO_2 .



Practice exercise 4A

1. Write down the symbols of the following radicals and indicate their valencies.

a) Carbonate	b) Sulphate
c) Hydroxide	d) Nitrate
e) Hydrogen carbonate	
2. Write down the symbols and charges of the following cations and anions.

<i>Cations</i>	<i>Anions</i>
a) Ammonium	e) Chloride
b) Sodium	f) Bromide
c) Calcium	g) Hydrogen sulphate
d) Aluminium	h) Phosphate
3. Write the formulae of the following compounds.

a) Potassium hydrogen carbonate	
b) Zinc nitrate	
c) Aluminium hydroxide	
d) Iron (II) chloride	
e) Calcium nitrate	
f) Ammonium sulphate	

4.2 Writing chemical equations

When writing chemical equations ensure the following:

- (i) Correct symbols of the elements (reactants and products).
- (ii) Correct state symbols of reactants and products.
- (iii) The equation is balanced.

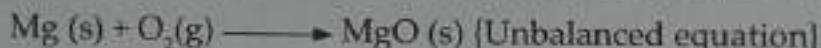
The numbers used in balancing chemical equations are actually the number of moles required for reactants and products. Balanced equations help us to predict the mass of reactants and products. For example, in a chemical factory, if a customer orders a product it is possible to calculate how much raw material is required to fulfil the customer's order.

Example 1

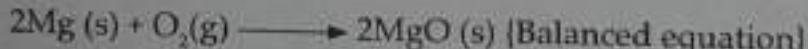
Write balanced equation for the reaction of magnesium with oxygen to form magnesium oxide.

Solution

- i. First write the symbols and formulae of the compound formed.



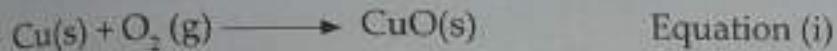
- ii. Check number of the atoms of each element in the equation if they are equal in the (reactants and products) sides. For example in above equation, there are more atoms of oxygen on the reactants side than on the product side.
- iii. To balance the equation, we must identify suitable (small) whole number values that will multiply atoms of the elements on both sides of the equation to make them equal. Write the number in front of each symbol. For example;



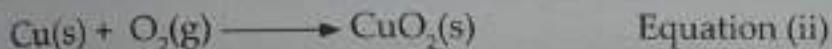
- Note:**
1. The plus (+) sign in equation does not mean "addition". It means to "react with"
 2. The arrow (\longrightarrow) is used to indicate formation of product. It is wrong to use equal (=) sign in chemical equations.
 3. We do not need to write 1 in chemical equations. It is believed to already exist.
 4. Remember to include the state symbols.
 - (s) means solid. (A solid can be precipitate or suspension)
 - (l) means liquid
 - (g) means gas
 - (aq) means aqueous (Substance dissolved in or containing water)
 5. Never balance an equation by writing a multiplying factor as a subscript.

Example 2

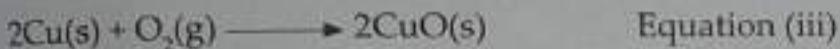
Write a balanced equation for the reaction of copper and oxygen solution -4



Equation (i) is unbalanced because there is one mole of oxygen atoms on the product side.



Equation (ii) is wrongly balanced. Why?



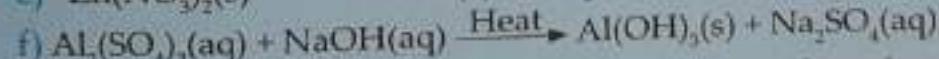
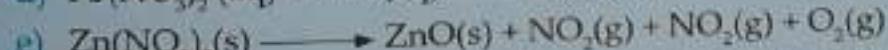
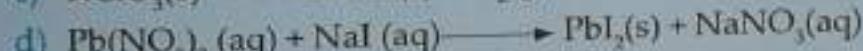
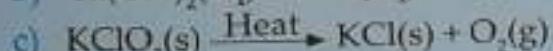
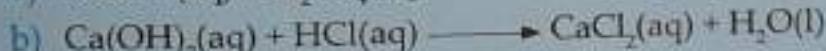
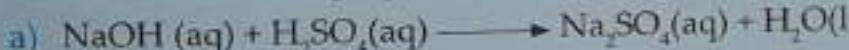
Equation (iii) is correctly balanced.

Note: For equation (ii) though the number of atoms of elements in both reactants side and product side are equal, the formula of copper (II) oxide is incorrect.

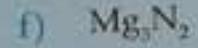
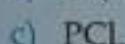
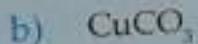
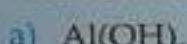


Practice exercise 4B

1. Balance the following equations:



2. What are the names of the following compounds whose formulae are:



4.3 Relative formula mass (R.F.M)

In Form one you learnt about relative atomic mass of elements (RAM).

Relative atomic mass has no units since it is a ratio of two masses. It is the average mass of one atom of the element-compared with $\frac{1}{12}$ th of the mass of one atom of carbon-12.

Relative formula mass is the sum total of relative atomic masses of all the atoms in a compound. Table 4.4 shows relative atomic masses of some common elements.

Table 4.4: Relative atomic masses of some common elements

Element	Symbol	Relative atomic mass
Hydrogen	H	1
Carbon	C	12
Nitrogen	N	14
Oxygen	O	16
Sodium	Na	23
Magnesium	Mg	24
Chlorine	Cl	35.5
Potassium	K	39
Calcium	Ca	40.1
Iron	Fe	55.8
Copper	Cu	63.5

Note: Relative atomic masses of elements are usually rounded off to whole numbers, to make calculations much easier.

Calculating relative formula mass of compounds

Step 1: Write the correct formula of the compound.

Step 2: Identify the relative atomic mass for all the atoms or ions in the compound.

Step 3: Add the relative atomic masses for the atoms or ions in that compound.

Example 1

Find the relative formula mass (R.F.M) of the following compounds.

- (a) Calcium chloride
- (b) Copper (II) hydroxide

(RAM: Ca = 40 Cl = 35.5 Cu = 63.5)

Solution

- (a) Calcium chloride

Step 1: Write the correct formula of the compound



Step 2: Add relative atomic masses of the ions in the compound

$$\text{R.F.M of } \text{CaCl}_2 = 40 + (35.5 \times 2)$$

$$= 40 + 71$$

$$= 111$$

Note: In the calculation, you must multiply RAM of chlorine atoms by 2 because there are two Cl in the formulae. Remember relative formula mass has no unit.

- (b) Copper (II) hydroxide

Formulae is $\text{Cu}(\text{OH})_2$

$$\text{R.F.M of } \text{Cu}(\text{OH})_2 = 64 + (2 \times 16) + (2 \times 1)$$

$$= 64 + 32 + 2$$

$$= 98$$

Note: We must double the R.A.M of atoms of elements in the brackets.

Example 2

Calculate the relative formula mass (R.F.M) of the following compounds.

- (a) Ammonium carbonate
- (b) Aluminium sulphate

(N = 14, H = 1, Al = 27, O = 16, C = 12, S = 32)

Solution

- (a) Formulae of ammonium carbonate is $(\text{NH}_4)_2\text{CO}_3$,

$$\begin{aligned}\text{R.F.M of } (\text{NH}_4)_2\text{CO}_3 &= (14 \times 2) + (2 \times 1 \times 4) + 12 + (16 \times 3) \\ &= 28 + 8 + 12 + 48 \\ &= 96\end{aligned}$$

- (b) Formulae of aluminium sulphate is $\text{Al}_2(\text{SO}_4)_3$,

$$\begin{aligned}\text{R.F.M of } \text{Al}_2(\text{SO}_4)_3 &= (27 \times 2) + (32 \times 3) + (3 \times 16 \times 4) \\ &= 54 + 96 + 192 \\ &= 342\end{aligned}$$



Practice exercise 4C

1. Find the relative formula mass of the following compounds.

- | | |
|----------------------------------|---------------------------------------|
| (a) $\text{Fe}(\text{OH})_2$ | (e) C_4H_{10} |
| (b) CaSO_4 | (f) NH_4NO_3 |
| (c) $(\text{NH}_4)_2\text{SO}_4$ | (g) $\text{CH}_3\text{CH}_2\text{OH}$ |
| (d) Cu_2O | (h) Fe_2O_3 |

2. Write down the formula of the following compounds and then find their relative formula mass.

- (a) Copper (II) nitrate
- (b) Iron (II) sulphate
- (c) Ammonium phosphate
- (d) Magnesium hydrogencarbonate.

4.4 The mole

In reactions, chemists deal with atoms, ions, molecules and electrons. Chemists are always interested to know the masses as well as the amount of these particles participating in a given reactions. The masses of these particles are usually so small, for example the mass of hydrogen is 1.4×10^{-24} g. Counting these particles individually or weighing them is also quite cumbersome. An Italian physicist called Amedeo Avogadro came up with a unit for measuring counting these particles called **mole**.

It is important to bear in mind that the term mole simply represents a collective number just like a dozen is used to mean 12 items or a decade referring to 10 years. Mole is taken to represent a large number value, that is 6.023×10^{23} particles. The number was established after series of experiments, an effort greatly attributed to Amedeo Avogadro. It is a fixed and constant number. It is referred to as **Avogadro's number** or **Avogadro's constant**. This number is represented as $L = 6.023 \times 10^{23}$.

Meaning of mole

The mole is the amount of substance that contains as many elementary particles as there are atoms in exactly 12.0 g of the carbon-¹² isotope. Particles here refer to **atoms**, **ions**, **electrons** or **molecules**. Therefore, we say one mole of the particles contains Avogadro's number of particles i.e. 6.023×10^{23} .

Always when talking about moles, clearly state the type of particles you are dealing with. For example;

1 mole of hydrogen atoms = 6.023×10^{23} H atoms

1 mole of sodium atoms = 6.023×10^{23} Na atoms

1 mole of chlorine molecules = 6.023×10^{23} Cl₂ molecules

1 mole of oxygen molecules = 6.023×10^{23} O₂ molecules

1 mole of silver ions = 6.023×10^{23} Ag⁺ ions

1 mole of iodide ions = 6.023×10^{23} I⁻ ions

1 mole of electrons = 6.023×10^{23} electrons

Note: The number 6.023×10^{23} is for any one mole of particle. Mole is abbreviated as mol.

Just as we have one, two, three, $\frac{1}{2}$ or $\frac{1}{4}$ pairs or dozens of things, we can also have 1, 2, $\frac{1}{2}$, $\frac{1}{4}$ moles of particles.

Class activity

Copy table 4.5 below and complete it by filling in the missing number of particles.

Table 4.5 Summary of the number of moles in response to number of particles

Number of moles	Number of particles
1	$1(6.023 \times 10^{23}) = 6.023 \times 10^{23}$
2	$2(6.023 \times 10^{23}) = 1.2046 \times 10^{24}$
3	$3(6.023 \times 10^{23}) =$
$\frac{1}{2}$	$\frac{1}{2}(6.023 \times 10^{23}) =$
$\frac{1}{4}$	$\frac{1}{4}(6.023 \times 10^{23}) =$

Note: Mole is just a quantity of substance. It is necessary to state the type of particles being referred to i.e. whether atoms, molecules, ions or electrons. For example, when dealing with oxygen clearly state if referring to a mole of oxygen atoms (O) or a mole of oxygen molecules (O₂).

Relationship between mole and mass of substance

Experiment 4.1

Aim: To count the number of particles in samples of sugar and maize flour.

Requirements

- Maize flour
- Sucrose (sugar)
- Petri dishes or saucers
- Weighing balance

Procedure

1. Place approximately the same amount of flour and sugar in petri dishes as shown in Fig. 4.1 below.



Fig 4.1: Sugar in petri dishes

2. Try counting the particles as long as you can.
 - What do you observe?
 - What can you conclude?
 - How can we know the number of particles in each sample?
3. Weigh each sample and record the mass as shown below.
 - Mass of flour = x g
 - Mass of sugar = y g

Discussion

You may have noticed that it is cumbersome to count the particles in a sample of flour or sugar. However, we can find out the number of particles in a sample of a substance from the mass of that sample. This mass is determined by weighing.

It has been determined experimentally that 12 g of carbon-12 contains 6.023×10^{23} atoms. This simply means that if we place 6.023×10^{23} atoms of carbon-12 on a balance, they would weigh 12 g.

Therefore; One mole (6.023×10^{23}) of carbon-12 atoms = 12 g. So instead of counting 6.023×10^{23} atoms of carbon, we can simply weigh 12 g of carbon - 12. This means that if you have 36 g or 3 moles of carbon-12, then you have 1.8069×10^{24} atoms of carbon-12.

In general scientists count atoms, molecules and ions by weighing, if we could count 6.023×10^{23} (1 mole) of atoms, and then place them on a balance, we would then get actual mass of atoms or molecular mass of substance in grams. Therefore the values of relative atomic mass or relative formula mass of substances are expressed in grams only after weighing the substances. Otherwise they should remain as relative masses without units.

Relationship between mole and relative masses of substances

Molar mass

Relative molecular mass and relative formula mass of substances are taken as equivalent to one mole of the substances. If we weigh one mole of a substance, the mass obtained is referred to as molar mass. The molar mass M is the mass of one mole of a substance expressed in grams per mole (g/mol).

When the relative mass of an element or compound is expressed in grams that mass is equivalent to one mole of the element or compound. Molar mass of any element always contains 6.023×10^{23} particles though the molar masses of the elements are different. This is because of the variation in weights (relative atomic masses) of atoms. Table 4.6 and 4.7 show relative masses of some substances and their molar masses.

Table 4.6: Molar and relative atomic mass of some elements

Element	Relative atomic mass	Molar mass	Number of particles	Number of moles
Carbon 12	12	12	6.023×10^{23}	1
Hydrogen ¹	1	1	6.023×10^{23}	1
Aluminium	27	27	6.023×10^{23}	1
Sulphur	32	32	6.023×10^{23}	1
Lead	207	207	6.023×10^{23}	1

Table 4.7: Relative molecular mass and relative formula mass of some elements and compounds

Molecules/Compound	Number of moles	Number of particles	Relative molecular/formula mass	Molar mass (grams)
H ₂	1	6.023×10^{23}	2	2
O ₂	1	6.023×10^{23}	32	32
Al ₂ (SO ₄) ₃	1	6.023×10^{23}	342	342
CO ₂	1	6.023×10^{23}	44	44
CuCO ₃	1	6.023×10^{23}	124	124

What conclusion do you draw from Table 4.6 and 4.7? Notice that the number of particles in one mole of substance is the same irrespective of their different relative masses.

Calculations involving moles

Calculating the number of particles in a given moles of an element or compound

When carrying out calculations involving number of particles, always bear in mind one mole of substance contains Avogadro's number or constant of particles, $L = 6.023 \times 10^{23}$. The particles can be atoms, electrons, ions or molecules.

Example 1

Find the number of atoms in:

- 3 moles of iron
- 0.25 moles of calcium
($L = 6.023 \times 10^{23}$)

Solution

- 1 mole of Fe contains 6.023×10^{23} atoms

Let the number of atoms in 3 moles be x

$$\begin{aligned}\therefore x &= \frac{3 \text{ moles} \times 6.023 \times 10^{23}}{1 \text{ mole}} \\ &= 18.069 \times 10^{23} \\ &= 1.8069 \times 10^{24} \text{ particles}\end{aligned}$$

- 1 mole of calcium contains 6.023×10^{23} atoms

Let the number of atoms in 0.25 moles of Ca be x atoms

Solving for x ,

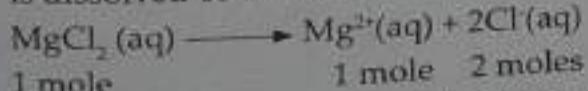
$$\begin{aligned}x &= \frac{0.25 \text{ mole} \times 6.023 \times 10^{23}}{1 \text{ mole}} \\ &= 1.506 \times 10^{23} \text{ atoms}\end{aligned}$$

Example 2

- How many magnesium ions are there in 1 mole of magnesium chloride?
- How many chloride ions are there in 0.5 mole of magnesium chloride?
($L = 6.023 \times 10^{23}$)

Solution

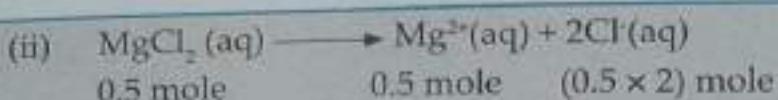
- The formula of magnesium chloride is MgCl_2 . Ions are set free when the salt is dissolved or melted.



1 mole of magnesium chloride when dissolved in water produces 1 mole of Mg^{2+} and 2 moles of Cl^- ions.

But 1 mole = 6.023×10^{23} Mg^{2+} ions

\therefore 1 mole of MgCl_2 contains 6.023×10^{23} magnesium ions.



From the equation 0.5 mole of MgCl_2 produce 1 mole of Cl^- ions

But 6.023×10^{23} chloride ions = 1 mole

\therefore 0.5 mole of MgCl_2 contains 6.023×10^{23} chloride ions.

Conversion of grams to moles and number of particles

Example 1

During laboratory preparation of oxygen 32 g of oxygen was collected. How many atoms were collected? ($\text{O} = 16$; $L = 6.023 \times 10^{23}$)

Solution

Note: 1. The values in the brackets are always given and must be used.

2. There are two methods we can use in solving such calculations. That is;

(i) First principle (statement) method.

(ii) Formula method,

Using first principle method

1 mole of oxygen (O) atoms = 16 g

But 1 mole of O_2 = (2×16) g

= 32 g

Therefore = 1 mole

1 mole of oxygen (O_2) = $2(6.023 \times 10^{23})$ atoms

(Remember one O_2 = 2 atoms of oxygen)

= 12.046×10^{23} atoms

= 1.2046×10^{24} atoms

Example 2

If 54 g of aluminium were obtained from aluminium ore, how many atoms of aluminium were obtained? ($\text{Al} = 27$; $L = 6.023 \times 10^{23}$)

Solution

First principle method

1 mole of Al = 27 g

y mole of Al = 54 g

Cross multiply and solve for y

$27 \text{ g} \times y = 54 \text{ g} \times 1 \text{ mole}$

$$y = \frac{54 \text{ g} \times 1 \text{ mole}}{27 \text{ g}}$$

= 2 moles of aluminium

1 mole of Al = 6.023×10^{23} atoms

2 moles = $2 \times 6.023 \times 10^{23}$ atoms = 1.2046×10^{24} atoms

Example 3

How many ions are there in 13 g of potassium ions K^+ ? ($K = 39$, $L = 6.023 \times 10^{23}$)

Solution

First principle method

$$1 \text{ mole of } K^+ \text{ ions} = 39 \text{ g}$$

$$y \text{ moles of } K^+ \text{ ions} = 13 \text{ g}$$

Cross multiply to solve for y

$$y \times 39 \text{ g} = 13 \text{ g} \times 1 \text{ mole}$$

$$y = (13 \text{ g} \times \frac{1 \text{ mole}}{39 \text{ g}})$$

$$= \frac{1}{3} \text{ mole}$$

$$\begin{aligned}\text{Number of } K^+ \text{ ions present} &= \frac{1}{3} \times 6.023 \times 10^{23} \\ &= 2.0 \times 10^{23} \text{ ions}\end{aligned}$$

Example 4

How many grams of sulphur contain:

(a) 6.0×10^{20} atoms

(b) 5.5×10^{23} atoms

$$(L = 6.0 \times 10^{23}, S = 32)$$

Solution

$$1 \text{ mole of sulphur (S)} = 6.023 \times 10^{23} \text{ atoms}$$

$$\text{Also, } 1 \text{ mole of S atoms} = 32 \text{ g}$$

$$32 \text{ g of S} = 6.023 \times 10^{23} \text{ atoms}$$

$$x \text{ g of S} = 6.023 \times 10^{20} \text{ atoms}$$

Cross multiply and solve for x

$$x \text{ g} \times 6.023 \times 10^{23} = 32 \text{ g} \times 6.023 \times 10^{20}$$

$$x = \left(\frac{32 \text{ g} \times 6.023 \times 10^{20}}{6.023 \times 10^{23}} \right) = 0.032$$

$$\therefore 6.0 \times 10^{20} \text{ atoms of S} = 0.032 \text{ g}$$

(b) $32 \text{ g of sulphur (S)} = 6.023 \times 10^{23} \text{ atoms}$

$$x \text{ g of S} = 5.5 \times 10^{23} \text{ atoms}$$

Cross multiply and solve for x

$$x = \left(\frac{32 \times 5.5 \times 10^{23}}{6.023 \times 10^{23}} \right)$$

$$\therefore 5.5 \times 10^{23} \text{ atoms of S} = 29.22 \text{ g}$$



Practice exercise 4D

- Find the number of atoms contained in the following elements.
 - 80 g calcium
 - 14.5 aluminium ($\text{Ca} = 40$, $\text{Al} = 27$, $L = 6.023 \times 10^{23}$)
- Given Avogadro's constant, $L = 6.023 \times 10^{23}$. Calculate the number of atoms in each of the following.
 - 15.5 sodium
 - 8 g magnesium ($\text{Na} = 23$, $\text{Mg} = 24$)
- Calculate the mass of
 - 1 atom of oxygen
 - 10 atoms of sodium ($\text{O} = 16$, $\text{Na} = 23$)
- An atom of a certain element X has a mass of 2.5×10^{-22} g. Find the relative atomic mass of X. ($L = 6.023 \times 10^{23}$)

Conversion of mass in grams to moles

Sometimes we may be required to convert mass of an element into moles. The following examples show how this can be easily done. We can use either the first principle method or formula method.

Example 1

Convert the masses of the following substances to moles.

- 0.12 g of carbon atoms.
- 0.24 g of magnesium atoms.
- 0.16 g of oxygen molecules.
- 0.8 g of oxygen atoms.
(C = 12, Mg = 24, O = 16)

Solution

First principle method

- 12 g of carbon atoms contain 1 mole
0.12 g of carbon contain $= x$ mole
Cross multiply and solve for x .

$$12 \text{ g} \times x \text{ mol} = 0.12 \text{ g} \times 1 \text{ mole}$$

$$x = (0.12 \text{ g} \times \frac{1 \text{ mole}}{12 \text{ g}}) \\ = 0.01 \text{ mole}$$

Therefore 0.12 g of carbon atoms = 0.01 mole

Formula method

$$\begin{aligned}\text{Moles} &= \frac{\text{Mass of substance given}}{\text{Molar mass of the substance}} \\ &= \frac{0.12}{12} \\ &= 0.01 \text{ mole}\end{aligned}$$

(b) First principle method

$$\begin{aligned}24 \text{ g of magnesium} &= 1 \text{ mole} \\ 0.24 \text{ g magnesium} &= y \text{ mole} \\ \text{Cross multiply and solve for } y \\ y \times 24 \text{ g} &= 0.24 \text{ g} \times 1 \text{ mole} \\ y &= \left(\frac{1 \text{ mole}}{24 \text{ g}} \times 0.24 \text{ g} \right) \\ &= 0.01 \text{ mole}\end{aligned}$$

Formula method

$$\begin{aligned}\text{Moles} &= \frac{\text{Mass of substance given}}{\text{Molar mass of the substance}} \\ &= \frac{0.24}{24 \text{ g}} \\ &= 0.01 \text{ mole}\end{aligned}$$

(c) Oxygen is a diatomic gas. 1 molecule of oxygen contains two atoms i.e. O₂.

First principle method

$$\begin{aligned}1 \text{ mole of oxygen atoms (O)} &= 16 \text{ g} \\ 1 \text{ mole of oxygen molecules, O}_2 &= 16 \times 2 = 32 \text{ g} \\ 32 \text{ g of oxygen molecules} &= 1 \text{ mole of oxygen (O}_2\text{) molecules} \\ 0.16 \text{ g of oxygen molecules} &= x \text{ moles of O}_2 \text{ molecules} \\ \text{Cross multiply and solve for } x \\ 32 \text{ g} \times x \text{ moles} &= 0.16 \text{ g} \times 1 \text{ mole} \\ x &= \left(0.16 \text{ g} \times \frac{1 \text{ mole}}{32 \text{ g}} \right) \\ &= 0.005 \text{ moles}\end{aligned}$$

Alternatively,

Using formula method

$$\begin{aligned}\text{Moles} &= \frac{\text{Mass of substance given}}{\text{Molar mass of the substance}} \\ &= \frac{0.16 \text{ g}}{16 \times 2 \text{ g}} \\ &= 0.005 \text{ moles}\end{aligned}$$

Example 2

Convert 71 g of chloride ions to moles.
(R.A.M Cl = 35.5, Fe = 56)

Solution

$$(a) \text{ 1 mole of } \text{Cl}^- \text{ ions} = 35.5 \text{ g}$$

$$x \text{ mole of } \text{Cl}^- \text{ ions} = 71 \text{ g}$$

Cross multiply and solve for x

$$x \times 35.5 \text{ g} = 71 \text{ g} \times 1 \text{ mole}$$

$$x = (71 \text{ g} \times \frac{1 \text{ mole}}{35.5 \text{ g}})$$

$$= 2 \text{ moles}$$



Practice exercise 4E

1. How many moles of atoms are present in:
 - (a) 6.9 g of potassium.
 - (b) 0.8 g of sulphur
 - (c) 71 g of chlorine molecules.
2. Calculate the number of moles of atoms in the following:
 - (a) 4 g of oxygen molecules.
 - (b) 30 g of helium.

Conversion of mass (in grams) of compounds to moles

Example 1

Suppose you have:

(a) 32 g of sulphur dioxide

(b) 15 g of aluminium sulphate

How many moles of each of the compounds do you have?

Solution

First principle method

First write the correct formula of the compound. Then work out the mass of 1 mole i.e. molar mass of the compound.

(a) 1 mole of sulphur dioxide, SO_2 = $32 + (16 \times 2) = 64 \text{ g}$

x moles of sulphur dioxide, SO_2 = 32 g

$$x = (32 \text{ g} \times \frac{1 \text{ mole}}{64 \text{ g}})$$

$$\approx 0.5 \text{ moles}$$

(b) 1 mole of $\text{Al}_2(\text{SO}_4)_3$
 $= (27 \times 2) + (32 \times 3) + 3(16 \times 4)$
 $= 342 \text{ g}$
 $x \text{ mole of } \text{Al}_2(\text{SO}_4)_3 = 15 \text{ g}$
 $x = (15 \text{ g} \times \frac{1 \text{ mole}}{342 \text{ g}})$
 $= 0.044 \text{ moles}$



Practice exercise 4F

How many moles are in:

- (a) 0.96 g of ammonium carbonate
- (b) 0.106 g of sodium carbonate
- (c) 9.9 g of zinc hydroxide
- (d) 16.2 g of carbon dioxide.

Conversion of moles to mass in grams

It is also easy to convert moles to mass in grams. Simply cross multiply and solve for the unknown value.

Example 1

A student bought x g of charcoal (carbon). This was the same as 0.1 mole. Find the value of x . ($C = 12$).

Solution

First principle method

$$1 \text{ mole of carbon atoms} = 12 \text{ g}$$

$$\therefore 0.1 \text{ moles of carbon atoms} = x \text{ g}$$

Cross multiply and solve for x

$$1 \text{ mol} \times X \text{ g} = 0.1 \text{ mole} \times 12 \text{ g}$$

$$\therefore x = 0.1 \text{ mole} \times \frac{12 \text{ g}}{1 \text{ mole}}$$

$$= 1.2 \text{ g}$$

Example 2

Find the mass of 0.5 mole of bromine atoms. ($\text{Br} = 80$)

Solution

$$1 \text{ mole of Br atoms} = 80 \text{ g}$$

$$0.5 \text{ mole of Br atoms} = x \text{ g}$$

Cross multiply and solve for x

$$1 \text{ mole} \times x \text{ g} = 0.5 \text{ moles} \times 80 \text{ g}$$

$$\begin{aligned}x &= \frac{80 \text{ g}}{1 \text{ mole}} \\&= 40 \text{ g}\end{aligned}$$



Practice exercise 4G

1. What is the mass of:
 - (a) 0.01 mole of C atoms?
 - (b) $\frac{1}{4}$ mole of Ca atoms?
2. What is the mass of $\frac{1}{5}$ mole of atoms of the following elements.
 - (a) Chlorine
 - (b) Aluminium

Conversion of moles of molecules or compounds to grams

Sometimes you may be required to convert moles of molecules to grams. To do that:

- (i) Write the correct formula of the compound or molecule.
- (ii) Add up the R.A.M of the atoms of elements in the compound or molecule, that is, find the formula mass.
- (iii) Express (convert) the number of moles in grams.

Example 1

How many grams are there in 9 moles of hydrogen gas?

Solution

First principle method

Formula of hydrogen gas is H_2 .

R.A.M of H = 1

$$1 \text{ mole of } \text{H}_2 = 1 \times 2 = 2 \text{ g}$$

$$\begin{aligned}9 \text{ moles of } \text{H}_2 &= x \text{ g} \\x &= 2 \times 9 \\&= 18 \text{ g}\end{aligned}$$

Example 2

Work out the number of grams in 0.5 mole of ethanol.
(C = 12, H = 1, O = 16)

Solution

Formula of ethanol is C_2H_5OH .

$$\begin{aligned}\text{Relative formula mass of ethanol} &= (2 \times 12) + (6 \times 1) + 16 \\ &= 24 + 6 + 16 \\ &= 46\end{aligned}$$

1 mole of ethanol, $C_2H_5OH = 46$ g

0.5 mole of ethanol = x g

Cross multiply and solve for x

$$\begin{aligned}x &= \frac{0.5 \text{ mole} \times 46 \text{ g}}{1 \text{ mole}} \\ &= 23.0 \text{ g}\end{aligned}$$

Hence 0.5 mole of ethanol has a mass of 23 g.

4.5 Molar gas volume

Gases are very light in density. It is very difficult to weigh and work with them. When heated, they expand rapidly. When under pressure they contract easily.

However, one aspect of gases we can easily measure is the volume of a gas. This can be done using a syringe, a measuring cylinder or a graduated gas jar as shown in Fig. 4.2.

The molar volume of a gas is defined as the volume occupied by one mole of the gas at standard temperature and pressure. One mole of any gas has been established to occupy the same volume at specified temperature and pressure.

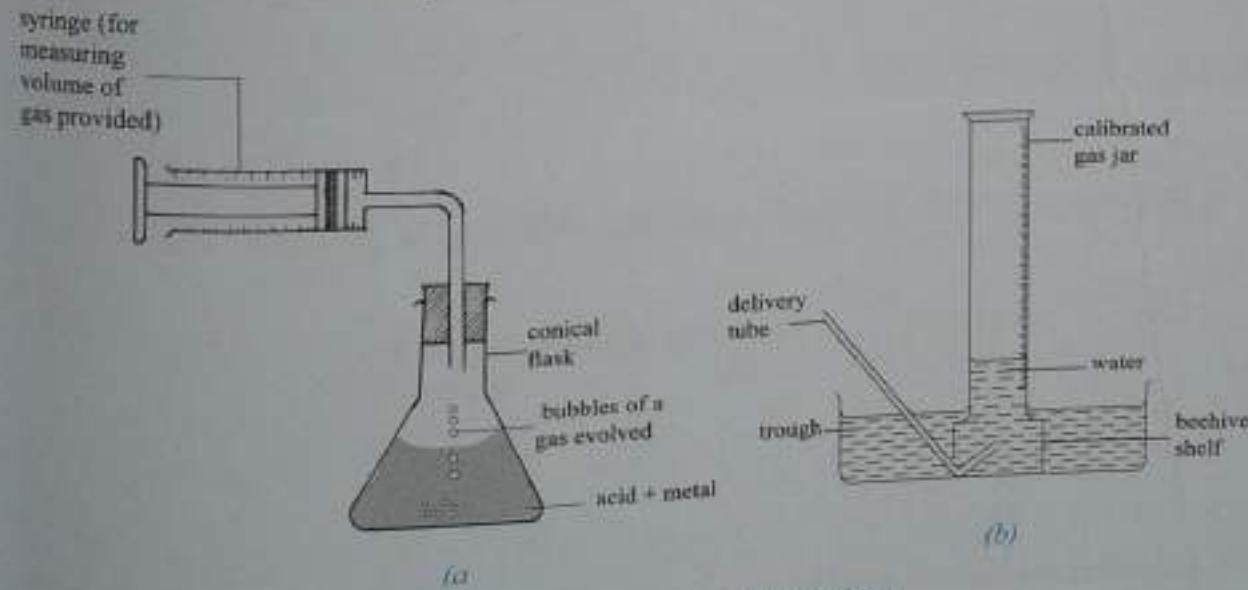


Fig 4.2: Set up for measuring volume of gas

Also equal volume of gases contain the same number of particles i.e. 6.023×10^{23} particles at the same temperature and pressure. This is the same for all gases under the same conditions of temperature and pressure.

How much is the molar volume of gas at standard temperature and pressure (s.t.p)?

Experiments have shown that one mole of any gas at 25°C (298 K) and 1 atmosphere pressure, occupy 24 dm³. These conditions are known as **room temperature and pressure (r.t.p)**. But one mole of gas occupies 22.4 dm³ at **standard temperature and pressure (s.t.p)**. Standard temperature and pressure is at 0°C (273K) and 1 atmosphere pressure. Because one mole of gas occupies the specified volume, that volume is known as the **molar volume or molar gas volume**.

If we know the densities of gases, using their relative molecular mass, it is possible to determine molar volumes. Let consider the following example to verify molar volumes of gases.

Example 1

Find the molar volume of hydrogen at s.t.p.

(H = 1.008; density of hydrogen is $\frac{0.09 \text{ g}}{\text{dm}^3}$)

Solution

Using the relationship of density, mass and volume, we can then find it's the molar volume of this gas at s.t.p.

$$\begin{aligned}\text{Density} &= \frac{\text{Mass}}{\text{Volume}} \\ 1 \text{ mole of H}_2 &= (1.008 \times 2) \text{ g} \\ &= 2.016 \text{ g} \\ \text{Volume} &= \frac{\text{mass}}{\text{Density}} \\ &= 2.016 \times \frac{1 \text{ dm}^3}{0.09} \\ &= 22.4 \text{ dm}^3\end{aligned}$$

Class activity

Copy Table 4.8. Calculate and fill the molar volumes of the gases.

Table 4.8: Molar gas volumes

Gas	Density (g/dm ³) (at s.t.p)	Relative atomic mass	Molar gas volume at s.t.p
N ₂	1.25	28	
CO ₂	1.81	44	
CO	1.15	28	

Note that scientists use cubic decimetre (1 dm³) as the unit for volume. One litre is equal to 1000 cm³ (i.e. 1 dm³ = 1L = 1000 cm³).

Calculations involving molar volume

Remember that 1 mole of a gas occupies 22.4 dm³ and 24 dm³ at s.t.p and r.t.p respectively.

Example 1

How many moles of hydrogen gas are there in 24 cm³ of hydrogen at room temperature and pressure?

Solution

Use same units of measurement. Do not mix.

1 mole of hydrogen gas occupy 24 dm³ at r.t.p

$$1000 \text{ cm}^3 = 1 \text{ dm}^3$$

X moles of hydrogen gas occupy 0.024 dm³ (24 cm³)

Cross multiply and solve for x

$$X = \frac{0.024 \text{ dm}^3}{24 \text{ dm}^3}$$

$$= 0.001 \text{ mole}$$

Example 2

What volume in cm³ does 0.01 moles of oxygen occupy at s.t.p? (Molar gas volume at s.t.p = 22.4 dm³).

Solution

1 mole of oxygen will occupy 22.4 dm³

0.01 mole of oxygen will occupy x dm³

$$X = (22.4 \times \frac{0.01 \text{ mole}}{1 \text{ mole}})$$
$$= 0.224 \text{ dm}^3$$

$$\text{Volume in cm}^3 = 0.224 \times 1000 \text{ cm}^3$$

$$= 224 \text{ cm}^3$$

Example 3

How many moles of atoms are there in 4.8 dm³ of nitrogen gas at r.t.p? (Molar gas volume at r.t.p = 24 dm³).

Solution

24 dm³ of nitrogen at r.t.p contains 1 mole of nitrogen molecules

4.8 dm³ of nitrogen gas would contain x mole

$$x = (4.8 \text{ dm}^3 \times \frac{1 \text{ mole}}{24 \text{ dm}^3})$$
$$= 0.2 \text{ mole}$$

Remember! nitrogen (N₂) is diatomic gas. Therefore mole of atoms is

$$2 \times 0.2 = 0.4 \text{ mole}$$

Example 4

A student collected 48000 cm³ of a diatomic gas Z at r.t.p. Find the:

- (a) moles of gas Z collected.

(b) mass of the gas collected.

(Molar volume at r.t.p = 24 dm³, R.A.M of gas Z = 16.0, L = 6.023 × 10²³)

Solution

1 mole of any gas occupies 24 dm³ (24 000 cm³) at r.t.p

x moles of gas occupy 48000 cm³

$$1000 \text{ cm}^3 = 1 \text{ dm}^3$$

Cross multiply and solve for x

$$x = \frac{48000 \text{ cm}^3}{24000 \text{ cm}^3}$$

$$= 2 \text{ moles}$$

The student collected 2 moles of gas Z

(b) Since gas Z is diatomic, its formula is Z₂.

1 mole of Z has mass = 16 × 2

$$= 32 \text{ g}$$

∴ 2 moles of gas collected has mass = 32 × 2 = 64 g



Practice exercise 4H

1. How many moles of molecules are there in the following gas volumes at r.t.p?
 - (a) 2.4 dm³ of oxygen gas
 - (b) 2.4 cm³ of nitrogen gas
2. What volume do these gases occupy at room temperature and pressure?
 - (a) 4 moles of hydrogen
 - (b) 0.1 moles of gas Y.
(Molar volume at r.t.p = 24 dm³)
3. How many grams of oxygen gas are in 56 dm³ of the gas at s.t.p? (O=16, Molar gas volume at s.t.p = 22.4 dm³).
4. 0.7 g of a liquid Y was vapourized to give 560 cm³ of gas at s.t.p. Find the relative formula mass of the liquid.
5. The relative formula mass of a gas is 17. What volume would this gas occupy at s.t.p? (Molar gas volume at s.t.p = 22.4 dm³).
6. The molar mass of gaseous compound XO₂ is 44 g. If this gas occupied 5.6 dm³ at s.t.p. Find the:
 - (a) number of moles
 - (b) number of atoms
 - (c) mass in grams of the gas collected.

4.6 Water of crystallisation

When saturated solutions of some salts e.g. copper (II) sulphate are gently heated and then slowly cooled large crystals will form. These crystals have definite shape with surfaces and edges. They incorporate water molecules within their structures that makes this possible. This water is called **water of crystallisation**. Salts with water of crystallisation are known as **hydrated salts**.

Hydrated ionic compounds have different number of water molecules within them. Table 4.9 shows examples of hydrated salts.

Table 4.9: Examples of hydrated salts

Name	Formula	Number of molecules of water of crystallisation
Magnesium sulphate -7-water	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	7
Sodium carbonate -10-water	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	10
Cobalt (II) chloride-6-water	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	6
Calcium (II) sulphate -5-water	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2
Copper (II) sulphate -5-water	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	5

When hydrated salts are heated they lose their water of crystallisation. It is possible to determine the mass and the percentage of water of crystallisation in hydrated ionic compounds.

Experiment 4.2

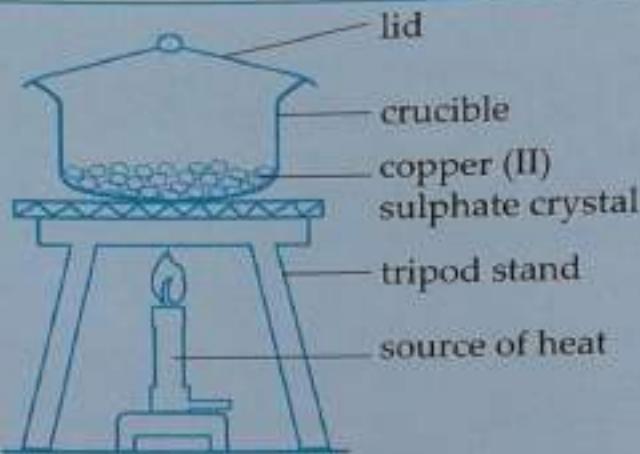
Aim: To determine water of crystallisation in hydrated copper (II) sulphate

Requirements

- Clean dry crucible and lid
- Weigh machine
- Pipe – clay triangle/wire gauze
- Tripod stand
- Bunsen burner
- A pair of tongs
- Copper (II) sulphate crystals

Procedure

1. Weigh an empty crucible plus its lid.
2. Put some copper (II) sulphate crystals in the crucible, cover with the lid and re-weigh.
3. Place the crucible with its content and the lid on the pipe-clay triangle on the tripod stand. First heat gently and later, strongly occasionally lifting the lid a little with a pair of tongs to drive off water of crystallization.



4. Allow the crucible and its contents and the lid to cool in dessicator and re-weigh them.
5. Heat the crucible and its contents again, cool and re-weigh. Repeat the heating until a constant mass is obtained.
6. Draw a table in your notebook. Record all the masses and observations made.
7. Calculate the mass of the water lost.
8. Calculate the mass of copper sulphate left.

Discussion

When the blue crystals of copper (II) sulphate were heated, after sometime they changed to a white powder. The white anhydrous powder that remained after heating weighed less.

Sample result

Mass of crucible and lid = w g

Mass of crucible + lid + blue hydrated copper sulphate = x g

Mass of crucible + lid + anhydrous white copper sulphate = y g

Mass of water expelled = (x - y) g

Mass of anhydrous copper sulphate = (y-w) g

$$\frac{\text{Mass of water expelled}}{\text{Anhydrous copper sulphate}} = \frac{n\text{H}_2\text{O}}{\text{CuSO}_4} = \frac{x-y}{y-w}$$

n representing number of water molecules is obtained by,

$$\frac{18n}{160} = \frac{x-y}{y-w}$$

$$n = \frac{x-y}{y-w} \times \frac{160}{18}$$

Percentage of water of crystallisation

$$= \frac{18n}{\text{CuSO}_4 \cdot n\text{H}_2\text{O}} \times 100 \%$$

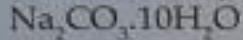
Conclusion

Anhydrous copper sulphate weighed less due to the mass of water of crystallisation lost from the crystals. When hydrated salts are heated they lose their water of crystallization.

Calculating percentage of water of crystallisation

Example 1

Calculate the percentage of water of crystallization in hydrated sodium carbonate,



(Na = 23, C = 12, O = 16, H = 1).

Solution

Relative formula mass of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = 286$

$$\begin{aligned}\text{Percentage of water} &= \frac{10\text{H}_2\text{O}}{\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}} \times 100\% \\ &= \frac{10 \times 18}{286} \times 100\% = 62.937\%\end{aligned}$$

Example 2

On heating 12.5 g of hydrated copper (II) sulphate, $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$, 8.0 g of anhydrous copper (II) sulphate remained. Calculate the percentage of water of crystallization in hydrated copper (II) sulphate.

Solution

Total mass of hydrated salt = 12.5 g

Mass of water lost on heating

$$12.5 - 8.0 = 4.5 \text{ g}$$

$$\text{Percentage of water of crystallization} = \frac{4.5}{12.5} \times 100\% = 36\%$$

Experiment 4.3

Aim: To investigate loss of water during heating of sugar

Requirements

- Clean dry crucible with lid
- Weigh machine
- Pipe clay triangle / wire gauge
- Tripod stand
- Bunsen burner
- Sugar

Procedure

1. Follow the steps as given in experiment 3.2 page 68.
2. Draw a table in your notebook and record your observations and masses.
3. Calculate the total mass lost.

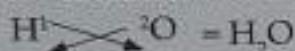
Discussion

Sugar (sucrose) has no water of crystallization.

Notice its formula $C_{12}H_{22}O_{11}$ also show no existence of water crystallisation

4.7 Formulae of compounds

You have already learnt how to write correctly formulae of compounds using symbols and valencies. For example, water is represented as:



From the formula of water, it shows us:

1 oxygen atom combines with 2 atoms of hydrogen to form one molecule of water. It implies that 1 mole of oxygen atoms combines with 2 moles of hydrogen atoms.

Given the R.A.M of H = 1, O = 16, we can say that 2 g of hydrogen combine with 16 g of oxygen atoms to form 1 mole of water.

Also from the formula, we deduce:

- The ratio of moles of atoms that constitute the compound.
- The quantity in grams of the elements in the compound.

So, if you know the number of grams of each element that form the compound, using their relative atomic masses, you can change the grams to moles. This will give us the ratio of moles in which the atoms combine. You can use the ratio to write down a formula. Such a formula is usually referred to as the **empirical formula (E.F.)**.

Empirical formula (E.F.)

When masons construct stone houses, they must mix cement, sand and water in certain proportions.



(a) Firm wall



(b) cracked wall

Fig. 4.2: An illustration to explain proportions of elements in a compound.

When the sand, cement and water are not mixed in correct proportions (ratios), the walls of the building are bound to crack as shown in Fig. 4.2(b) and may finally collapse. This represents the situation in the composition of atoms in a compound. The atoms in the compound must combined in certain fixed ratios for them to remain stable.

otherwise such compounds would be unstable and not being able to exist. Empirical formula of a compound shows the simplest whole number ratio of the moles of atoms of the different elements in a compound.

Experiment 4.4

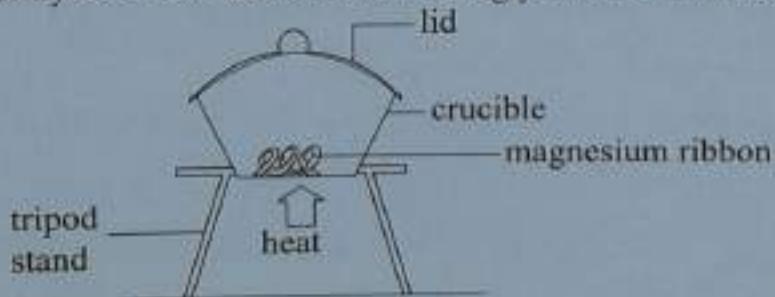
Aim: To determine empirical formula (E.F) of magnesium oxide

Requirements

- Crucible and the lid
- Magnesium ribbon
- Weigh machine
- Bunsen burner
- Emery paper/steel wool
- Tripod stand

Procedure

1. Weigh an empty crucible plus the lid and record the mass.
2. Clean about 15 cm of magnesium ribbon thoroughly using emery paper or steel wool.
3. Coil up the magnesium ribbon and place it into the crucible.
4. Weigh the crucible and the lid again and record this mass.
5. Heat gently for a few seconds then strongly for a few minutes.



6. Remove the Bunsen burner, lift the lid slightly to let in air and quickly replace the lid to avoid loss of the white smoke. The white smoke is the magnesium oxide (MgO).
7. Repeat step 6 several times until no more magnesium flares.
8. Remove the lid and heat strongly for a few minutes, then stop heating.
9. Allow the crucible plus its contents to cool and re-weigh them. Record this mass.
 - (i) Can you suggest any experimental errors that may contribute to getting a wrong empirical formula?
 - (ii) What do you conclude from the result after re-weighing?

Discussion

When the lid is lifted, magnesium glows brighter. Finally a white ash is formed. The white ash is magnesium oxide. It weighs more than magnesium ribbon metal.

Below is a sample of results likely to be obtained and how to use the results to determine the empirical formula.

Mass of crucible + lid	= 25.00 g
Mass of crucible + lid + magnesium before heating	= 25.24 g
Mass of crucible + lid + magnesium oxide after heating	= 25.40 g
Mass of magnesium	= 0.24 g
Mass of crucible + lid + magnesium oxide after cooling	= 25.40 g
Mass of oxygen in the oxide = (25.40 – 25.24) g	= 0.16 g

Calculating empirical formula of the magnesium oxide

We can use the idea of moles as follows;

a) Number of moles of an element = $\frac{\text{Mass of an element}}{\text{Relative atomic mass of the element}}$

b) Number of moles of a compound = $\frac{\text{Mass of compound}}{\text{Relative formula mass of the compound}}$

Elements	Mg	O
Composition by mass in grams	0.24	0.16
Get moles reacting by dividing mass of each element by its R.A.M	$= \frac{0.24}{0.24}$	$= 0.01$
Divide by smaller number to get whole number moles	$= \frac{0.01}{0.01}$	$= \frac{0.01}{0.01}$
Mole ratio	1	1

From the calculation, it tells us that 1 mole of magnesium atoms combines with 1 mole of oxygen atoms in the ratio of 1:1 to form magnesium oxide, MgO.

1:1 is the simplest whole - number ratio of the moles of atoms in the compound. The formula MgO is the empirical formula (E.F).

Note:

1. Due to experimental errors in weighing and another possible reaction of the magnesium ribbon with nitrogen in the air to form magnesium nitride, there may be variation in experimental results and theoretical value.
2. Empirical formula does not usually give exact number of the different atoms in the molecule of the compound.

Example 1

When a sample of hydrocarbon (X) was analysed, it was found to contain 12 g of carbon and 4 g of hydrogen. Determine the empirical formula of this hydrocarbon. (C = 12, H = 1).

Solution

Elements	C	H
Composition by mass in g	12	4
Get reacting moles by dividing by R.A.M of each element	$\frac{12}{12} = 1$	$\frac{4}{1} = 4$
Divide the moles by the smallest value	$\frac{1}{1} = 1$	$\frac{4}{1} = 4$
Mole ratio	1	4

Therefore, empirical formula (E.F) of the hydrocarbon (X) is CH_4 .

Calculating empirical formula using percentage composition

So far the examples considered in calculating empirical formula use mass of the elements. It is also possible to determine empirical formula of compounds using the percentage composition as shown in the following examples.

Example 2

When compound containing carbon and hydrogen was analysed, it was found to contain 75% of carbon and 25% of hydrogen. Find its simplest formula.

(R.A.M: of C = 12, H = 1).

Solution

Element	C	H
Composition by mass in %	75	25
Get reacting moles by dividing by R.A.M	$\frac{75}{12} = 6.25$	$\frac{25}{1} = 25$
Divide by the smallest value	$\frac{6.25}{6.25} = 1$	$\frac{25}{6.25} = 4$
Mole ratio	1	4

Therefore, empirical formula of the compound is CH_4 .

Example 3

14.82 g of a hydrocarbon contains 12.26 g of carbon. Find the empirical formula of this hydrocarbon.

Solution

A hydrocarbon has hydrogen and carbon atoms. If C = 12.26 g, the rest is hydrogen.

$$\begin{aligned}\text{Mass of H} &= (14.82 - 12.26) \text{ g} \\ &= 2.56 \text{ g}\end{aligned}$$

Element	C	H
Composition by mass (g)	12.26	2.56
Get reacting moles by dividing by RAM	$\frac{12.26}{12} = 1.02$	$\frac{2.56}{1} = 2.56$
Divide by the smallest value to get mole ratio	$\frac{1.02}{1.02} = 1$	$\frac{2.56}{1.02} = 2.5$
Multiply by 2 to get whole number mole ratios	$(1 \times 2) = 2$	$(2.5 \times 2) = 5$

Thus empirical formula is C_2H_5

Note: We do not round off 2.5 to 3. To get a whole number, multiply both ratios by a certain factor to get whole numbers. In this case, we multiply both sides by 2.

Example 4

When 100 g of a sample of a hydrated salt was analysed, it was found to contain 25.6 g of copper, 12.8 g sulphur, 25.6 g of oxygen and the rest was water of crystallisation. Calculate the empirical formula of the salt. (R.A.M: Cu = 64, S = 32, O = 16, H = 1)

Solution

Note: Water of crystallisation $x(H_2O)$ is incorporated in the crystals as molecules. So we should calculate the moles of water indicated (x) in the crystals as shown below.

$$\text{Mass of water} = 100 - (25.6 + 12.8 + 25.6) = 36 \text{ g}$$

Element	Cu	S	O	xH_2O
Composition by mass (g)	25.6	12.8	25.6	36
Get reacting moles by dividing by RAM	$\frac{25.6}{64} = 0.4$	$\frac{12.8}{32} = 0.4$	$\frac{25.6}{16} = 1.6$	$\frac{36}{16} = 2$
Divide by the smallest value to get mole ratio	$\frac{0.4}{0.4} = 1$	$\frac{0.4}{0.4} = 1$	$\frac{1.6}{0.4} = 4$	$\frac{2}{0.4} = 5$
Mole ratio	1	1	4	5

Therefore, the empirical formula of the hydrated salt is $CuSO_4 \cdot 5H_2O$



Practice exercise 41

- Calculate the empirical formula of each of the following compounds using the percentages of the elements given.
 - C = 73.5%, H = 10.20%, O = 16.3%
 - Ca = 40%, C = 12%, O = 48%
- 20.0 g of iron compound contains 14 g iron and the rest is oxygen. Find the empirical formula of the compound. (Fe = 56, O = 16)

Molecular formula (M.F)

The molecular formula of a compound shows the actual number of atoms of the various elements present in one molecule of that compound.

To determine the molecular formula of a compound, we need to know the empirical formula and the relative molecular mass (R.M.M) or relative formula mass (RFM) of the compound. Molecular formula is obtained by multiplying the empirical formula by a whole number, n. That is,

$$M.F = (E.F)n$$

The following examples show how to calculate the molecular formula of compounds.

Example 1

Sodium metal burns in excess oxygen. It burns with a bright yellow flame and forms a yellow oxide that contains 59% sodium. The relative molecular mass of the oxide is 78. What is the molecular formula of the oxide? (RAM: Na=23, O=16)

Solution

Percentage of oxygen is $100 - 59 = 41\%$

Element	Na	O
Composition by mass in %	59	41
Get reacting moles by dividing by RAM	$\frac{59}{23} = 2.57$	$\frac{41}{16} = 2.56$
Divide by the smallest value to get mole ratio	$\frac{2.57}{2.56} = 1$	$\frac{2.56}{2.56} = 1$
Mole ratio	1	1

The empirical formula (E.F) of the oxide is NaO .

The relative mass of empirical formula, $NaO = 23 + 16 = 39$

The molecular mass is given by

$$(NaO)_n \approx 78$$

$$39n \approx 78$$

$$n = \frac{78}{39}$$

$$= 2$$

Therefore molecular formula is $(NaO)_2$, which is Na_2O_2 .

Example 2

A compound Q contains 76.5% carbon, 10.2% hydrogen by mass and the rest is oxygen. Its relative molecular mass, M, is 98. Calculate the molar mass of Q.

(R.A.M: C = 12, H = 1, O = 16).

Solution

Note: If you have understood how we proceed in these calculations, you may omit some details as shown in the following solution.

$$\text{The percentage of oxygen} = 100 - (76.5 + 10.2) = 16.3$$

Element	C	H	O
Composition by mass in %	76.5	10.2	16.3
Get reacting moles by dividing by RAM	$\frac{76.5}{12} = 6.375$	$\frac{10.2}{1} = 10.2$	$\frac{16.3}{16} = 1.018$
Divide by the smallest value to get mole ratio	$\frac{6.375}{1.018} = 6.26$	$\frac{10.2}{1.018} = 10.02$	$\frac{1.018}{1.018} = 1$
Mole ratio	6	10	1

Empirical formula is $C_6H_{10}O$

$$\begin{aligned}\text{Relative mass of E.F.} &= (6 \times 12) + (10 \times 1) + (1 \times 16) \\ &= 72 + 10 + 16 \\ &= 98 \\ n &= \frac{98}{98} = 1\end{aligned}$$

Molecular formula is $(C_6H_{10}O)1 = C_6H_{10}O$

Note: It is possible for the molecular formula of a compound to be equivalent to its empirical formula as seen in the example 2 above.

Practice exercise 4J

- Calculate the molecular formula (M.F.) of a compound made up of 85.7% carbon and 14.3% hydrogen. The molecular mass of the compound is 28.
- An oxide of iron contains 70% iron and the rest is oxygen. Calculate the empirical formula of the oxide. If its relative molecular mass is 160, find its molecular formula. ($C = 12$, $H = 1$, $Fe = 56$, $O = 16$).
- A compound contains 40% carbon, 6.67% hydrogen and the rest is oxygen. If the relative molecular mass of the compound is 180, what is its molecular formula?

4.8 Concentration of solutions

The term **concentration** refers to the amount of solute dissolved in a specific volume of solvent. In a given amount of water, the more solute is dissolved, the more concentrated the solution becomes. If the solution contains a little solute, it is described as dilute. Similarly, if a large volume of water is added to a small amount of solute, then the solution becomes very dilute.

Concentration is usually expressed in number of moles of solute dissolved per 1000 cm³ of solution.

$$1000 \text{ cm}^3 = 1 \text{ dm}^3 = 1 \text{ litre}$$

Remember! The total volume of the solute plus the solvent must be equal to 1000 cm³. This is why a 1 dm³ volumetric flask is used in preparing molar solutions.

When one mole of a solute is dissolved in water and the volume of the solution made up to 1 dm³ the solution is said to be a **molar solution**.

A concentration of one mole per cubic decimetre is usually written as **1 mol/dm³** or **1 mol dm⁻³** or **1M**. Concentration expressed this way is also referred to as **molarity** of the solution. The molarity of solution is abbreviated as M. Therefore, a molar solution contains **1 mole of solute per dm³ solution**.

Expressing concentration of solutions

The three common ways of expressing concentration of solutions are:

- (i) Grams per volume.
- (ii) Moles per volume, usually in 1dm³.
- (iii) Concentration in percentage.

Concentration in grams per dm³

The concentration (or molarity) can also be expressed in grams per cubic decimetre (g dm⁻³). We may first calculate the concentration in mol dm⁻³ and then convert to g dm⁻³.

Example 1

53 g of anhydrous sodium carbonate was dissolved in 2 dm³. Calculate the concentration in g dm⁻³. (Na = 23, C = 12, O = 16)

Solution

Using first principle method

Remember! Standard volume for concentration is 1 dm³

Formula of sodium carbonate is Na₂CO₃

Step 1: Work out relative formula mass of Na₂CO₃,
 $= (2 \times 23) + (1 \times 12) + (3 \times 16) = 106$

Step 2: Calculate the number of moles as follows:

$$1 \text{ mole of Na}_2\text{CO}_3 = 106 \text{ g}$$

$$x \text{ moles of Na}_2\text{CO}_3 = 53 \text{ g}$$

Cross multiply and solve for x

$$x = (53 \text{ g} \times \frac{1 \text{ mol}}{106 \text{ g}})$$
$$= 0.5 \text{ moles}$$

Step 3: Calculate the concentration in mol dm⁻³ using the number of moles.

0.5 mole was dissolved in 2 dm³.

y moles were dissolved in 1 dm³

Cross multiply and solve for y

$$y = (0.5 \text{ mole} \times \frac{1 \text{ dm}^3}{2 \text{ dm}^3})$$
$$= 0.25 \text{ mol dm}^{-3}$$

Step 4: Finally, convert mol dm⁻³ to g dm⁻³ as follows:

$$1 \text{ mole of Na}_2\text{CO}_3 = 106 \text{ g}$$

$$0.25 \text{ mole of Na}_2\text{CO}_3 = 0.25 \text{ mole} \times \frac{106 \text{ g}}{1 \text{ mole}}$$
$$= 26.5 \text{ g}$$

Therefore concentration expressed in g per dm³ = 26.5 g dm⁻³

Concentration in moles per volume (mol dm^{-3})

- A solution containing 2 moles in 1000 cm^3 (1 dm^3), has a concentration of 2 mol dm^{-3} or simply 2M .
- A solution which contains 0.5 moles of solute dissolved in 1 dm^3 solution is expressed as 0.5 mol dm^{-3} or 0.5 M .

Concentration expressed as a percentage

Concentration of solutions can also be expressed as a percentage. This is very common with strong mineral acids. It is indicated on the bottle label, for example 50% concentration or 98% concentration.

Another example is the alcoholic beverages consumed. The concentration of alcohol in alcoholic drinks is expressed as a percentage of the volume of the liquid. The value of the percentage of alcohol can vary from 0 to 70% or even higher. This quantity is measured by weight or volume.

For example, if an alcoholic drink contains 15% pure ethanol, it is labelled 15% alcohol by volume. This is usually abbreviated as 15% Abv. The rest is water.

Examples of alcoholic beverages and their estimated alcohol by volume (Abv) guides:

- Beers 2-7% or higher % Abv as is applicable
- Wines 10-15% Abv
- Spirits 20 - 40%. Abv

Ethanol, popularly known as alcohol, is the active ingredient in alcoholic beverages. Ethanol is the only alcohol the body can withstand and only when consumed in relatively small volumes mixed with water. It is also used as fuel and a solvent.

Remember! Excessive consumption of alcohol is harmful for one's health. It can cause liver cirrhosis, impairs vision and loss of coordination of the body among other side effects.



Practice exercise 4K

1. What is the molarity of a solution containing:
 - (a) 3 moles per dm^3 .
 - (b) 0.25 moles in 1000 cm^3 .
 - (c) 2 moles in 2 dm^3 .
2. Express the following molarities as concentration in g dm^{-3} .
 - (a) 0.2 M potassium hydroxide.
 - (b) 0.1 M nitric acid solution.
3. Calculate the mass in grams of each compound in each of the following solutions.
 - (a) 80 cm^3 of 0.5 M sodium hydroxide
 - (b) 100 cm^3 of 1 M potassium hydroxide.
R.A.M. P = 39, Na = 23, O = 16, H = 1
4. What is the concentration, in mol dm^{-3} of 100 cm^3 a solution containing 9.8 g of sulphuric acid?

- Drivers are advised to obey the motto 'DDD' i.e. Drinking? Don't Drive! Or Driving? Don't Drink! Explain briefly why this motto must be obeyed.
- (a) A bottle containing an alcoholic drink is labelled 70% Abv. Which is the higher content, water or alcohol and by what percentage?
 (b) Give four harmful effects of drunkenness.

4.9 Preparation of standard solutions

A solution whose concentration is known is called a **standard solution**.

Suppose your teacher asks you to prepare 250 cm³ of 1 mol dm⁻³ (1M) sodium hydroxide for a chemistry lesson. How would you prepare this solution?

How to prepare a standard solution

Step 1: Work out required moles.

1 M means 1 mole in 1000 cm³

Therefore,

If 1000 cm³ = 1 mole

250 cm³ = x moles

Cross multiply and solve for x

$$x = 1 \text{ mole} \times \frac{250 \text{ cm}^3}{1000 \text{ cm}^3}$$

$$= 0.25 \text{ moles}$$

Step 2: Work out R.F.M of sodium hydroxide (NaOH)

$$\begin{aligned} \text{R.F.M of NaOH} &= 23 + 16 + 1 \\ &= 40 \end{aligned}$$

$$1 \text{ mole of NaOH} = 40 \text{ g}$$

$$0.25 \text{ moles of NaOH} = y \text{ g}$$

Cross multiply and solve for y

$$\therefore y = (40 \text{ g} \times \frac{0.25}{1 \text{ mole}})$$

$$= 10 \text{ g}$$

Step 3: Now weigh 10 g of sodium hydroxide pellets and put in a 250 cm³ volumetric flask, dissolve in distilled water and make the solution up to 250 cm³ mark with distilled water.

Experiment 4.5

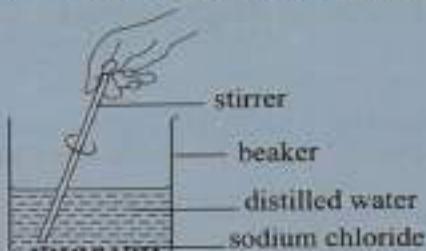
Aim: To prepare a standard solution

Requirement

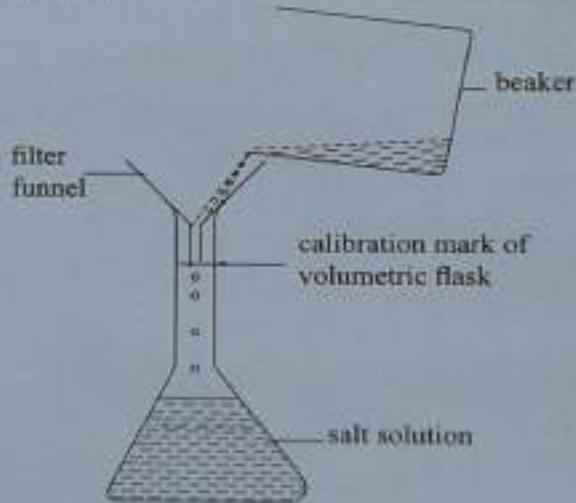
- Weighing balance
- 1 dm³ volumetric flask
- Stirrer/glass rod
- Reagent bottle
- Distilled water
- Beaker
- Sodium chloride
- Filter funnel

Procedure

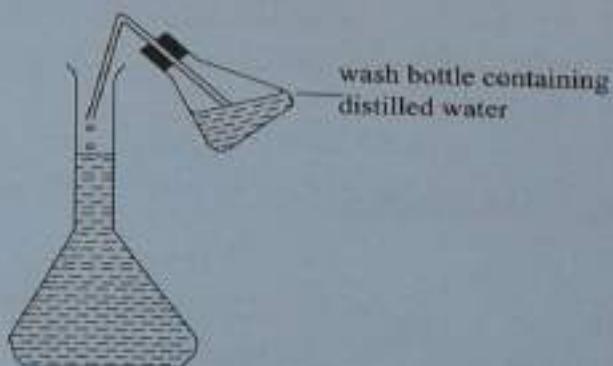
1. Weigh 58.5 g of sodium chloride crystals.
2. Place 400 cm³ of distilled water in a beaker.
3. Add the salt into the water, stirring continuously until all the salt dissolves.



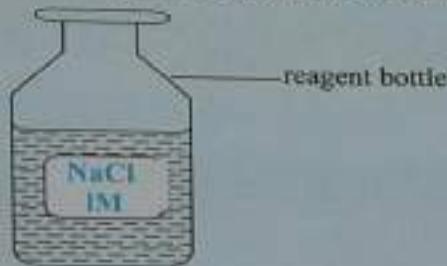
4. Using a filter funnel, transfer the salt solution into a 1 dm³ volumetric flask as shown in Fig. 4.- (b).



5. Rinse the beaker with distilled water carefully and add the solution into the flask.
6. Add more distilled water and shake the flask well. Add more water until the solution level is just below the calibration mark. Using a wash bottle, add more distilled water drop by drop until the bottom of the meniscus is at the same level with calibration mark.



7. Use a stopper to cover the flask and invert it several times to make sure the solution mixes thoroughly.
8. Transfer the solution into reagent bottle and label it 1M NaCl as shown below.



Questions

- Did all the salt dissolve in the water?
- Write the formula of sodium chloride.
- Using the relative atomic masses, find the molar mass of sodium chloride.
- What can we conclude from this experiment?

Discussion

I

One mole of sodium chloride is 58.5 g.

Therefore when we dissolve this amount (58.5 g) of salt in distilled water and make the solution up to 1000 cm^3 , the molarity or concentration of the solution is 1 mol dm^{-3} or 1M.

II

Suppose this much of solution 1000 cm^3 (1 dm^3) was not needed and only 100 cm^3 of the 1 M solution was requested for, how much salt should we dissolve to make 1M solution?

Solution

Remember this;

1M solution means that 1 mole of a substance is dissolved in 1 dm^3 (1000 cm^3).

For our case, the substance is NaCl.

1 mole of NaCl = 58.5 g

This means 58.5 g of NaCl are in 1000 cm^3 of the solution

x g of NaCl must be present in 100 cm^3 to constitute 1 M solution

Cross multiply and solve for x

$$x = (58.5 \text{ g} \times \frac{100 \text{ cm}^3}{1000 \text{ cm}^3}) \\ = 5.85 \text{ g}$$

Therefore to make 100 cm^3 of 1M NaCl; add 5.85 g of NaCl in about 60 cm^3 of distilled water and stir to dissolve. Add more water to make 100 cm^3 of the solution.

Concentration and dilution

Recall that concentration refers to the amount of solute in a specific volume of solvent. When more solvent e.g. water is added to a given concentrated solution, it is said to be diluted. Let us now investigate what happens to a solution when different quantities of a solvent are added to a solution.

Experiment 4.6

Aim: To investigate concentration and dilution

Requirements

- Copper(II) sulphate crystals or potassium manganate (VII)
- Beaker
- Stirring rod
- Distilled water

Procedure

1. Label four 250 cm^3 beakers A, B, C and D respectively.
2. Place equal amounts of crystals (either copper(II) sulphate or potassium manganate(VII)) into each beaker. Add 50 cm^3 to each beaker, stir to dissolve.
3. Add 50 cm^3 of water into beaker A, 100 cm^3 of water into beaker B, 150 cm^3 of water into beaker C and 200 cm^3 of water into beaker D. Stir the mixture in well each beaker.

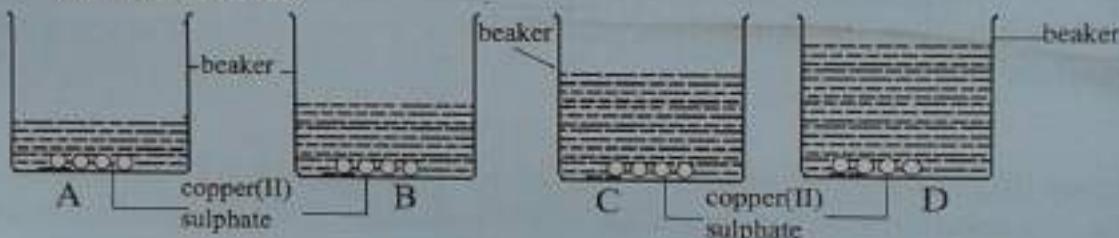


Fig. 4.6 Diluting a solution

- What do you observe?
- Record your observations.
- What conclusions can you draw from your observations?

Discussion

It was observed that as more quantities of water were added to the initial mixtures, the colour becomes more increasingly faded. This indicates that the concentration of the solution was getting more diluted as higher quantities of water were being added to the concentrated solution. That is the particles of solute continually gets fewer in comparison to the amount of solvent molecules in the solution.

The dilution principle is applied in such areas as mixing of concentrated juices and diluting the concentrated mineral acids to required concentration for use in laboratories.

Dilution law

You should have noticed that as a solution gets diluted, the number of moles of solute in the solution does not change. However, the volume of the solution changes i.e. increases while, the concentration of the solution decreases.

Now, if the initial concentration is taken as C_1 and the initial volume as V_1 , the number of moles of solute is obtained as;

$$C_1 \times V_1 = \text{Moles}$$

For the diluted solution, let concentration be C_2 and the new volume by V_2 , the number of moles is obtained as follows;

$$C_2 \times V_2 = \text{Moles}$$

Since number of moles of solute remain the same in the initial solution and diluted solution

Then

$$C_1 \times V_1 = C_2 \times V_2 \quad \text{or} \quad C_1 V_1 = C_2 V_2$$

This relationship is called the **dilution law**. It can be used to calculate the concentration after dilution C_2 as well as the new volume V_2 .

Example 1

How much water must be added to 5 cm³ of 6.0 M HCl to dilute the acid to 0.1M?

Solution

$$C_1 = 6.0 \text{ M} \qquad V_1 = 5.0 \text{ cm}^3$$

$$C_2 = 0.1 \text{ M} \qquad V_2 = ?$$

Using $C_1 V_1 = C_2 V_2$,

$$V_2 = \frac{C_1 V_1}{C_2}$$

$$V_2 = 6.0 \times \frac{5.0}{0.1}$$

$$= 300 \text{ cm}^3$$

Note: This does not mean that 300 cm³ of water must be added, but that the total volume of solution must be made up to 300 cm³.

Therefore volume of water to be added $(300 - 5) \text{ cm}^3 = 295 \text{ cm}^3$

Example 2

Suppose 180 cm³ of a 2.0 M solution is diluted to 1.0 dm³, what will be the concentration (molarity) of the resulting solution?

Solution

$$C_1 V_1 = C_2 V_2$$

$$\begin{aligned}
 C_2 &= \frac{C_1 V_1}{C_2} \\
 &= (180 \times \frac{2.0}{1000}) \text{ M} \\
 &= 0.36 \text{ M or } 0.36 \text{ mol dm}^{-3}
 \end{aligned}$$



Practice exercise 4L

- If 2 dm^3 of 5.0 mol dm^{-3} solution was diluted to 6 dm^3 find the concentration (molarity) of the diluted solution.
- The concentration of sulphuric acid in a laboratory is 18.4 mol dm^{-3} . What volume of the acid should be used to prepare a 500 cm^3 solution of 2 mol dm^{-3} ?
- If 175 cm^3 of 2.0 M solution is diluted to 5.0 dm^3 , what will be the molarity of the solution.

4.10 Acid-base titration

Acid reacts with a base to form salt and water. This reaction is referred to as **neutralisation** reaction. Neutralisation reactions can be done very precisely by a process known as **titration** in a laboratory.

Titration is the process of adding a solution from a burette into a standard solution. The standard solution is usually placed in a conical flask. An indicator is used to show the point at which the reaction becomes complete. The point at which a reaction is complete is called the **end-point or equivalence point**. The volume of the solution being added from the burette is called **titre**. The volume transferred by the pipette into the conical flask is known as an **aliquot**.

Apparatus used when titrating

There are special apparatus used in titration. Pipettes and burettes deliver accurate volumes and exact amounts of solutions we are dealing with. Titration experiments are also known as **volumetric analysis**.

A pipette delivers fixed and exact volumes of liquid or solution. A burette helps to add accurate amount of liquid or solution for complete neutralisation. Table 4.10 shows apparatus used in volumetric analysis and their uses.

Table 4.10: Common apparatus used in volumetric analysis and their uses

Apparatus	Use
Weigh machine	To weigh solids to be dissolved.
Measuring cylinder	To add solution into the burette.
Volumetric flask	To make solutions of known concentration.
Pipette	To deliver fixed volumes of liquid or solution into conical flasks.
Burette	To release small amounts of solutions into the conical flask.

Beaker	To collect and pour solutions into the burette.
Funnel	To facilitate pouring solutions into the burette.
White tile or paper	To help in the observation of colour change in the flask more clearly.
Dropper	To add 2-3 drops of an indicator into the conical flask.

Handling titration apparatus

Burettes and pipettes are expensive apparatus. These apparatus must be handled with a lot of care to avoid breakage.

Filling a pipette

- Wash the pipette thoroughly with water and then rinse it with the solution given, i.e. the one you are supposed to fill the pipette with.
- Suck the solution up the pipette well above the calibration mark. It is recommended to suck the solution from a tilted conical flask to avoid air bubbles entering into the pipette as shown in Fig. 4.3. Use a pipette filler to fill the pipette.

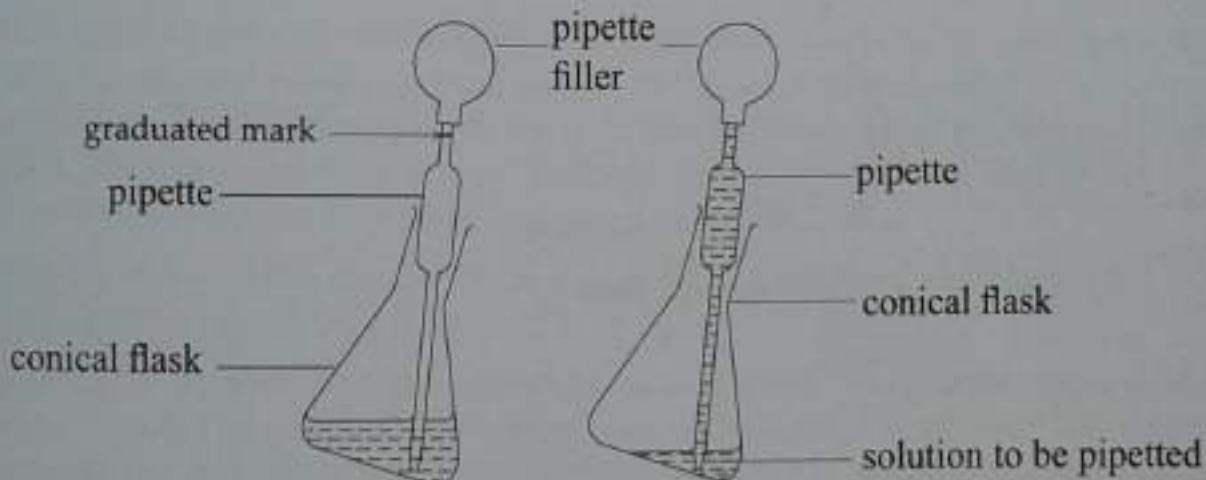


Fig. 4.3: Correct method of filling a pipette with a filler

- Note that when the solution falls below the mark, you have to re-fill all over again. This wastes time. To avoid this, hold the pipette upright and read the bottom of the meniscus. See Fig. 4.4.
- Allow the solution to run out into the conical flask. Do not force out the little amount of solution left in the pipette as the pipette is graduated with this allowance.

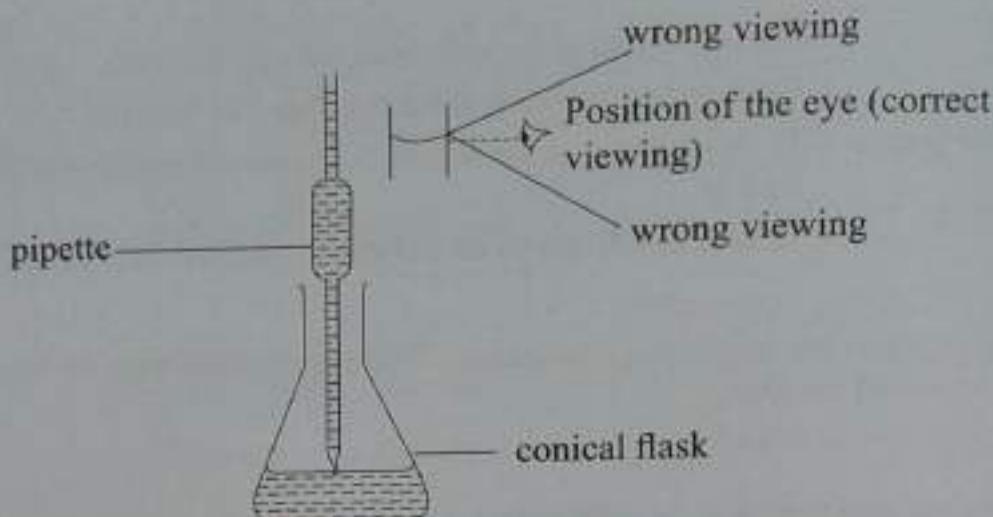


Fig. 4.4: Correct reading of pipette

- Add 2 - 3 drops of the indicator as shown in Fig. 4.5.

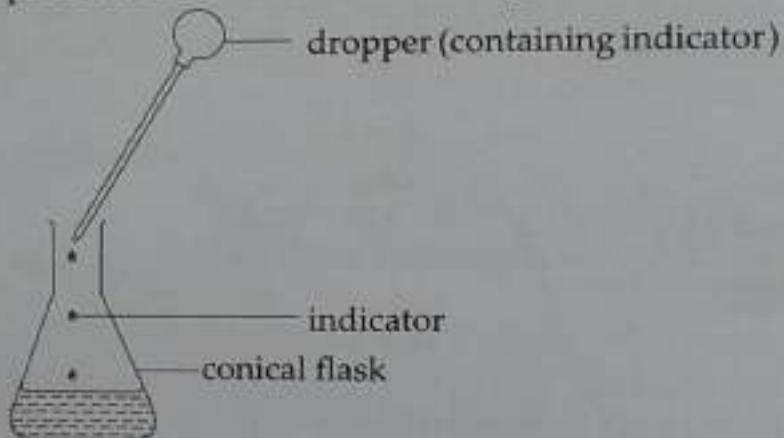


Fig. 4.5: Adding drops of indicator into the standard solution.

Filling and running a burette

A burette is calibrated from the top downwards i.e. 0 cm³ at the top and 50 cm³ at the bottom near the tap. Examine the burette and note that the divisions are 0.1 cm³.

- Wash the burette with distilled water and then rinse it with the given acid solution or the solution to be added to the burette.
- Clamp the burette to the stand in an upright position.
- Using a filter funnel and a beaker, fill the burette with the acid or the solution to be used up to above the 0 cm³ graduation mark. When filling the burette, hold the funnel with one hand so that air can escape as you fill the burette otherwise air will hold the acid in the funnel and when you lift the funnel, the acid quickly fills the burette and spills over. See Fig. 4.6.

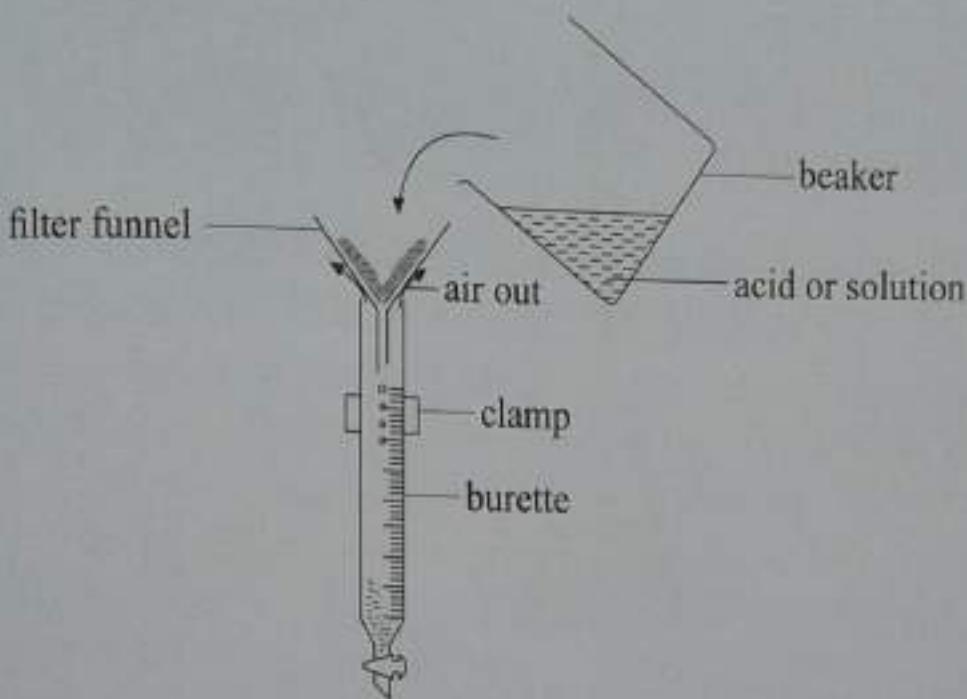


Fig. 4.6: Correct way of filling a burette

- Place a white tile or paper under the conical flask to clearly see the colour changes.
- Run the acid into the conical flask, 1 or 2 cm^3 at a time, fairly quickly. After every addition, swirl the flask, keeping the eye on the solution in the flask to see any new colour change. When you swirl the flask and the new colour developing persists for a while, the end point is near. Add one drop of the acid at a time until you get a permanent colour. This is the end-point of the titration.
- Read and record the volume of the acid used immediately, to the nearest 0.1 cm^3 . Record your results in, a table similar to Table 4.11.
- Repeat the titration two more times using a different clean conical flask. Add the same number of drops of the indicator as used in the first titration. However, if you use the same flask, you must wash it thoroughly with distilled water and then rinse with a little of the solution you intend to suck into the pipette.

Note: The first volume obtained should guide you to get the second volume fairly quickly. For example if your first titre volume was 25.0 cm^3 , you may add 21 cm^3 quickly while shaking the flask. Then add the acid dropwise while swirling the conical flask until you get the same permanent colour change as in previous titration.

- Repeat the titration using the second volume as a guide to the volume required. You can add the acid until you are about 1 cm^3 from the end point, then you add the acid drop by drop. Fig. 4.7. illustrate these steps.

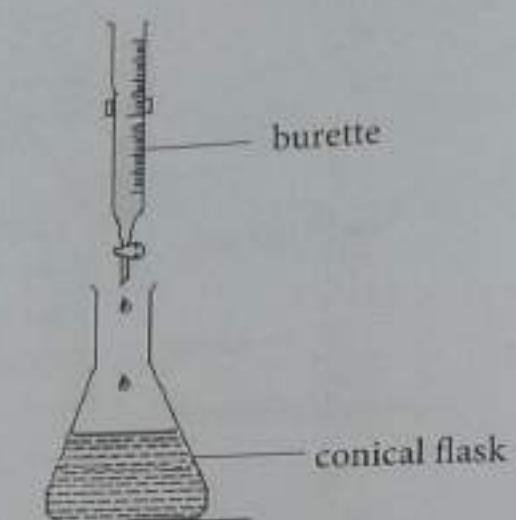


Fig. 4.7 Titration process

- Find the average of any two or three values for the volume of the acid added, which differ by not more than $\pm 0.2 \text{ cm}^3$. In other words, the three titrations should be fairly consistent.

Table 4.11: Record of volume of titration results

Burette readings	1	2	3
Final burette reading	21.5	43.2	21.1
Initial burette reading	0.0	22.0	0.0
Volume of acid used (cm^3)	21.5	21.2	21.1

Calculate the average volume of the acid used and show your working.

$$\begin{aligned}\text{Average volume of acid used} &= \frac{21.1 + 21.1}{2} \\ &= 21.15 \text{ cm}^3\end{aligned}$$

Note: The value 21.5 is omitted because it is way off the acceptable variance of ± 0.2 . If you got values such as 24.2 cm^3 , 24.5 cm^3 and 24.6 cm^3 which two values would you use for getting the averages? You would use 24.5 and 24.6 because the difference between them is not more than 0.2 cm^3 .

Most students do the experiment fairly well up to and including getting the average of the acid (or any other solution) used from the burette. But, some may not know how to use the values obtained to proceed with further calculations. The following examples show how we are suppose to answer typical examination questions on volumetric analysis.

Example 1

You are provided with a solution A which was made by dissolving 5.3 g dm^{-3} of sodium carbonate, Na_2CO_3 . Solution B has hydrochloric acid in 1 dm^{-3} solution.

You are required to:

- Calculate the molarity of the sodium carbonate solution.
- Standardise solution B using solution A, i.e. find its concentration in mole per dm³. (Na = 23; O = 16; C = 12)

Procedure

- Fill the burette with dilute hydrochloric acid provided.
- Pipette 25.0 cm³ of solution A and transfer it into the conical flask.
- Add 2 - 3 drops of methyl orange indicator. Observe the colour change.
- Titrate until you get the end-point. How would you tell that the end-point has been reached?
- Repeat the titration 2 to 3 times to get fairly consistent values.
- Record your values as in a table like the one shown below.

Burette reading	1	2	3
Final burette reading			
Initial burette reading			
Volume of solution B used (cm ³)			

Note the initial colour of indicator in the sodium carbonate and stop adding the acid when you get a different colour. It will change from yellow to pink.

- Find the volume of the acid that reacted.
- Standardise solution B using solution A.
- Find the molarity of the sodium carbonate.

Calculating using titration results

Example 1

The following is a sample titration results and how it is used in calculation thereafter.

Burette readings	1	2	3
Final burette readings	22.5	44.4	25.8
Initial burette reading	0.0	22.5	0.0
Volume of solution B used (cm ³)	22.5	25.9	25.8

- Calculate the average volume of solution B used. Show your workings.

$$\frac{25.9 + 25.8}{2} = 25.85 \text{ cm}^3$$

- Write an equation for the reaction.



- Calculate moles of solution A and solution B used.

From the equation we get the mole ratio of the reactants, moles of the sodium carbonate (solution A) and moles of the acid (solution B).

- (a) First find the mole of solution A whose volume (25.0 cm^3) and concentration (5.3 g dm^{-3}) are known as follows:

$$\begin{array}{ll} 1 \text{ mole of } \text{Na}_2\text{CO}_3 & = (2 \times 23) + 12 + (3 \times 16) = 106 \text{ g} \\ x \text{ mole of } \text{Na}_2\text{CO}_3 & = 5.3 \text{ g} \end{array}$$

Solving for x

$$\begin{aligned} x &= (5.3 \text{ g} \times \frac{1 \text{ mole}}{106 \text{ g}}) \\ &= 0.05 \text{ mole} \end{aligned}$$

Thus, molarity of solution A is 0.05 mol dm^{-3} or 0.05 M

- (b) Mole contained in solution A;

If 1000 cm^3 of solution A contains 0.05 mole

25 cm^3 of solution A used in titration would contain y mole

Solving for y,

$$\begin{aligned} y &= (25 \text{ cm}^3 \times \frac{0.05 \text{ mole}}{1000 \text{ cm}^3}) \\ &= 0.00125 \text{ mole} \end{aligned}$$

- (c) Mole of acid

Mole ratio from the equation, $\text{Na}_2\text{CO}_3 : \text{HCl} = 1 : 2$

Moles of HCl = 0.00125×2

$$= 0.0025 \text{ mole}$$

This means that 25.85 cm^3 of HCl used contains 0.0025 mole

1000 cm^3 of the HCl would contain x moles.

Solving for x,

$$\begin{aligned} x &= 0.0025 \text{ mol} \times \frac{1000 \text{ cm}^3}{25.85 \text{ cm}^3} \\ &= 0.0967 \text{ mole} \end{aligned}$$

Therefore the concentration of HCl is $0.0967 \text{ mol dm}^{-3}$

Example 2

You are provided with:

- Solution M which is 0.5 M hydrochloric acid.
- Solution N containing 5.3 g of a metal carbonate $X_2\text{CO}_3$ dissolved in 250 cm^3 .
- Distilled water and a volumetric flask.
- Methyl orange indicator.
- Titration apparatus.

$$(\text{Na} = 23; \text{C} = 12; \text{O} = 16)$$

You are required to determine the:

- (i) Concentration (molarity) of solution N in
 - (a) moles per dm^3
 - (b) g dm^{-3}
- (ii) Relative atomic mass of X

Solution

You solve this question by titration.

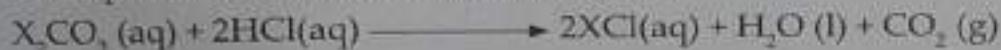
Pipette 25 cm³ of solution N and transfer it into a conical flask. Add 2-3 drops of the indicator. As shown in example 1, get 3 concordant values i.e. values that are close to each other. Suppose you obtained values as shown in the table below.

Burette readings	1	2	3
Final burette reading	22.0	43.9	25.8
Initial burette reading	0.0	22.0	0.0
Volume of acid reading (cm ³)	22.0	21.9	25.8

Calculate the average volume of solution M used.

$$\frac{21.9 + 22.0}{2} = 21.95 \text{ cm}^3$$

The equation for reaction that occurred is:



Ionic equation



Note: That we can use either of the equations.

From the instructions given, we can calculate the moles of HCl in the average volume used (21.95 cm³) since the concentration of HCl is given, 0.5 M.

Moles in the volume of acid used:

1000 cm³ contain 0.5 moles of HCl

21.95 cm³ contain x moles of HCl

Cross multiply and solve for x,

$$x = 0.5 \times \frac{21.95 \text{ cm}^3}{1000 \text{ cm}^3}$$

$$= 0.01 \text{ moles of HCl}$$

Moles of X₂CO₃ used:

The mole ratio of X₂CO₃: HCl is 1 : 2

Since amount of acid is twice that of X₂CO₃ in the reaction.

$$\text{Mole of X}_2\text{CO}_3 = \frac{0.01}{2} \text{ moles}$$

$$= 0.005 \text{ moles}$$

This means that 25 cm³ of X₂CO₃ used in titration contained 0.005 mole.

(a) Moles of X₂CO₃ in 1000 cm³ (1 dm³) = x mole

$$x = \frac{0.005 \text{ mole} \times 1000 \text{ cm}^3}{25 \text{ cm}^3}$$

$$= 0.2 \text{ mole}$$

The concentration (molarity) of X₂CO₃ is 0.2 mol dm⁻³ or 0.2 M.

- (b) 250 cm^3 of solution N contained 5.3 g
 1000 cm^3 of solution N would contain y grams
 Cross multiply and solve for y

$$y = \frac{5.3 \text{ g} \times 1000 \text{ cm}^3}{250 \text{ cm}^3}$$

$$= 21.2 \text{ g dm}^{-3}$$

Concentration is 21.2 g dm^{-3} .

250 cm^3 of solution X_2CO_3 = 5.3 g

$$1000 \text{ cm}^3 \text{ of solution } \text{X}_2\text{CO}_3 = \frac{5.3 \text{ g} \times 1000 \text{ cm}^3}{250 \text{ cm}^3}$$

$$= 21.2 \text{ g}$$

Molar mass of X_2CO_3

$$0.2 \text{ mole} \longrightarrow 21.2 \text{ g}$$

$$1 \text{ mole} \longrightarrow \frac{21.2 \times 1 \text{ mole}}{0.2 \text{ mole}}$$

$$= 106 \text{ g}$$

$$\therefore 2x + 12 + 48 = 106$$

$$2x = 106 - 60$$

$$= 46$$

$$x = 46 \div 2$$

$$= 23$$

4.11 Calculating percentage yield of a reaction

The actual amount of product formed during reactions can be expressed in percentage. This is important in establishing output of industrial processes.

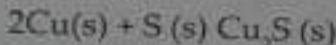
Percentage yield is calculated using the following formula:

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$

Example 1

In an experiment, 2.4 g of copper metal were heated with excess sulphur to yield 2.25 g of copper (I) sulphide. What is the percentage yield of this reaction? ($\text{Cu} = 63.5$, $\text{S} = 32$).

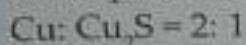
Solution



From the equation,

$$\begin{aligned} \text{Moles of copper that reacted} &= \frac{\text{mass of copper given}}{\text{molar mass of copper}} \\ &= \frac{2.4}{63.5} \\ &= 0.0378 \text{ mole} \end{aligned}$$

Mole ratio in the equation can be used to calculate the expected number of moles of the product.



$$\text{Expected moles of Cu}_2\text{S to be formed} = \frac{0.0378}{2} \text{ mole}$$

$$= 0.0189 \text{ mole}$$

$$\text{R.M.F of Cu}_2\text{S} = (2 \times 63.5) + 32$$

$$= 159$$

$$1 \text{ mole of Cu}_2\text{S} = 159 \text{ g}$$

$$\text{Expected yield of Cu}_2\text{S} = 159 \text{ g} \times 0.0189 = 3.00519 \text{ g}$$

$$\text{Percentage yield of Cu}_2\text{S} = \frac{2.25 \text{ g}}{3.0051 \text{ g}} \times 100\%$$

$$= 74.87\%$$

Example 2

When 12.35 g of copper (II) carbonate was heated in a crucible, 7.0 g of copper (II) oxide was produced. Calculate the percentage yield of copper (II) oxide.

(C = 12, O = 16, Cu = 63.5)

Solution



1 mole 1 mole 1 mole

$$\text{R.F.M of CuO} = (63.5 \times 1) + (16 \times 1) = 79.5$$

$$\text{R.F.M of CuCO}_3 = 63.5 + 12 + (16 \times 3) = 123.5$$

From the equation

123.5 g of CuCO₃ is expected to yield 79.5 g of CuO

Therefore 12.35 g of CuCO₃ would yield

$$= 12.35 \text{ g} \times \frac{79.5 \text{ g}}{123.5 \text{ g}}$$

$$= 7.95 \text{ g of CuO}$$

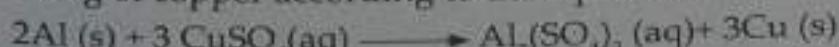
If the actual yield is 7.0 g

$$\text{Percentage yield of CuO} = \frac{7.0}{7.95} \times 100\%$$

$$= 88.0504\%$$

Example 3

2.34 g of aluminium reacted with excess copper (II) sulphate solution to produce 3.89 g of copper according to the equation:



What was the percentage yield of copper? (Al = 27, Cu = 63.5)

Solution

From the equation we can calculate the actual yield of copper.

2×27 g of Al would yield 3×63.5 g of Cu

54 g of Al = 190.5 g of Cu

2.34 g of Al would yield x g of Cu

Solving for x,

$$x = 2.34 \text{ g} \times \frac{190.5 \text{ g}}{54 \text{ g}} \\ = 8.255 \text{ g of Cu}$$

$$\text{Percentage yield of copper} = \frac{3.89 \text{ g}}{8.255 \text{ g}} \times 100\% \\ = 47.123\% \text{ of Cu}$$



Practice exercise 4M

1. Calcium carbonate can be decomposed by heating according to the following equation.



What is the percentage yield of calcium oxide in this reaction if 12.6 g of calcium oxide (CaO) is obtained on heating 25.9 g of CaCO_3 is heated.

2. Calculate the percentage yield of iron in a reaction where 67.3 g of iron(III) oxide reacts with excess of carbon monoxide to produce 41.8 g of iron according to the equation:



3. When 54.8 g of silicon (IV) oxide is heated with an excess of carbon, 32.5 g of silicon carbide is produced besides the carbon monoxide gas. What is the percentage yield of this reaction?



4. Calculate the percentage yield of copper in a reaction in which 1.56 g of aluminium and an excess of copper (II) sulphate react to produce 2.58 g of copper according to the following equation.



5. When 42 g of magnesium carbonate reacts with excess dilute hydrochloric acid, at room temperature and pressure, 7 dm^3 of carbon (IV) oxide, is produced.

Calculate the percentage yield of this reaction.



(C = 12, Si = 28, Fe = 56, Al = 27, O = 16, S = 32, Mg = 24; Molar gas volume at r.t.p = 24 dm^3)

4.12 Limiting reagent

Reactants must react in given mole ratios in order for the reactants to be all used up. Sometimes in a reaction, the amounts of reactants provided for may not be in their recommended mole ratio according to stoichiometric equation. In this case, amount of one of the reactants will be left over once the reaction has taken place. Also the amount of the products produced by such a reaction is expected to be equally restricted by the amount of the reactant that has been completely used up in the reaction.

The reactant that is completely used up in reaction while the other reactant is still available is called the **limiting reagent**. The unfinished reactant (reagent) in a reaction after it has come to an end is known as excess **reagent/reactant**.

Lets consider the following example:



According to the stoichiometric equation above, one mole of nitrogen gas reacts with three moles of hydrogen gas to yield two moles of ammonia gas. Now, if one mole of nitrogen and four moles of hydrogen are reacted, it means one mole of hydrogen would be left unreacted. This means that even if more hydrogen is added to the reaction system, it will have no net effect on the amount of product formed since no more nitrogen is available in the system to react with the added hydrogen. In this case the amount of product formed by the reaction is limited/controlled by the **amount of the limiting reagent (reactant)**. The limiting reagent in this reaction is nitrogen and the excess reagent is hydrogen.

Example 1

Magnesium and oxygen react to form magnesium oxide according to the equation.



If 6 g of magnesium and 2 g of oxygen are available for a reaction, determine the limiting reagent, the excess reagent and the mass of magnesium oxide formed.

(O = 16, Mg = 24)

Solution

$$\begin{aligned}\text{Moles of Mg used} &= \frac{\text{mass of Mg given}}{\text{molar mass of Mg}} \\ &= \frac{6 \text{ g}}{24 \text{ g}} \\ &= 0.25 \text{ mole}\end{aligned}$$

$$\begin{aligned}\text{Moles of O}_2 \text{ used} &= \frac{2 \text{ g}}{32 \text{ g}} \\ &= 0.0625 \text{ moles}\end{aligned}$$

From the equation, the mole ratio is;

2 moles of Mg require 1 mole of O₂ for a complete reaction.

0.25 mole of Mg would require

$$\frac{0.25}{2} = 0.125 \text{ moles of oxygen}$$

The amount of oxygen available is 0.0625 mole, which is less than the required amount of 0.125 mole. Therefore oxygen is the limiting reagent.

If 0.0625 moles of O₂ is used; mole of Mg required is,

$$(0.0625 \times 2) = 0.125 \text{ moles of Mg}$$

However, amount of Magnesium available is 0.25 mole, which means magnesium is in excess, by $(0.250 - 0.125) = 0.125$ mole. Magnesium is therefore the excess reagent.

Moles of MgO produced is equivalent to moles of Mg used = 0.125 mole

$$\text{R.F.M of MgO} = 24 + 16 = 40$$

$$\text{Mass of magnesium oxide formed} = 0.125 \times 40 = 5.0 \text{ g}$$

Example 2

Mercury reacts with bromine to produce mercury (II) bromide according to the following equation.



If 2.15 g of Hg is reacted with 1.56 g of bromide, calculate:

- The mass of limiting reagent used.
- The mass of HgBr₂ formed
- The mass of the reactant which remain in excess.

$$(\text{Br} = 80, \text{Hg} = 200)$$

Solution

(i) R.M.M of Br₂ = $80 \times 2 = 160$

From the equation, 200 g of Hg reacts with 160 g of bromine.

Now, if 200 g of Hg reacts with 160 g of bromine

Then 2.15 g of Hg would require

$$\frac{2.15 \times 160}{200 \text{ g}}$$

$$= 1.72 \text{ g of bromine}$$

But the mass of bromine available is only 1.56 g, therefore bromine is the limiting reagent.

1.56 g of bromine would require

$$\frac{1.56 \text{ g} \times 200}{160 \text{ Hg}}$$

$$= 1.95 \text{ g of Hg}$$

(ii) R.F.M of HgBr₂ = $(200 \times 1) + (80 \times 2) = 360$

160 g of bromine would yield 360 g of HgBr₂

Now 1.56 g of bromine (Br₂) would yield

$$\frac{1.56 \text{ g} \times 360 \text{ g}}{160 \text{ g}}$$

$$3.51 \text{ g of HgBr}_2$$

(iii) Mercury is excess by $(2.15 - 1.95) \text{ g} = 0.2 \text{ g}$



Practice exercise 4N

1. Flourine element can be prepared according to the following reaction equation.

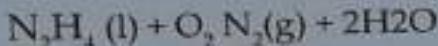


If 5.32 g of K_2MnF_6 is mixed with 8.75 g of SbF_5 ,

- (a) Identify the limiting reagent and the excess reagents.
- (b) Calculate the mass of flourine element produced.
- (c) What mass of the excess reagent remained?

(F = 19, K = 39, Mn = 55, Sb = 122)

2. Hydrazine is used in rocket fuel. It reacts with oxygen as follows.



In a particular rocket engine, 2.29 g of hydrazine and 3.14 g of oxygen are available for reaction.

- (a) Find the limiting reagent.
- (b) Determine the reagent that is in excess and by how much.
- (c) Calculate the mass of water produced

(H = 1, N = 14, O = 16)

3. Magnesium and chlorine react according to the following equation.



If 20 g of magnesium and 20 g of chlorine are available for reaction, determine:

- (a) The limiting reagent.
- (b) The mass of MgCl_2 formed.

4. When sodium is placed in water, it reacts violently to produce hydrogen gas and form sodium hydroxide solution.

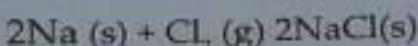
- (a) Write a balanced chemical equation for this reaction.

- (b) If 9.2 g of sodium reacts completely, calculate the mass of gas that would be produced.

- (c) What mass of water would react completely with 4.6 g of sodium.

- (d) If 1 kg of sodium was placed in 300 cm³ of water, which reactant would be used up first.

5. Sodium and chlorine react according to the following equation.



If 12.5 g of sodium and 25.5 g of chlorine are available for reaction, determine:

- (a) the limiting reagent
- (b) the mass of sodium chloride formed.

6. Sulphur (IV) oxide gas reacts with water to form an acid. If 32 g of sulphur (IV)oxide reacts with 18 g of water,
- How much H_2SO_4 would be produced?
 - Which reactant is in excess and by how much?

Revision Exercise 4



- Write the formulae of the following compounds from the name given and calculate their formula masses.
 - Ammonium phosphate
 - Iron(II) sulphate
- Calculate the volume of ammonia in dm^3 at r.t.p needed to produce 40 g of ammonium nitrate when it is reacted with nitric acid.
- Calculate the mass of:
 - 0.5 mol sodium hydroxide
 - 0.1 mol magnesium nitrate
- Calculate the percentage by mass of nitrogen in each of the following compounds.
 - NaNO_3
 - $\text{Ca}(\text{NO}_3)_2$
- A hydrocarbon has a relative molecular mass of 42. It has the following composition carbon 85.7% and hydrogen 14.3%. Find its molecular formula.
- On analysis, a compound of iron and oxygen was found to contain 6.4 g of iron and 5.5 g oxygen. Its relative molecular mass is 160. Find the molecular mass of the oxide.
- 25 cm^3 of a solution containing 4 g/ dm^{-3} of NaOH reacts with 50 cm^3 of a solution of hydrochloric acid. Calculate the molarity of the acid.
- In a titration experiment, a student pipetted 25.0 cm^3 of ammonia solution and titrated with 0.1 M HCl. If the average volume of acid used was 36.30 cm^3 calculate the concentration of ammonia solution in:
 - mol dm^{-3}
 - g dm^{-3}
- A hydrated salt contains 55.9 % water of crystallization. The relative formula mass of the anhydrous salt is 142. Find the number of molecules of water of crystallization.

10. Calculate the empirical formula of a compound which contains 20.15% iron, 11.51% sulphur, 23.02% oxygen and 45.33% water of crystallization.
11. 3.2 g of methane were completely burned in oxygen.
- How many moles of carbon dioxide were produced?
 - What is the volume of oxygen required to burn the 3.2 g methane completely?
12. Calculate the volume at r.t.p and mass of
- 0.06 mole of SO_2
 - 0.04 mole of H_2 (Molar gas volume at r.t.p = 24 dm^3)
13. (a) 1.2 dm^3 of nitrogen gas contain how many;
- Atoms?
 - Molecules?
- (b) Calculate the number of moles of molecules in 600 cm^3 of carbon dioxide at s.t.p.
($L = 6.023 \times 10^{23}$, molar gas volume at s.t.p = 22.4 dm^3)



Success criteria

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

- Define the terms exothermic and endothermic in relation to heat changes.
- Describe temperature changes in exothermic and endothermic reactions and processes involved.
- Draw energy level diagrams for exothermic and endothermic reactions.
- Describe energy changes involved in bond breaking and bond formation processes.
- Determine whether the reaction is exothermic or endothermic using bond energies.

5.1 Heats of reactions

We have seen that most chemical reactions are accompanied by changes of heat energy. For example the Haber process and Contact process produces a lot of heat energy. There are also some reactions which absorbs heat energy from the surroundings.

In this topic, we are going to look at how these heat energy changes take place in various physical and chemical processes. Heat changes are of great importance to chemists in controlling and monitoring various industrial process in order to achieve optimum yield.

5.2 Exothermic and endothermic reactions

The word **exothermic** describes a process that releases energy in the form of heat. Exothermic reactions usually feel hot because they are giving out heat. The term **endothermic** reactions describes a process that absorbs energy in the form of heat. Endothermic usually feel cold because it is taking heat away from the surroundings.

An exothermic reaction is one that releases heat and cause the surroundings temperature to rise while an endothermic reaction is one that absorbs heat and causes the surroundings temperature to fall. Table 5.1 shows examples of exothermic and endothermic processes.

Table 5.1: Some examples of exothermic and endothermic reactions

Exothermic process	Endothermic process
Formation of ice cubes (freezing water).	Melting ice cubes.
Condensation of rain from water vapour.	Evaporation of water.
A burning candle.	Melting solid salts.

Mixing water and strong acid.	Mixing water and ammonium nitrates.
Adding water to anhydrous salt.	Losing water from a hydrated salt.
Combining atoms to form a molecule.	Splitting a molecule to individual atoms.
Neutralization reaction.	Photosynthesis.
Combustion of fuels such as wood, coal and oil.	Decomposition of limestone.
Ionization of atoms.	Baking bread.

5.3 Temperature changes in exothermic and endothermic reactions

Experiment 5.1

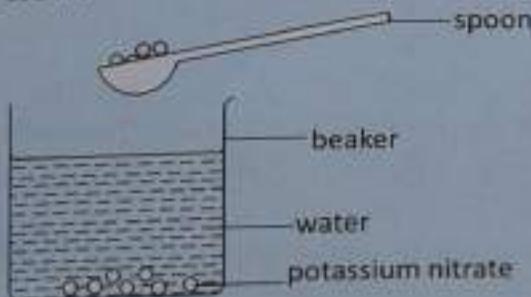
Aim: To investigate what happens when potassium nitrate/ammonium nitrate is dissolved in water.

Requirements

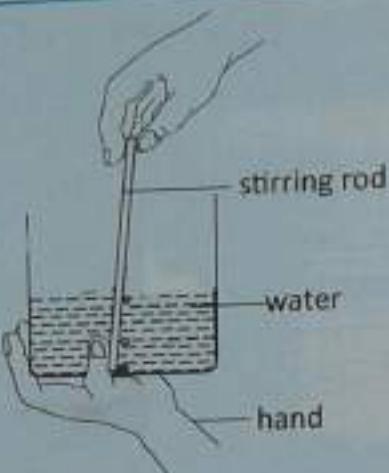
- Beaker
- Glass rod
- Ammonium nitrate/potassium nitrate
- Water
- Thermometer
- Spoon/spatula
- Stirring rod

Procedure

1. Put about 25 cm³ of water in a beaker.
2. Add 3 spatula-endfuls of ammonium nitrate or potassium nitrate into the beaker as shown below.



3. Hold the beaker in the palm of your hand as shown below as you stir the mixture using a glass rod.



- What do you observe?
4. Record your observations in your notebook.
- What do you feel on your palm?
 - Is heat energy being taken from your hand or given out to your hand?
 - What do you conclude?
5. Repeat the experiment but stir the solution with a thermometer.
- Caution:** Make sure the thermometer does not touch the side or bottom of the beaker to avoid breakage.
6. Copy Table 5.2 in your notebook and record the initial and final temperatures of the solution.

Table 5.2: Changes in temperature when dissolving potassium nitrate/ammonium nitrate

Initial temperature of water (°C)	
Final temperature of solution (°C)	

- What do you conclude from the above temperature readings?

Discussion

When potassium nitrate is dissolved in water heat energy is absorbed from its surroundings. In this case, its surroundings include the beaker, glass rod, the thermometer, air around, and your palm.

This explains why your palm felt cold and the temperature of the solution became lower than the initial temperature of the water when measured using a thermometer. This is an endothermic reaction. In endothermic reactions, heat energy is absorbed and the temperature of the surroundings decreases or fall. Loss of energy is a result of interaction between a system and its surroundings. The beaker and its contents is the system. An endothermic reaction is a reaction which takes in heat from the surroundings.

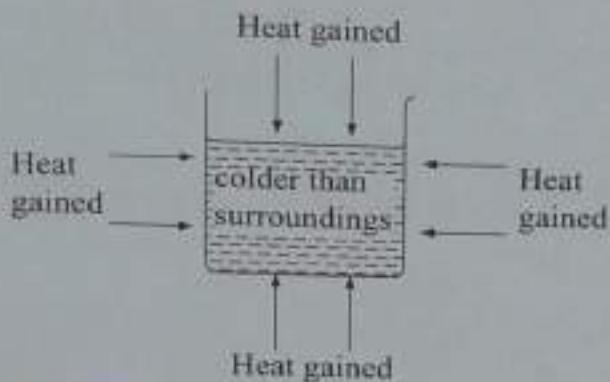


Fig. 5.1: An example of endothermic reaction.

Experiment 5.2

Aim: To investigate what happens when sodium hydroxide pellets are dissolved in water.

Caution: Sodium hydroxide pellets or its solution are highly corrosive. They should not come into contact with your skin.

Requirements

- Boiling tube
- Thermometer
- Stirring rod
- Sodium hydroxide (pellets)
- Distilled or tap water

Procedure

1. Half-fill the boiling tube with water.
2. Measure and record the temperature of the water.
3. Add 3-4 sodium hydroxide pellets into the water and stir.
4. Using the thermometer note and record the temperature of the solution.
Does the boiling tube feel cold or hot?
5. Copy Table 5.3 in your notebook and record your results.
 - Does the reaction absorb or give out heat?
 - What do you conclude?

Table 5.3: Changes in temperature when dissolving NaOH pellets in water

Initial temperature of water (°C)	
Final temperature of sodium hydroxide solution (°C)	

Discussion

When sodium hydroxide is dissolved in water, heat energy is released to the surroundings. The surrounding is the thermometer, the beaker, the air around and your palm. This is the reason why your palm feels warm. The temperature of the solution is higher than that of the water and pellets before dissolution. This is an **exothermic reaction**. In exothermic reactions, heat energy is given out and the temperature of the surroundings increases or rises.

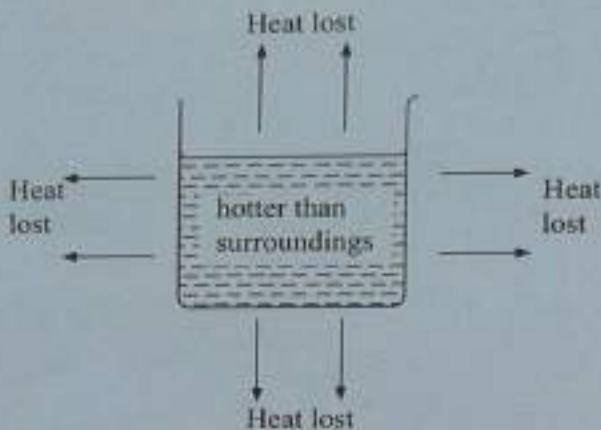


Fig. 5.2: Heat loss to the surroundings in an exothermic reaction.

The beaker and its contents is the system and the surrounding is everything else around it. An exothermic reaction is a reaction in which heat energy is produced and released to the surroundings.

Fig 5.3 gives an analogy to assist us understand endothermic and exothermic processes.

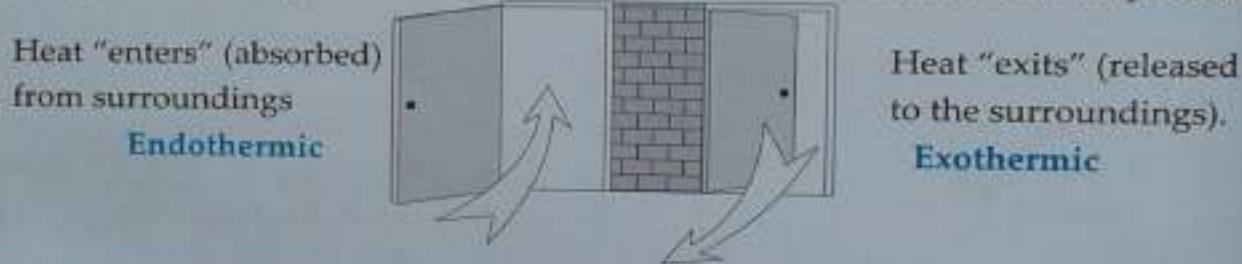


Fig. 5.3: Analogy of absorption and evolution of heat energy in endothermic and exothermic reactions.

In endothermic reactions the products are at a higher energy level compared to the reactants, while in an exothermic reactions products are at a lower energy level compared to the reactants.



Practice exercise 5A

1. Compare exothermic and endothermic reactions in terms of heat change with the surroundings.
2. A student during an experiment dissolved potassium nitrate in water. The equation for the reaction which occurs is:-

$$\text{KNO}_3(\text{s}) \longrightarrow \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \quad \Delta H = 34.6 \text{ kJ}$$
 - (a) What sign would you assign the ΔH value, positive or negative? Explain.
 - (b) What does the symbol ΔH signify in a reaction?
3. Indicate whether the following process are exothermic or endothermic.
 - (a) Respiration.
 - (b) Photosynthesis.
 - (c) Combustion of petrol in car engine.

Enthalpy of neutralisation

The term **enthalpy** refers to heat content of a substance

Experiment 5.3

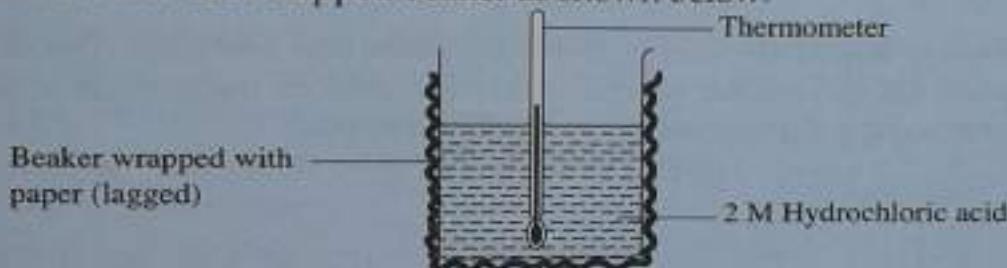
Aim: To find the enthalpy change during neutralization reaction.

Requirements

- 250 cm³ beaker wrapped with cotton wool or newspaper leaf
- Thermometer (-10°C to 110°C)
- 50 cm³ measuring cylinder
- 2M sodium hydroxide
- 2M hydrochloric acid
- Distilled water

Procedure

- (i) Using a measuring cylinder, measure 50 cm³ of 2M hydrochloric acid and transfer into the wrapped beaker as shown below.



- (ii) Note the temperature of the acid. Record it in Table 5.4 as T₁.
- (iii) Rinse well the measuring cylinder with distilled water.
- (iv) Using the measuring cylinder, measure 50.0 cm³ of 2M sodium hydroxide solution.
- (v) Take the temperature reading of sodium hydroxide and record it in Table 5.4 as T₂.
- (vi) Find the average temperature of the acid, T₁ and the alkali, T₂, i.e. $\frac{T_1 + T_2}{2} = T_3$ and record in Table 5.4.
- (vii) Pour sodium hydroxide solution, (NaOH) carefully into the hydrochloric acid, (HCl) in the wrapped beaker.
- (viii) Stir the mixture of the two solutions carefully for a while with the thermometer (do not touch the sides of the beaker with the thermometer to prevent breakage).
- (ix) Record the highest temperature reached, T₄ in Table 5.4.
- (x) Find temperature change by subtracting T₄ - T₃.
 - Does the temperature rise or fall?
 - Is the reaction exothermic or endothermic?
 - Write chemical and ionic equations for the reaction.
 - Will the sign of ΔH for this reaction be +ve or -ve? Give a reason for your answer.

Table 5.4: Results of temperatures reading in neutralisation reaction

	°C	K
Temperature of the acid, T_1		
Temperature of the alkali, T_2		
Average temperature of the two solutions, $\frac{T_1 + T_2}{2} = T_3$		
Highest temperature of solution reached, T_4		
Temperature change, $(T_4 - T_1) = \Delta T$		

Note: You can repeat the experiment using the following pairs:

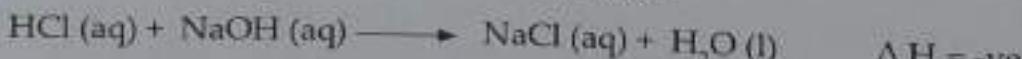
- (i) 2M nitric acid and potassium hydroxide.
(ii) 2M hydrochloric acid and ammonium hydroxide.
(iii) 2M ethanoic acid and sodium hydroxide. Write chemical and ionic equations for the reaction in (i) and (ii).

Discussion

Temperature rise would be seen in these neutralisation reactions. This shows that these reactions are exothermic reactions. ΔH is therefore negative. It is possible to calculate the enthalpy change, using the known volumes.

Table 5.5: Specimen results

	°C	K
Temperature of hydrochloric acid, T_1	22.5	295.5
Temperature of sodium hydroxide, T_2	22.0	295.0
Average temperature of the two solutions, $\frac{T_1 + T_2}{2} = T_3$	22.25	295.25
Highest temperature reached, T_5	35.5	308.5
Temperature change, ΔT ($T_5 - T_3$)	13.25	13.25

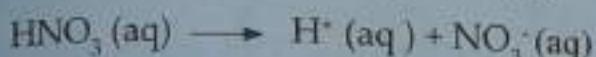


Ionic equation:

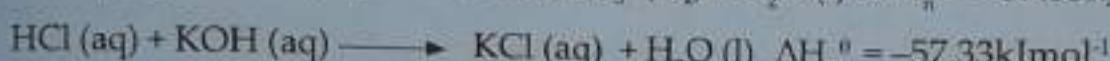
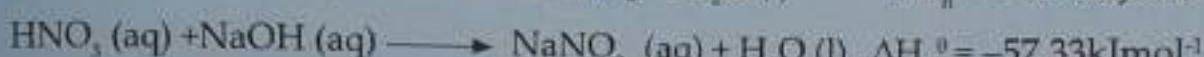
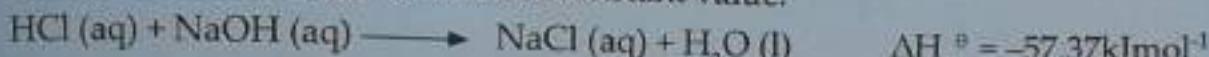


Note: That when we measure the temperature change when a known volume of an acid is neutralised by a known volume of an alkali, we can actually calculate the enthalpy change for that neutralisation reaction then proceed and calculate the molar enthalpy change of neutralisation. Experiments have shown that for strong acids and strong alkali reactions, the value of the heat energy liberated is about 57 kJ mol^{-1} . This is because all strong acids and alkalis are **completely dissociated** in aqueous solution.

Examples:

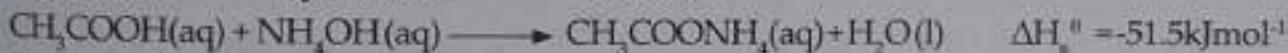
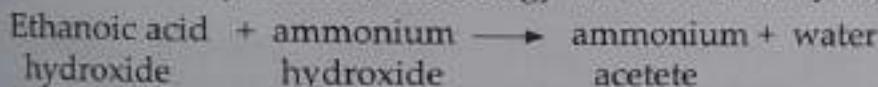


For neutralisation reactions involving strong acids and strong bases, the enthalpy change in the reactions is almost a constant value.



When a strong acid e.g. hydrochloric acid is neutralised by a weak base e.g. aqueous ammonia (ammonium hydroxide), slightly less heat energy is produced. The energy released is about 52.2 kJ mol^{-1} .

When both the acid and the alkali are weak, the heat liberated is much lower, for example, when weak ethanoic acid is neutralised by weak aqueous ammonia (ammonium hydroxide), the energy released is 51.5 kJ mol^{-1} .



The enthalpy change is low because some energy, approximately $+5.5 \text{ kJ}$, must be used to ionise ethanoic acid and ammonium hydroxide. Consequently, less energy is liberated.



Practice exercise 5B

- Define the term enthalpy change of neutralisation.
- Explain why the quantity of heat liberated when one mole of hydrochloric acid, HCl, is neutralised by one mole of sodium hydroxide, is the same quantity as when one mole of nitric acid, is used instead of hydrochloric acid.

5.4 Energy level diagrams for exothermic and endothermic reactions

An energy level diagram is a graphical representation of the heat change involving products and reactants after the reaction. Fig 5.4(a) and 5.4(b) shows energy level for exothermic and endothermic reactions respectively.

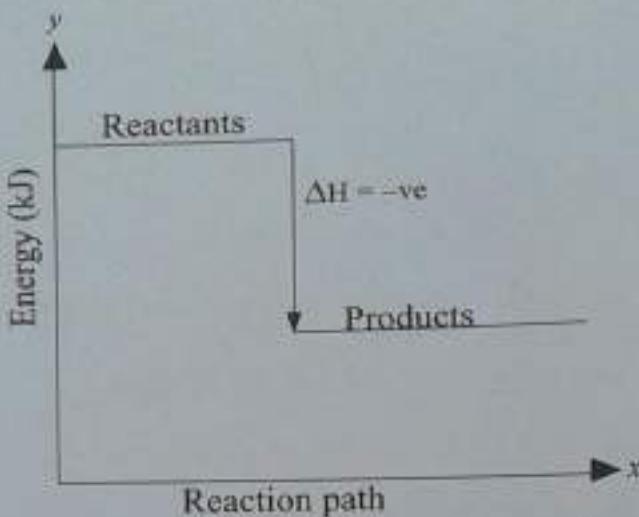


Fig. 5.4: (a) Energy level diagram for an exothermic reaction

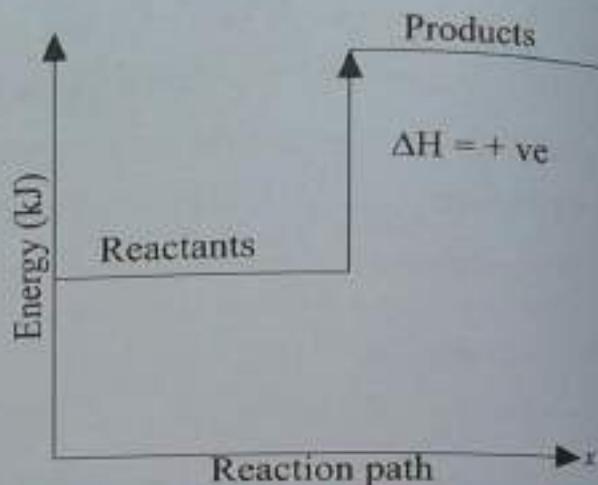


Fig. 5.4: (b) Energy level diagram for endothermic reaction

The x-axis in the energy level diagram shows the progress of the reaction from reactants to products while y-axis shows the heat content of the system.

If the graph is drawn to scale, we can calculate the heat change (ΔH) as follows.

$$\text{Heat change } (\Delta H) = H_{\text{products}} - H_{\text{reactants}}$$

If the heat change is $-ve$, then that particular reaction is exothermic. That is, heat energy of the products is lower than the reactants. Heat energy is evolved in the process. See Fig. 5.4(a). From Fig. 5.4(b), the heat content of the products is higher than that of the reactants. Hence the heat change will be a **positive (+ve) value** and the reaction is **endothermic**. For example, assuming that the value of reactants from the graph above is 10 kJ and that of the product is 50 kJ.

The heat change (ΔH) will be:

$$\begin{aligned} \text{Heat change, } \Delta H &= H_{\text{products}} - H_{\text{reactants}} \\ &50 - 10 = +40 \text{ kJ} \end{aligned}$$

The heat value is +40 kJ hence the reaction is endothermic.

- Note:**
1. The notation of heat change is ΔH . The difference in the level of reactants and products represents either the heat energy absorbed from or released to the surroundings during the reaction.
 2. You may encounter the word enthalpy during our discussions. It simply means heat. Also enthalpy change is equivalent to **heat change**.

Class activity

Draw energy level diagrams to represent the following processes.

- Burning of a candle.
- Photosynthesis.
- Use ΔH to show whether it is negative or positive in each case above.

Energy level diagrams for neutralisation reactions

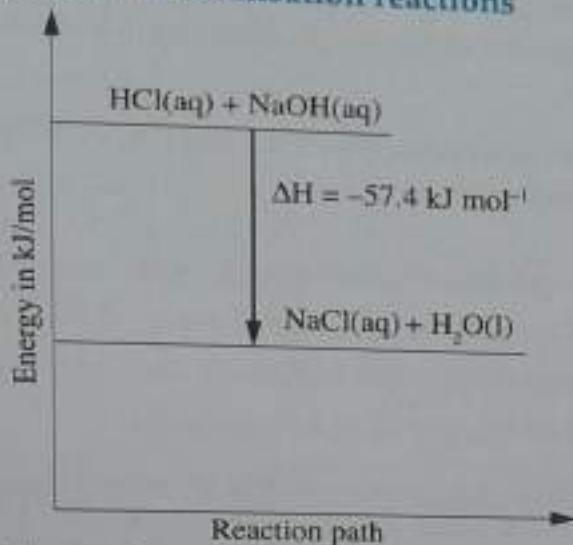


Fig. 5.5: Energy level diagram for neutralisation reaction between hydrochloric acid and sodium hydroxide

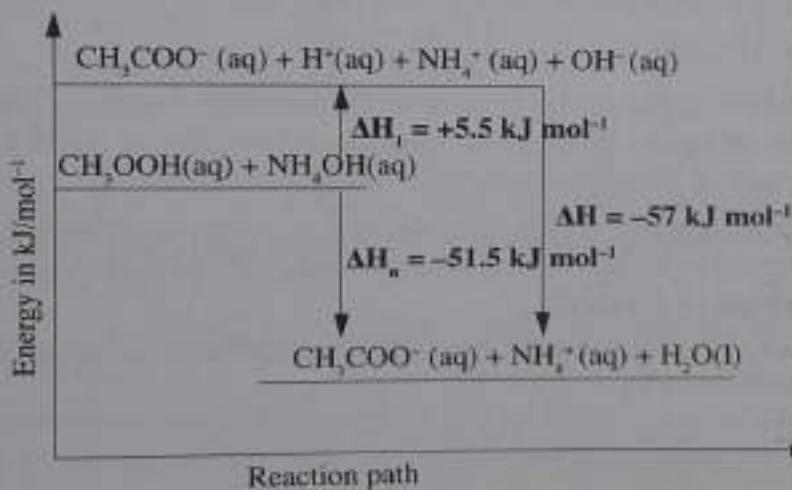


Fig. 5.6: Energy level diagram for the reaction of ethanoic acid and ammonium hydroxide

5.5 Energy changes in Bond breaking and formation processes

In every reaction (chemical process) the bonds are broken and new bonds are formed. Bond breaking absorbs energy therefore it is an **endothermic** process. In bond formation, energy in form of heat is released, therefore it is an **exothermic** process. Enthalpy changes in chemical processes can be determined through experiments.

The value of enthalpy change, (ΔH) for a reaction depends on the physical conditions under which the measurement is done. Just as we indicate the state symbols of the substances involved in a reaction depending on the temperature of the surrounding, the value of ΔH depends on the pressure under which the measurements are made. The changes for most reactions are carried out under conditions known as the **standard conditions** for the reaction. These conditions have been chosen as follows:

Standard temperature = 25°C (298K).

Standard pressure = 1 atmosphere.

Whenever enthalpy (heat changes) are measured under the above stated standard conditions, they are called **standard enthalpies** of the reactions. The special symbol $^\circ$ is used as a superscript for ΔH .

ΔH° is the symbol for **standard enthalpy**. The superscript " indicates that the enthalpy change is measured under standard conditions.

Examples of standard enthalpies of reactions include:

ΔH_f° denotes the standard enthalpy of formation.

ΔH_c° denotes the standard enthalpy of combustion.

ΔH_n° denotes the standard enthalpy of neutralisation.

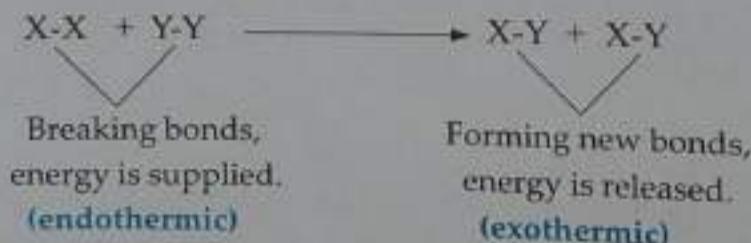
To determine the final quantity of energy released or absorbed during a reaction, first find the amount of energy used to start the reaction and amount of energy released by the end of the reaction. Then compare the two amounts of energies obtained to see whether the energy used to start the reaction is more or less than the energy obtained. Let us now learn how to determine bond energy changes in chemical processes.

Bond energies calculation

Every chemical bond has a particular bond energy associated with it. This bond energy varies with the type of bond. Known bond energies would be used to calculate the overall energy changes of reactions.

Energy must be absorbed to break bonds but energy is released during bond formation. The difference between the energy absorbed and energy released is the overall enthalpy change of reaction.

Let us consider the following general reaction where diatomic molecules of X_2 react with diatomic molecules of Y_2 .



Would you say the reaction is exothermic or endothermic?

Assume the bond energies for the different type of bonds above are the ones provided in Table 5.6.

Table 5.6: Specimen bond energies

Bond	'Amounts' of energy required to break bond / released when bond is formed (kJ mol^{-1})
$X-X$	435
$Y-Y$	240
$X-Y$	430

To break bond between X – X, the energy required	= 435 kJ mol ⁻¹
To break bond between Y – Y, the energy required	= 240 kJ mol ⁻¹
Total energy required	= 675 kJ mol ⁻¹

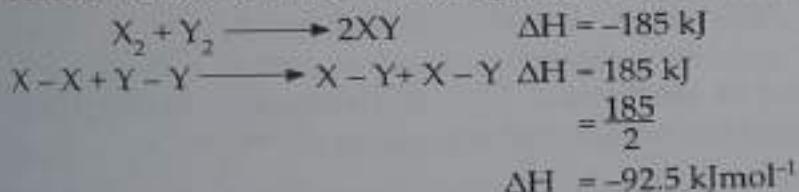
As we discussed earlier, in an endothermic reaction ΔH has a positive value. Since bond breaking is endothermic, the value should be written as +675 kJ mol⁻¹.

Forming a bond between X – Y, energy released	= 430 kJ mol ⁻¹
Forming another bond between X – Y, energy released	= 430 kJ mol ⁻¹
Total energy released	= 860 kJ mol ⁻¹

Since bond formation is an exothermic reaction, the value should be written as -860 kJ mol⁻¹.

As we have seen, we got 185 kJ more than we 'invested' when two (X-Y) bonds in two XY molecules were formed. That is $860 - 675 = 185$ kJ.

Note: If we use ΔH notation, we must insert a negative sign in front of the answer i.e. -185 kJ to show that energy was released. Here, the negative sign indicates that the reaction is exothermic and the equation can be written as



Now, let us consider another general reaction given as follows:



Using the bond energy values in Table 5.7, find out whether the reaction above is exothermic or endothermic.

Remember! That to break bonds for reactants, energy must be supplied (endothermic) and when bonds for products are formed, energy is released (exothermic).

Table 5.7: Sample bond energies

Bond	Energy used to break bond / released when bond is formed in kJ mol ⁻¹
A–A	435
B–B	497
A–B	463

Compare your work with the following solution.

To break the bond between A–A the amount of energy required = 435 kJ mol⁻¹

To break the bond between B–B the amount of energy required = 497 kJ mol⁻¹

The total amount of energy required = 932 kJ

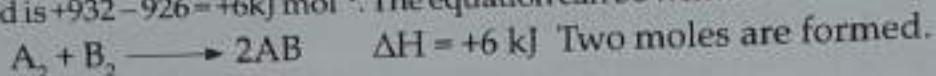
Bond breaking is an endothermic process. Therefore, the value should be assigned a positive sign i.e. +932 kJ mol⁻¹

The amount of energy released to form the two bonds between A – B = $463 \times 2 = 926 \text{ kJ mol}^{-1}$

Total amount of energy required = 926 kJ

Bond formation is an exothermic process. The value should be assigned a negative sign i.e. -926 kJ mol^{-1} .

Note that we get less energy when bonds are formed. We spent 932 kJ and got 926 kJ. We have 'lost' 6kJ of energy. This energy has been absorbed by the system. The energy absorbed is $+932 - 926 = +6 \text{ kJ mol}^{-1}$. The equation can be written as follows:



Therefore $\Delta H = \frac{6 \text{ kJ}}{2 \text{ mol}} \Delta H = +3 \text{ kJ/mol or } +3 \text{ kJmol}^{-1}$.

A reaction where less energy is released than supplied is an endothermic reaction. Note, that the energy released is less by 6 kJ for every 2(A–B) bonds formed.

When particles such as atoms combine to form molecules, they do so by forming covalent bonds while ions combine by forming ionic bonds. Once this has happened, energy is stored in the chemical bonds linking the atoms or ions. This energy stored in the bonds of the molecules of a substance is called **potential energy**. For example, when hydrogen atoms combine to form hydrogen molecules, energy is released in form of heat energy. The reaction is **exothermic**. Due to the energy released, the hydrogen molecules formed contain less energy and are said to be stable.



Bond formation is an exothermic process

To break the covalent bonds, energy must be supplied.



Breaking bonds is an endothermic process

Due to energy absorbed when separating the molecules, free atoms possess more energy than the molecules. Therefore, free atoms are highly unstable. This is why hydrogen does not exist as separate atoms. The energies required to break the covalent bonds of hydrogen molecules is exactly equal to that released when the separate atoms combine to form molecules. This obey the principle of law of conservation of energy. The energy required to break covalent bonds between atoms have been determined experimentally. These energies are called **bond dissociation energies**. Table 5.8 shows some of bond dissociation energies.

Table 5.8: Some bond dissociation energies

Bond	Bond energies (kJ mol^{-1})
C–H	413
C–C	346
N–H	389
H–H	436
Cl–Cl	242
H–Cl	431

Bond	Bond energies (kJ mol ⁻¹)
Br—Br	193
C—Cl	339
H—Br	365
C—Br	280

Notice from Table 5.8 that some bonds are stronger than others.

- (i) Which is the strongest bond from Table 5.8? Explain.
- (ii) Which is the weakest bond from Table 5.8? Explain.

The covalent bond between the hydrogen atoms is the strongest. This is because the hydrogen atoms are very small (i.e. the atomic radius is very small), therefore, the nuclei attract the shared pair of electrons very strongly. Hence, the bond requires a lot of energy to break. The atomic radius of chlorine atom is large. The attraction of the shared pair of electrons by the nuclei of chlorine atoms is relatively weak. Therefore, the bond is weak and requires less energy to break.

Now, let us see how bond energies are used to determine the enthalpy of formation of some compounds.

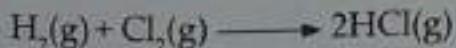
Enthalpy of formation

Enthalpy of formation is the enthalpy change that occurs when one mole of a substance is formed from its elements under standard conditions.

Enthalpy of formation of hydrogen chloride

Determine the bonds to be broken and the new bonds to be formed. We know that hydrogen chloride is made of hydrogen and chlorine atoms. We are also aware that hydrogen and chlorine are both diatomic gases. Their respective atoms are linked by strong covalent bonds. Therefore, the reaction needs energy to start it off. This energy is required to break the bonds of the reactants (endothermic). When products are formed, new bonds are formed between H and Cl atoms. Formation of bonds is an exothermic reaction. We are expected to find out from the reaction below whether breaking the bonds require more energy than the energy released during bond formation. Refer to bond energies in Table 5.8.

Step 1: First write the reaction equation as follows:



or



Step 2: Draw the energy level diagram for enthalpy of formation of HCl

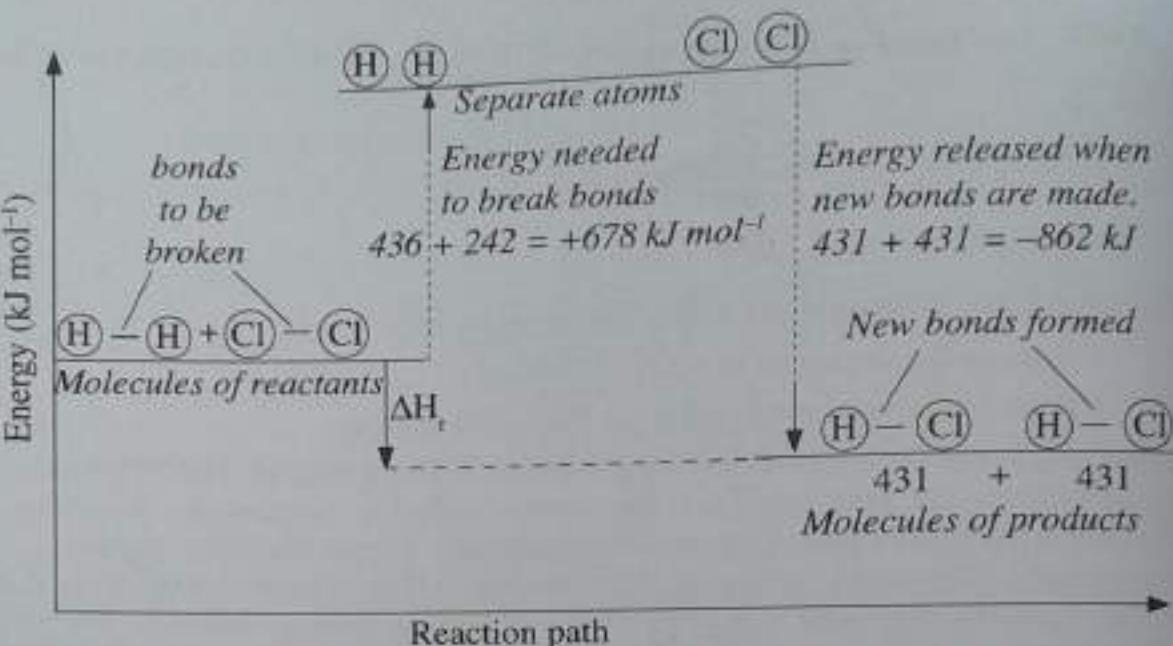


Fig 5.7: The reaction of hydrogen and chlorine involves first breaking of bonds of the reactants. Then formation of new bonds of products.

Step 3: Calculating the ΔH of formation of HCl

We start by looking at how many H – H and Cl – Cl bonds are broken and how many H–Cl bonds are formed. Then determine how much energy is spent to break these bonds. The total energy needed to break these bonds, is the energy needed to start off this reaction. We get this energy by adding up the bond energies as shown below.

$$\begin{aligned} \text{One H-H bond} &\longrightarrow 1 \times (\text{H-H}) \text{ bond dissociation energy} \\ &= 1 \times 436 = +436 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{One Cl-Cl bond} &\longrightarrow 1 \times (\text{Cl-Cl}) \text{ bond dissociation energy} \\ &= 1 \times 242 = +242 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Total energy needed} = 436 + 242 = +678 \text{ kJ}$$

Note: The +ve signs are necessary because breaking bonds is an **endothermic** process.

The total energy released during bond formation is obtained as follows:

$$\begin{aligned} \text{Two H-Cl bonds} &\longrightarrow 2 \times (\text{H-Cl}) \text{ bond dissociation energy} \\ &= 2 \times 431 = -862 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Total energy released} = -862 \text{ kJ}$$

Note: The -ve sign must be written in front of the number because bond formation is an **exothermic** process.

We got more energy when making new bonds than spent when breaking bonds. Heat of reaction, ΔH , = energy difference

$$\Delta H_r = \left(\text{sum of energy released when new bonds are formed} \right) - \left(\text{sum of energy needed to break bonds in reactants} \right)$$

$$\therefore \Delta H_r = 862 - 678 \\ = -184 \text{ kJ}$$

\therefore 184 kJ of energy is released when 2 moles of hydrogen chloride are formed.
Therefore, the enthalpy of formation for HCl is, $\frac{-184 \text{ kJ}}{2} = -92 \text{ kJ mol}^{-1}$

Practice exercise 5C

1. (a) Hydrogen and bromine react to form hydrogen bromide. Write an equation for the reaction.

(b) Energy to break H – H = 435 kJ

Energy to break Br – Br = 193 kJ

Energy to form H – Br = 365 kJ

(i) Calculate the overall enthalpy change for the reaction.

(ii) Is the overall reaction exothermic or endothermic? In terms of ΔH notation, insert the correct value in equation 1 (a) above.

2. Hydrogen burns in air to form steam.



(a) Which bonds are broken?

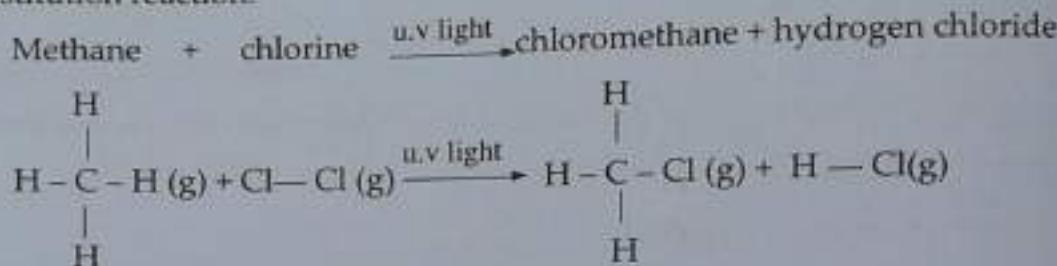
(b) Use the bond energies in the following table to calculate ΔH for the reaction.

Bond	Bond energy (kJ mol^{-1})
H – H	436
O = O	489
O – H	464

(c) Re-write the equation and include ΔH .

Determining the enthalpy of formation of chloromethane from methane gas and chlorine gas

Methane is the first member of the hydrocarbons homologous series called alkanes. Alkanes undergo substitution reaction where one or more of the hydrogen atoms of an alkane, in this case methane, can be substituted by a halogen atom i.e. chlorine in the presence of ultraviolet light to form chloromethane as shown below. This is an example of a substitution reaction.



- Is this an exothermic or endothermic reaction?

This reaction first involves breaking bonds of the reactants then formation of new bonds of the products as shown in Fig. 5.8.

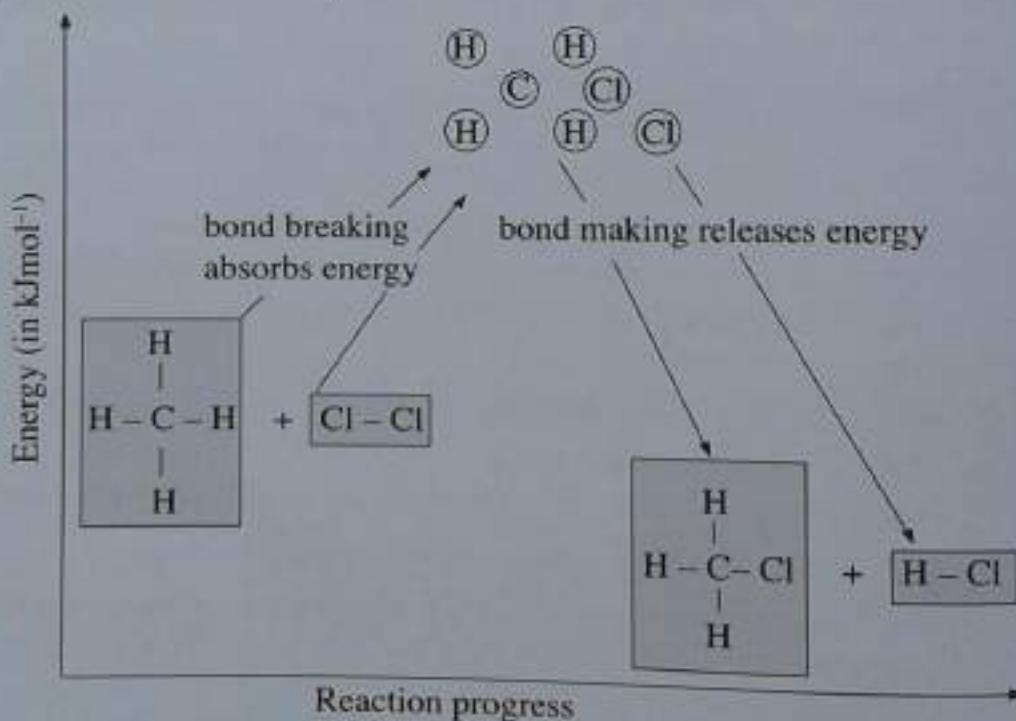


Fig. 5.8 Reaction of methane with chlorine

Note that:

- All the four C–H bonds in methane and one Cl–Cl are broken (endothermic).
 - When the products are formed, the following bonds are formed.
 - Three (3) C–H
 - One (1) C–Cl
 - One (1) H–Cl
- exothermic

Let us use the bond energies given in Table 5.8 to calculate ΔH for this reaction.

Reactants bonds broken

Four C – H = $4 \times 413 = + 1652$ kJ

One Cl – Cl = $1 \times 242 = + 242$ kJ

Total energy needed = + 1894 kJ

Products bonds formed

Three C – H = $3 \times 413 = - 1239$ kJ

One C – Cl = 1×339

= - 339 kJ

One H – Cl = $1 \times 431 = - 431$ kJ

Total energy given out = - 2009 kJ

Enthalpy of formation = $\left(\begin{array}{l} \text{sum of energy released} \\ \text{when bonds are broken.} \end{array} \right) - \left(\begin{array}{l} \text{sum of energy needed} \\ \text{to break bonds.} \end{array} \right)$

$$\therefore \Delta H = 2009 - 1894$$

$$= -115\text{kJ}$$

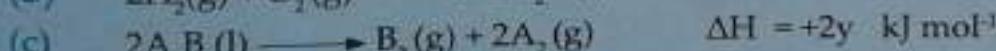
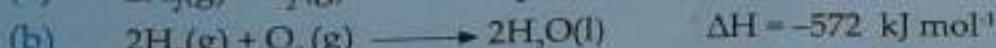
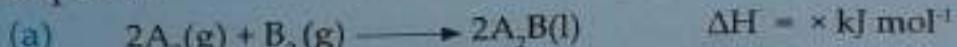
The reaction is therefore exothermic.



Practice exercise 5D

- Which of the following reactions are exothermic and which ones are endothermic?

Explain.



- Ethane can be halogenated using bromine to form 1,2-dibromoethane in presence of sunlight. Use the values given in Table 5.8 to calculate the enthalpy change, ΔH of this reaction.

Energy level diagrams showing activation energy

For a reaction to take place, energy must be supplied to start off the reaction.

This energy is called **activation energy** (E^*).

Activation energy (E^*) is the minimum amount of energy required for a reaction to take place.

Can you imagine anybody placing a sufuria with water on a cooker without lighting the fuel? Will she or he manage to cook? What do you think lighting the fuel does. Study the energy level diagram for burning charcoal in fig 5.9.

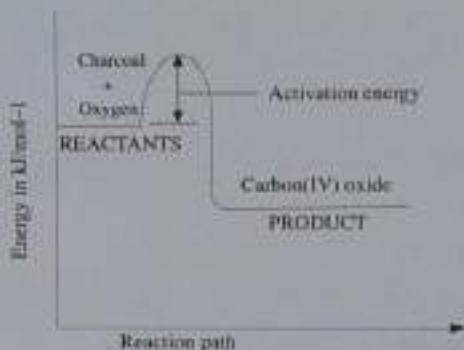


Fig. 5.9: Energy level diagram showing activation energy for(exothermic reaction)

The energy level diagram above shows that we need certain amount of energy to get the reaction started. This energy is called **activation energy**. Without activation energy, reaction cannot proceed. This explains why we need to light the fuel before we can cook. Lighting provides activation energy needs to initiate the reaction between carbon and oxygen, which provides heat used during cooking i.e.



We can also draw an energy level diagram of an endothermic reaction as shown in fig. 5.10 below. The diagram shows that dissolution of potassium nitrate is an endothermic process and activation energy is needed for reaction to begin.

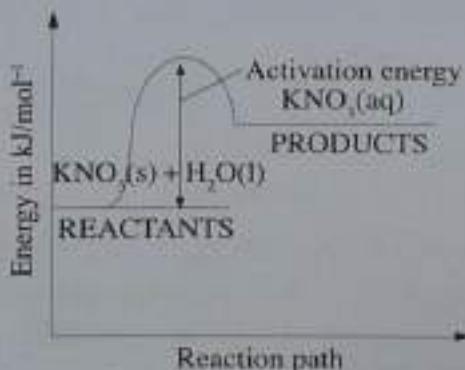


Fig. 5.10: Energy level diagram showing the activation energy endothermic reaction

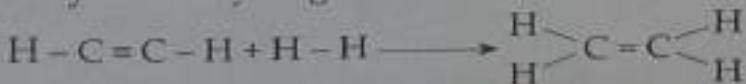
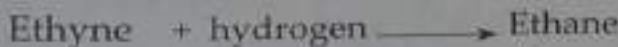
Practice exercise 5E

1. Define activation energy.
2. Draw energy level diagram showing activation energy for:
 - (a) Burning of candle.
 - (b) Photosynthesis.

Revision Exercise 5

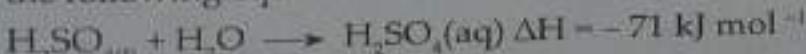


- (a) Differentiate between endothermic and exothermic reactions.
 (b) List five examples of endothermic and exothermic reaction.
- A student from Lake secondary school wanted to determine enthalpy of combustion when a hydrocarbon with formula C_6H_{14} was burnt. The following are the results of the experiment done.
 Mass of water = 100 g
 Initial temperature = $17.0\text{ }^{\circ}\text{C}$
 Final temperature = $57.0\text{ }^{\circ}\text{C}$
 Mass of hydrocarbon burned = 0.43 g
 Specific heat capacity = $4.18\text{ kJ kg}^{-1}\text{ K}^{-1}$
 - Name the hydrocarbon used.
 - Write a balanced equation of the burning of the hydrocarbon.
 - Calculate the heat given out in kJ when 0.43 g of carbon is burn in air.
 - What is the mass of 1 mole of the hydrocarbon.
 - Calculate the number of moles of the compound that was burnt.
- Explain the meaning of the following symbols.
 - ΔH_f^\ominus
 - ΔH_c^\ominus
- Draw an energy level diagram for an exothermic reaction and endothermic reaction.
- List the conditions at standard enthalpy.
- Calculate the overall energy released during hydrogenation of ethyne to ethene. Use the bond energy given below.



Bond	Energy (kJ mol^{-1})
H - H	435
C - H	413
C ≡ C	835
C - C	611

- Dissolving concentrated sulphuric acid is an exothermic process as shown in the following equation.



Draw an energy level diagram for dissolution of concentrated sulphuric acid.

Topic 6:

Alkanols

Success criteria

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

- (a) Identify the functional group of alkanols.
- (b) Draw and name the structure of the first ten unbranched alkanols.
- (c) Write the molecular formula of alkanols given the number of carbon atoms.
- (d) Explain the physical properties of alkanols.
- (e) Describe the chemical reactions of alkanols.
- (f) Classify alkanols as primary, secondary and tertiary.
- (g) Describe methods of preparing alkanols.
- (h) Explain uses of ethanol.



In Form two, we learnt that hydrocarbons are compounds which contain carbon and hydrogen only. We also learnt that the hydrocarbons are grouped into families which form homologous series. The members in the same homologous series have similar physical and chemical properties. Some of the homologous series that we learnt about include:

- Alkanes — saturated hydrocarbons with a general formula C_nH_{2n+2} .
- Alkenes — unsaturated hydrocarbons with a double bond and a general formula C_nH_{2n} .

Alkynes — are unsaturated hydrocarbons with a triple bond with a general formula C_nH_{2n-2} where $n = 1, 2, 3, \dots$

We are going to learn about other homologous series which contain oxygen in addition to carbon and hydrogen, that is, alkanols and alkanoic acids.

Alkanols as a homologous series

- Members of this series contain -OH as the functional group.
- All the names of alkanols end with -ol.
- They have a general formulae of ROH or $C_2H_{2n+1}OH$.
- Each member differs from the preceding one by a $-CH_2-$ group (methylene group).
- They show gradual change in physical properties such as melting points and boiling points as the hydrocarbon chain represented by R gets bigger.
- They have similar physical and chemical properties.

6.1 Functional groups of alkanols

Alkanols are organic compounds. They are also known as **alcohols**. The alkanols form a homologous series with -OH as the functional group. They may be regarded

as being derived from an alkane by replacing one of the hydrogen atoms with an -OH group. Alkanols are saturated organic compounds.

A functional group is an atom or combination of atoms which gives an organic molecule its distinctive and characteristic properties. The functional group is linked to the concept of a homologous series. Homologous series is a group of molecules with the same general formula and the same functional group.

Any molecule which contains the functional group -OH is a member of the alkanol family. Usually it is restricted to cases where the C atom attached to the -OH has no other heteroatom (atom other than C or H) attached to it.

Class activity 1

Using your knowledge of naming of alkanes and their condensed formulae:

- Write the first 5 names of alkanols.
- Identify the functional group of the alkanols named in (a) above.

6.2 General formula and nomenclature of alkanols

The general formula of alkanols is ROH, where R is an alkyl group. Alkyl group is the name given to a group of atoms remaining when one of the hydrogen atom of an alkane is removed. For example,

When we remove one hydrogen atom from:

- Methane (CH_4), we get methyl (CH_3) group.
- Ethane (CH_3CH_3), we get ethyl (CH_2CH_3) group and
- Propane ($\text{CH}_3\text{CH}_2\text{CH}_3$), we get propyl ($\text{CH}_3\text{CH}_2\text{CH}_2$) group.

In this case methyl, ethyl and propyl are examples of alkyl groups. They are represented by letter R in abbreviated form as ROH.

To get the number of carbon and hydrogen atoms represented by R in the general formula, we use another formula

$\text{C}_n\text{H}_{2n+1}\text{OH}$, where n can be 1, 2, 3, 4, ...

Naming alkanols

The names of members of this homologous series are obtained by replacing the suffix -e of the corresponding alkane by -ol. For example, when n = 1 in alkanes, the name is **methane**. In this example, if we replace the suffix -e in methane with -ol, the name becomes **methanol**. It is the first member of the family of alkanols.

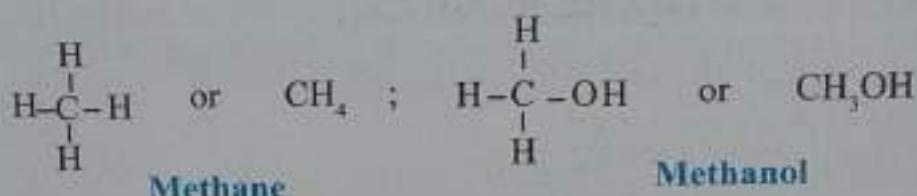
Class activity 2

Using the general formula, $\text{C}_n\text{H}_{2n+1}\text{OH}$, for alkanols, write the condensed formula for the first six members of alkanols. The first one has been done for you as an example.

1. CH_3OH - Methanol

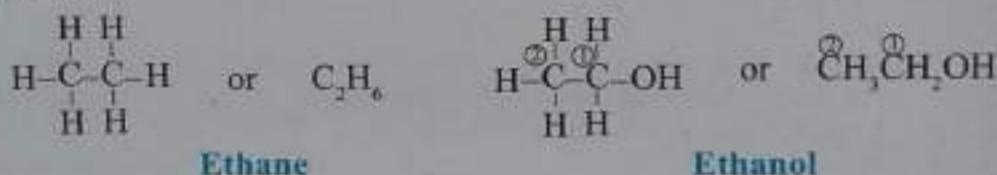
We can use the general formula $C_nH_{2n+1}OH$ to also determine the structural formula of each member of this family as follows. For methanol $n = 1$, we substitute in the formula to get $C_1H_{(2 \times 1)+1}OH$ which gives CH_3OH which gives CH_3OH . This is the molecular formula of methanol.

Methanol is almost the same as methane in structure. The difference is that we replace one of the hydrogen atoms in methane with hydroxyl group, $-OH$.

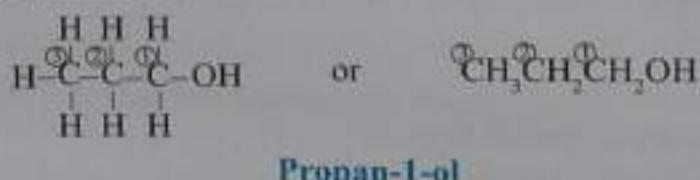


Note: The hydroxyl group can replace any of the four hydrogen atoms in methane.

When $n = 2$, the molecular formula becomes $C_2H_{(2 \times 2)+1}OH$ or C_2H_5OH . The name of this alkanol is derived from ethane, where one hydrogen atom is replaced by $-OH$ as shown below.



When $n=3$, the molecular formula will be C_3H_7OH . The name is propan-1-ol and the structure is as shown below.



In case of two similar alkyl groups present in a molecule the prefix di- is used, prefix tri- is used for three similar alkyl groups, while tetra - is used for four similar alkyl groups. The number of carbon atoms gives alkanol its name which is derived from corresponding parent alkane.

For the first two members of the alkanol family we do not indicate the position of the functional group in the structure. However, from third member of homologous series of alkanols, the position of the carbon atom to which the functional group is attached is indicated. When numbering the carbon chain ensure that the carbon atom attached to functional group ($-OH$) is assigned lowest possible value.

Practice exercise 6A

1. Write the formula of alkanols where $n = 6, 7, 8, 9$ and 10 .
2. Name the alkanols in (1) above.

Molecular and structural formula of alkanols

Molecular formula shows the actual number of atoms of each element in a molecule, with any functional group present. Structural formula shows the arrangement of atoms carbon by carbon, with the attached hydrogens and functional groups. There is also skeletal formula which show the bonds of the carbon skeleton only, with any functional groups but, the hydrogen and carbon atoms are not shown.

Table 6.1: Names, formulae and structures of some alkanols

Name	Molecular formula	Structural formula
Methanol	CH_3OH	$ \begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{OH} \\ \\ \text{H} \end{array} $
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	$ \begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H} - \text{C} - & \text{C} - \text{OH} \\ & \\ \text{H} & \text{H} \end{array} $
Propan-1-ol	$\text{C}_3\text{H}_7\text{OH}$	$ \begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H} - \text{C} - & \text{C} - & \text{C} - \text{OH} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array} $
Butan-1-ol	$\text{C}_4\text{H}_9\text{OH}$	$ \begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H} - \text{C} - & \text{C} - & \text{C} - & \text{C} - \text{OH} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array} $
Pentan-1-ol	$\text{C}_5\text{H}_{11}\text{OH}$	$ \begin{array}{ccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & \\ \text{H} - \text{C} - & \text{C} - & \text{C} - & \text{C} - & \text{C} - \text{OH} \\ & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array} $
Hexan-1-ol	$\text{C}_6\text{H}_{13}\text{OH}$	$ \begin{array}{cccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H} - \text{C} - & \text{C} - \text{OH} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array} $
Heptan-1-ol	$\text{C}_7\text{H}_{15}\text{OH}$	$ \begin{array}{cccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & & \\ \text{H} - \text{C} - & \text{C} - \text{OH} \\ & & & & & \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array} $

Octan-1-ol	$C_8H_{17}OH$	$ \begin{array}{ccccccccc} & H & H & H & H & H & H & H & H \\ & & & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & & & \\ & H & H & H & H & H & H & H & H \end{array} $
Nonan-1-ol	$C_9H_{19}OH$	$ \begin{array}{cccccccccc} & H & H & H & H & H & H & H & H & H \\ & & & & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & & & & \\ & H & H & H & H & H & H & H & H & H \end{array} $
Decan-1-ol	$C_{10}H_{21}OH$	$ \begin{array}{cccccccccc} & H & H & H & H & H & H & H & H & H \\ & & & & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & & & & \\ & H & H & H & H & H & H & H & H & H \end{array} $

Table 6.2: Condensed formula and the skeletal formula

Name	Condensed formula	Skeletal formula
Methanol	CH_3OH	$\diagup OH$
Ethanol	CH_3CH_2OH	$\begin{array}{c} \diagup \\ \diagdown \end{array} OH$
Propan-1-ol	$CH_3CH_2CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \end{array} OH$
Butan-1-ol	$CH_3(CH_2)_2CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \\ \diagdown \end{array} OH$
Pentan-1-ol	$CH_3(CH_2)_3CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \end{array} OH$
Hexan-1-ol	$CH_3(CH_2)_4CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \\ \diagdown \end{array} OH$
Heptan-1-ol	$CH_3(CH_2)_5CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \end{array} OH$
Octan-1-ol	$CH_3(CH_2)_6CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \\ \diagdown \end{array} OH$
Nonan-1-ol	$CH_3(CH_2)_7CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \\ \diagdown \\ \diagup \end{array} OH$
Decan-1-ol	$CH_3(CH_2)_8CH_2OH$	$\begin{array}{c} \diagup \\ \diagdown \\ \diagup \end{array} OH$

Note:

The IUPAC rules demand that the position of the -OH group be included in the name. This is why the number 1 is included in propan-1-ol to show that functional group is attached to fixed or terminal carbon of the straight-carbon chain. The same applies to all other alkanols. These alkanols whose molecular formulae and structural formulae end with an -OH group are called **primary** alkanols, that is the carbon carrying the -OH group is attached to only one other carbon atom.

6.3 Classification of alcohols

Alcohols can be classified as primary, secondary or tertiary. The classification is based on the location of the hydroxyl group.

Primary alcohol

If the hydroxyl group is attached to a carbon atom attached to only one other carbon atom, then the alcohol is a primary alkanol (1°).

Example

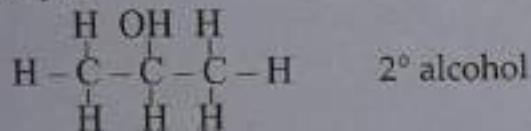


Butan-1-ol

Secondary alcohol

When the hydroxyl group is attached to a carbon atom which is bonded to two other carbon atoms, then the alcohol is called a secondary alcohol (2°).

Example

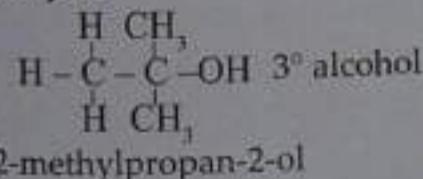


Propan-2-ol

Tertiary alcohol

If the carbon atom bonded to the hydroxyl group is also bonded to three other carbon atoms, then the alcohol is tertiary alcohol.

Example



The structural differences between primary, secondary and tertiary alcohols cause differences in their chemical behaviors. Alcohols molecules may contain one, two, three or many hydroxyl groups.



Practice exercise 6B

1. Define the following terms
 - (a) Molecular formula.
 - (b) Homologous series.
2. State the three classes of alkanol.

6.4 Preparation of ethanol

(a) Preparing ethanol by fermentation of sugars

Experiment 6.1

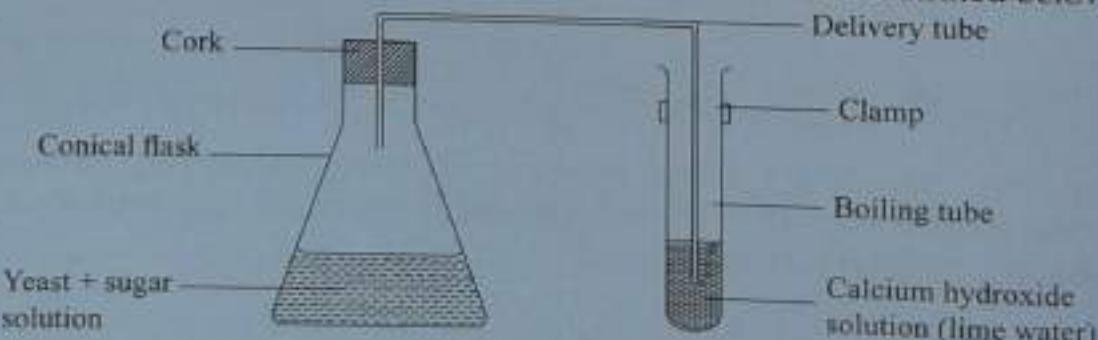
Aim: To prepare ethanol in the laboratory by fermentation of glucose.

Requirements

- Delivery tube
- Cork
- Conical flask
- Boiling tube
- Glucose or any other sugar solution
- Yeast
- Calcium hydroxide solution

Procedure

1. Place sugar solution mixed with yeast in a conical flask.
2. Connect a delivery tube with a tight fitting cork onto the conical flask and boiling tube containing calcium hydroxide solution as illustrated below.



3. Keep the set up in an undisturbed place for about 3 to 4 days.
 - What do you observe after 4 days? Explain your observations.
 - What is the role of yeast in this process?

- What do you conclude from the above observations?
 - What happens to the calcium hydroxide after 4 days?
 - What gas is produced in the above experiment?
4. Pure ethanol is obtained by fractional distillation of the mixture formed.

Discussion

The reactions whereby sugars are converted to alcohol and carbon dioxide are referred to as **fermentation reactions**. Ethanol is prepared in the laboratory by the fermentation of glucose or any other sugar solution using enzymes, in this case, the yeast. Bacteria and yeast cells produce enzymes, that catalyse reactions in the organic materials. The process of fermentation can be summarised as follows:

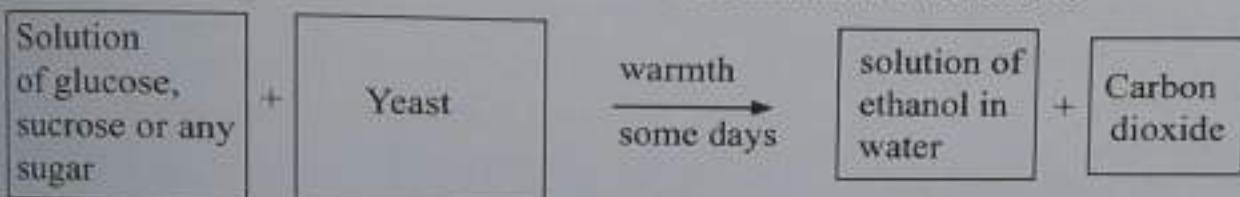
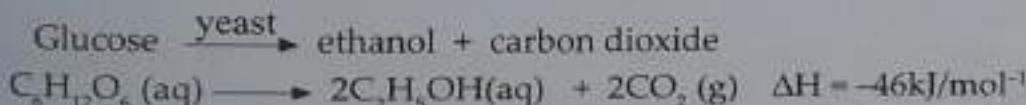


Fig 6.1 Summary of the process of fermentation

Glucose is finally converted to ethanol and carbon dioxide. The equation for the reaction can be summarised as follows:

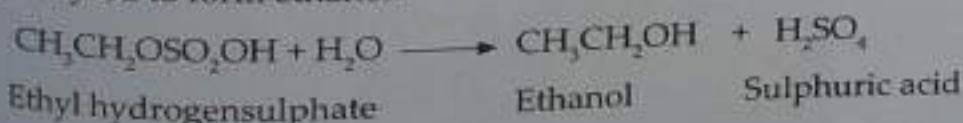


(b) From reaction between ethene and steam

Ethanol is prepared by hydrating ethene in presence of acid catalyst. Alcohols are produced industrially by hydrating alkenes in the presence of an acid catalyst such as concentrated sulphuric acid. Cold concentrated sulphuric acid reacts with ethene as shown below:



When cold water is added and the mixture warmed the ethyl hydrogen sulphate is hydrolysed to form ethanol.

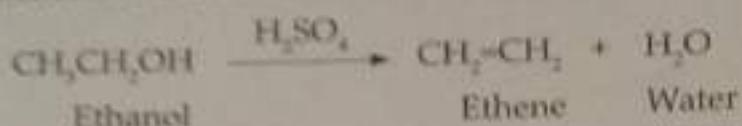


Overall reaction



Reactivity of alkanols and the reaction products are determined by the location of the hydroxyl groups. The reactions are reversible, because alkanols will undergo elimination reaction. When alkanols undergo elimination reactions, the elements of

water are removed (dehydration). This reaction is one of the methods used to prepare alkenes. When ethanol is heated in presence of an acid catalyst, ethene is formed.



Secondary and tertiary alcohols are more easily dehydrated than primary alcohols.

Experiment 6.2

Aim: To prepare Kachasu brew.

Requirements

- Germinated maize
- Winnowing basket
- Sugar
- Water
- Drum and small tins
- Firewood and matchstick
- Tin
- Pipe

Procedure

1. Half germinated maize is dried and then pounded. This is followed by winnowing to remove the wastes.
2. The mixture of fine half-germinated maize and sugar are then immersed in cold water and left for some days for fermentation to take place.
3. Water is then drained from the mixture.
4. Then a fire is prepared with firewood to heat up the drained water in the drum up to its boiling point.
5. This allows the alcohol vapour to escape from the drum and passes through a pipe attached to it.
6. Alcoholic vapour is collected in a tin. This changes its state back to water to form Kachasu.



Kachasu brewed in a drum and collected in a tin

Remember! Kachasu is an alcoholic drink. Like other alcohols, it affects ones health. We should avoid taking Kachasu brew!

6.5: Properties of alkanols

Generally alkanols have neutral pH. They are poor conductors of electricity. The first three are miscible in water. The rest are immiscible. Table 6.3 shows the trends in physical properties of alkanols.

Physical properties of alkanols

- The melting point and boiling points of alkanols increases down the homologous series.
- Solubility of alkanols decreases down the group.
- Density of alkanols increases down the group.
- The higher alkanols containing 4 to 10 carbon atoms are some how viscous.
- Volatility decreases down the group.

Table 6.3: Trends in physical properties of alkanols

Name	Melting point °C	Boiling point °C	Density g cm ⁻³	Solubility in water
Methanol	-98	65	0.791	Soluble
Ethanol	-117	78.5	0.789	Soluble
Propan-1-ol	-127	97	0.803	Soluble
Butan-1-ol	-89.5	117	0.810	Fairly soluble
Pentan-1-ol	-79	138	0.814	Slightly soluble
Hexan-1-ol	-55.6	157	0.814	Slightly soluble
Heptan-1-ol	-34	176	0.822	Slightly soluble
Octan-1-ol	-15	195	0.825	Slightly soluble
Nonan-1-ol	-7	212	0.827	Slightly soluble
Decan-1-ol	6	228	0.829	Slightly soluble

The melting and boiling points of alkanols increase with **increase in relative molecular mass**. As the molecular mass increases, the intermolecular forces of attraction between molecules increase. As these forces increase, more energy is needed to overcome them.

This increases the melting and boiling points. The intermolecular forces include **hydrogen bonding** and **van der Waals forces**. There is **hydrogen bonding** between the oxygen atom and hydrogen atom that forms when two molecules of alkanols come close to each other.

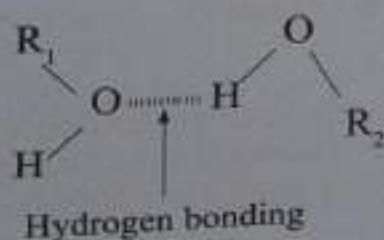


Fig. 6.2: Two molecules of alkanol joined by hydrogen bonding

Because of these hydrogen bonds, alkanols have higher melting points than hydrocarbons of the same number of carbon atoms. In order to break the hydrogen bonds, more heat energy is required hence raising their melting point. More energy is also needed to make the constituent alkanol molecule to leave the liquid and form a gaseous vapour. So, the boiling points are also much higher.

The densities increase with increase in relative molecular mass. This is because of the increase in intermolecular forces of attraction between molecules making them very close to each other. This reduces the volume occupied by the molecule.

The alcohols show a steady change in physical properties that occurs when moving up the homologous series. The hydroxyl group (OH) affects the physical properties of any molecule that it is part of. For example ethanol with relative molecular mass of 46 is less volatile and a liquid at room temperature compared to other compounds with similar relative molecular mass like propane with a relative molecular mass of 50.5 which is gaseous at room temperature.

Table 6.4 Comparison of R.M.M and boiling points of different compounds.

Compound	R.M.M	Boiling points
Ethanol	46	351
Chloromethane	50.5	249
Propane	44	231

The cause of ethanol's anomalous properties is hydrogen bonding that forms between OH groups of adjacent ethanol molecules, giving ethanol (alkanols) relatively high intermolecular forces therefore its low volatility. The influence of the OH group is less significant up the homologous series.

Hydrogen bonding between OH groups also has an effect on the viscosity of alcohols, particularly those with more than one OH group in their molecule. For example ethanol has viscosity of 1.06×10^{-3} Nsm $^{-2}$ at 298K, about the same as water, but propane -1, 2, 3 -triol (glycerin) is very thick and sticky with viscosity of 942×10^{-3} Nsm $^{-2}$ at the same temperature, because of interaction between its molecules which carry three OH groups.



Practice exercise 6C

1. Explain the trends in melting and boiling points of the first ten alkanols.
2. Compare the melting and boiling points of alkanols to those of alkanes with the same number of carbon atoms. Give reasons for your answer.

Chemical properties of alkanols

Alkanols form a homologous series with similar chemical properties. Lets carry out the following experiment to investigate the chemical properties of ethanol.

Experiment 6.3

Aim: To determine the chemical properties of ethanol.

Requirements

- Bottle tops/evaporating basins
- Test tubes
- Beaker
- Universal indicator
- Blue and red litmus papers
- Sodium metal
- Concentrated sulphuric acid
- Ethanoic acid
- Acidified potassium dichromate (VI)
- Acidified potassium manganate (VII)

Procedure

Table 6.5: Investigation of chemical properties of ethanol

Procedure	Observations	Conclusions
1. Place a few drops of ethanol into a bottle top and ignite.		
2. Place about $2\text{-}3 \text{ cm}^3$ of ethanol in a test tube. Add about 3 drops of universal indicator. Test with blue and red litmus papers.		
3. Place about $2\text{-}3 \text{ cm}^3$ of ethanol in a test tube. Add a very small piece of sodium metal. Test for any gas produced with a burning splint.		
4. Place about $2\text{-}3 \text{ cm}^3$ of ethanol in a test tube. Add an equal amount of ethanoic acid. Add two drops of concentrated sulphuric acid and heat. Pour the resulting mixture into about 70 cm^3 of water in a beaker. Smell the product.		
5. Place about $2\text{-}3 \text{ cm}^3$ of ethanol in a test tube. Add about 5 cm^3 of acidified potassium manganate(VII) to the test tube. Warm gently.		
6. Repeat step 5 but add acidified potassium dichromate(VI).		

Questions

- What colour changes occurred on the indicators?
- What is the pH of ethanol?
- Which gas is produced when sodium reacts with ethanol?

Discussion

(a) Combustion of ethanol

When ethanol is ignited in plentiful supply of air or oxygen, it burns with almost an invisible blue flame to produce carbon dioxide and water.



(b) Reaction of ethanol with sodium

When sodium metal reacts with ethanol, it forms a compound called sodium ethoxide. Effervescence occurs and a colourless gas which burns with a 'pop' sound is produced. The gas is hydrogen. The reaction is similar to the reaction of sodium with water but is much slower and less vigorous.



Ethanol also reacts with other metals such as potassium to produce the corresponding ethoxide and hydrogen gas.

Note: This reaction is also possible with other alkanols. The general equation of the reaction of alkanols with metals is:

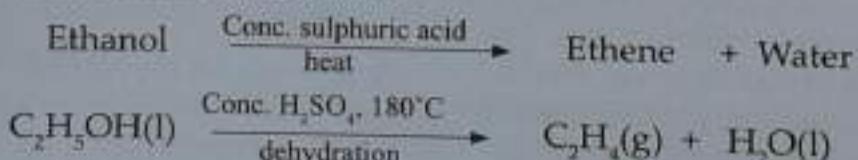


Where, R – alkyl group of the reacting alkanol.

M – metal such as potassium or sodium.

(c) Reaction of ethanol with concentrated sulphuric acid

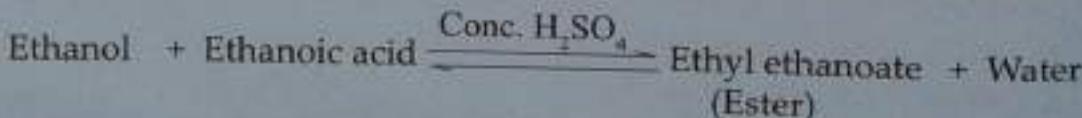
Concentrated sulphuric acid reacts with ethanol at 180°C to form ethene and water. This is a **dehydration** reaction. This is the reverse of hydration reaction used to produce ethanol from ethene.



Note: At 140°C another organic compound known as **ether** is formed.

(c) Ester formation

Alkanols react with alkanoic acids (to be discussed later in detail) to form compounds called **esters**. For example, ethanol reacts with ethanoic acid in the presence of a few drops of concentrated sulphuric acid (catalyst) to form a substance with a characteristic sweet and fruity smell called **ethyl ethanoate**. This substance is an ester.





The process of ester formation is called **esterification**. Esterification is reversible reaction, the ester formed can be converted back to the parent alkanol and alcanoic acid by hydrolysis process.

Note: The name of ester is derived from the reactants; in this case, the respective alkanol and alcanoic acid. In our example above; the name comes from ethanol and ethanoic acid respectively.

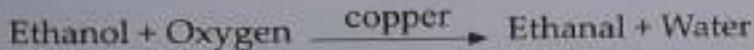
6.6 Oxidation of ethanol

(a) Reaction of ethanol and atmospheric oxygen - combustion

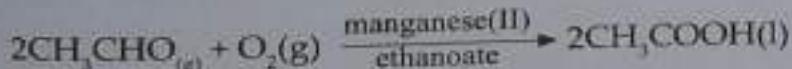
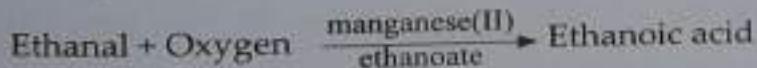
Ethanol like all alcohols undergoes oxidation when burnt in plentiful supply of air or oxygen. It burns with a smokeless flame to produce carbon dioxide and water.



Oxidation can also be carried out in two stages by passing alkanol e.g ethanol as vapour with air over heated copper catalyst in the first stage.



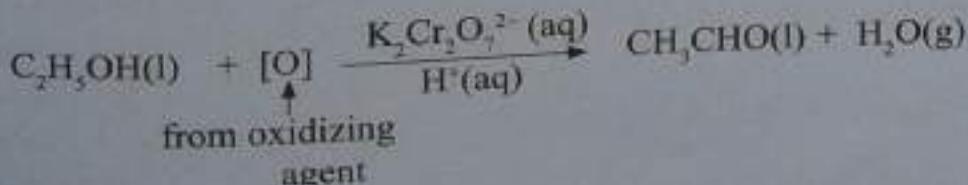
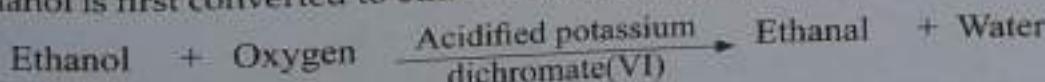
In second stage, manganese(II) ethanoate is used as a catalyst.



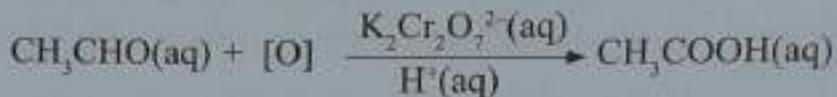
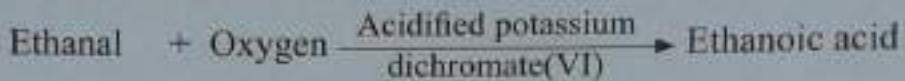
(b) Oxidation of ethanol using oxidising agents

Potassium dichromate(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$) and potassium manganate(VII) are the oxidising agents. When acidified potassium dichromate(VI) is added to ethanol, the colour changes from orange to green. When acidified potassium manganate(VII) (KMnO_4) is added to ethanol, the purple colour changes to colourless. They oxidise ethanol to ethanoic acid. The oxidation of ethanol is a two-step process.

- Ethanol is first converted to **ethanal**. This is a slow process.



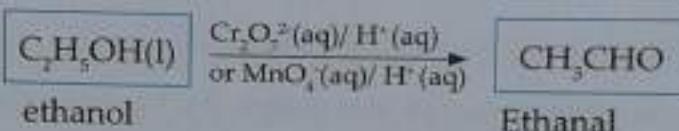
2. Then rapid conversion of ethanal to ethanoic acid.



Note:

- If ethanol is allowed to come into contact with air, it can be oxidised by atmospheric oxygen to ethanoic acid. This dilute ethanoic acid is commonly referred to as **vinegar**. The souring of ethanol was the original method of making vinegar.
- Oxygen from the air can slowly oxidise ethanol in beer. If the bottle is not tightly corked and a lot of carbon dioxide escapes, ethanol is oxidised making the beer go 'flat'.

Summary of reaction of ethanol



Summary of ethanol oxidation



You can control how far the alcohol is oxidized by controlling the reaction conditions.

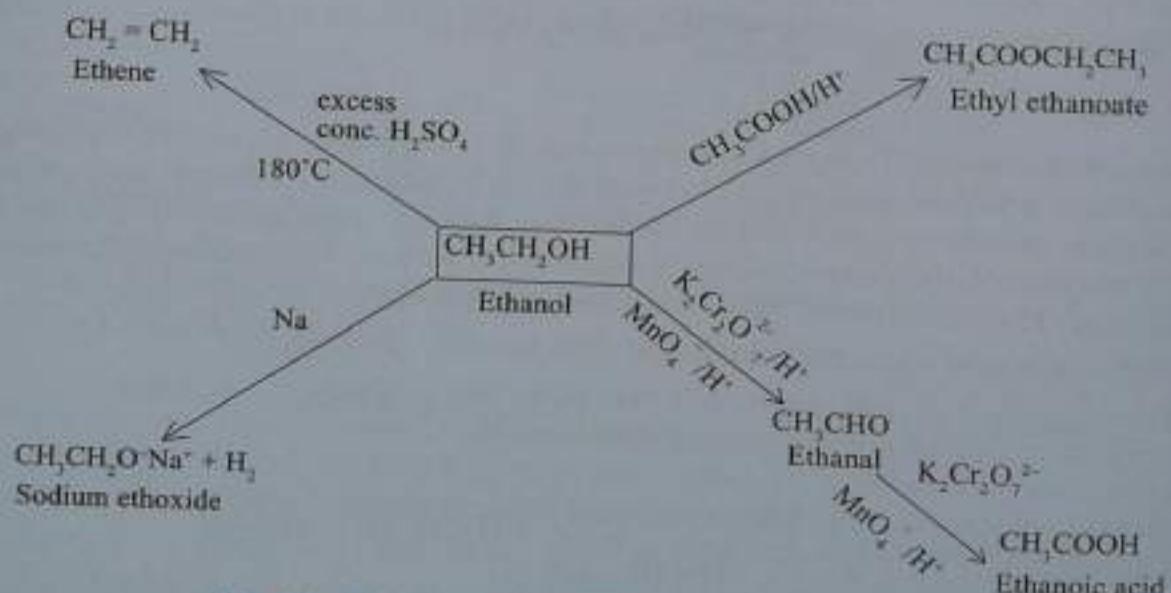


Fig. 6.3: Flow chart showing some of the reactions of ethanol

Uses of ethanol

1. Used as a solvent e.g it is a good solvent for iodine.
2. Used in the manufacture of varnishes, ink, glues and paints.
3. Used in the manufacture of deodorants, perfumes, this is because it evaporates quickly.
4. Ethanol is used in alcoholic drinks, e.g beer, wines and spirits.
5. As an antiseptic in specified concentrations.
6. As a fuel when it is blended with gasoline to form gasohol. On small scale, ethanol in form of methylated spirit is used in spirit lamps.
7. Moderate consumption of alcohol has numerous health benefits such as greater protection against heart diseases, decrease common cold infections and improvement in factors that influence blood clotting.

Dangers of excessive consumption of alcoholic drinks

1. Alcoholism (addiction) which can destroy physical and emotional health.
2. Causes of some cancers are directly attributed to excess alcohol consumption which include: liver cancer, mouth cancer, pharynx, esophagus and pancreatic cancers.
3. Cardiac problems, people who drink excessively can develop high blood pressure. Heat muscle damage as a result of drinking too much alcohol can cause fatal heart failure or stroke.
4. Miscarriages. Pregnant women can suffer miscarriages if they continue to take alcohol or give birth to babies that have fetal alcohol syndrome.
5. Suicide. Alcohol as depressant can influence one to commit suicide or suffer serious injury.
6. Liver cirrhosis, this is a disease associated with long-term alcohol abuse.
7. Risky sexual behaviours leading to unwanted pregnancy, HIV and AIDS and other sexually transmitted infections.
8. Loss of employment leading to poverty.

Revision Exercise 6



1. How does the reactivity of sodium with ethanol compare with the reaction of sodium with water? Name the gas produced each case?
2. Write a chemical equation for the reaction between ethanol and ethanoic acid in the presence of concentrated sulphuric acid.
3. Explain using an equation what happens when ethanol is burnt in air.
4. State the physical properties of ethanol.
5. List three uses of ethanol.
6. Draw the structures of:
 - (a) Octan-1-ol.
 - (b) Hexan-1-ol.
7. Write the molecular formula and draw the structures of:
 - (a) Pentan-1-ol.
 - (b) Heptan-1-ol.
8. Why is it dangerous to drink methylated spirit?
9. Ethanol (C_2H_5OH) can be made by fermentation of glucose ($C_6H_{12}O_6$)
 - (a) Write a balanced equation for the fermentation of glucose.
 - (b) Yeast must be added to glucose solution in order for fermentation to occur. Explain why yeast is needed.
 - (c) If the temperature during fermentation is increased to $70^\circ C$, the reaction slows down and then stops completely. Explain why this happens.
 - (d) An increase in temperature from $25^\circ C$ to $35^\circ C$ will increase the rate of reaction. Explain this using collision theory of particles.
10. Methanol, (CH_3OH) and ethane (CH_3CH_3), have almost the same molecular mass. Explain why the boiling point of methanol is $65^\circ C$ while that of ethane is $-88.6^\circ C$.

Topic 7:

Alkanals and Alkanones

Success criteria

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

- (a) Identify the functional groups of alkanals and alkanones.
- (b) Draw and name the structures of the first five alkanals and alkanone.
- (c) Describe the sources and properties of alkanals and alkanones.
- (d) Carry out a test to distinguish alkanals from alkanones.
- (e) Describe the uses of alkanals and alkanones.



Alkanals and alkanones molecules are characterized by the presence of a carbonyl group. A carbonyl group consists of an oxygen atom doubly bonded to a carbon atom, $\text{C}=\text{O}$.

Carbonyl group is one of the most important functional groups in organic chemistry and biochemistry due to its capability to undergo wide variety of reactions. This group is present in alkanals (also called aldehydes) and alkanones (also called ketones). The carbon atom of the carbonyl group must be connected to two other atoms or groups.

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

7.1 Alkanals

The general formula of alkanals is RCHO . Where R represents an alkyl group e.g. CH_3 , CH_3CH_2 , $\text{CH}_3\text{CH}_2\text{CH}_2$ - except in methanal. In methanal, R represents hydrogen (H).

Nomenclature of Alkanals

The name of the alkanal is derived from the parent alkane with same number of carbon atoms. Then the suffix '-e' from the parent alkane is replaced by suffix '-al'.

The longest continuous carbon chain is numbered such that the carbon which is in the carbonyl group is always number 1.

Table 7.1: Names, formulae and structures of the first five alkanals

Name	Condensed formula	Structural formulae	Molecular formulae
Methanal	HCHO	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$	HCHO
Ethanal	CH_3CHO	$\begin{array}{c} \text{H} & \text{O} \\ & \parallel \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & & \\ \text{H} & & \end{array}$	CH_3CHO

Name	Condensed formula	Structural formulae	Molecular formulae
Propanal	$\text{CH}_3\text{CH}_2\text{CHO}$	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{O} & \\ & & & \parallel & \\ \text{H}- & \text{C} & - & \text{C} & - \text{H} \\ & & & & \\ & \text{H} & \text{H} & & \end{array}$	$\text{C}_2\text{H}_5\text{CHO}$
Butanal	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{H} & \text{O} \\ & & & & \parallel \\ \text{H}- & \text{C} & - & \text{C} & - \text{C} - \text{H} \\ & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{C}_3\text{H}_7\text{CHO}$
Pentanal	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{O} \\ & & & & & \parallel \\ \text{H}- & \text{C} & - & \text{C} & - & \text{C} - \text{C} - \text{H} \\ & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{C}_4\text{H}_9\text{CHO}$

7.2 Alkanones

The general formula of alkanones is $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}'$, where R and R' are alkyl groups that have the same or different numbers of carbon atoms.

Nomenclature of alkanones

The parent name of the alkanones is derived from corresponding alkane with similar number of carbon atom. The suffix '-e' from the parent alkane is replaced by the suffix '-one'. The numbering of the carbon atoms of alkanones begins at the end nearer to the carbonyl group. For example, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ Pentan-2-one

For alkanones with five or more carbon atoms, the number of the carbon attached to the carbonyl group is given.

Table 7.2 Names, formulae and structures of the first four alkanones

Name	Condensed formulae	Structural formulae	Molecular formulae
Propanone	CH_3COCH_3	$\begin{array}{ccccc} & \text{H} & \text{O} & \text{H} & \\ & & \parallel & & \\ \text{H}- & \text{C} & - & \text{C} & - \text{H} \\ & & & & \\ & \text{H} & \text{H} & & \end{array}$	$\text{C}_3\text{H}_6\text{O}$
Butanone	$\text{CH}_3\text{CH}_2\text{COCH}_3$	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{O} & \text{H} \\ & & & \parallel & \\ \text{H}- & \text{C} & - & \text{C} & - \text{C} - \text{H} \\ & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{C}_4\text{H}_8\text{O}$
Pentan-2-one	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{H} & \text{O} & \text{H} \\ & & & & \parallel & \\ \text{H}- & \text{C} & - & \text{C} & - & \text{C} - \text{C} - \text{H} \\ & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{C}_5\text{H}_{10}\text{O}$
Penta-3-one	$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	$\begin{array}{ccccc} & \text{H} & \text{H} & \text{O} & \text{H} & \text{H} \\ & & & \parallel & & \\ \text{H}- & \text{C} & - & \text{C} & - & \text{C} - \text{C} - \text{H} \\ & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	$\text{C}_5\text{H}_{10}\text{O}$

7.3 Structural differences between alkanals and alkanones

Alkanals

Alkanals have alkyl carbon chains (R-) attached to the carbonyl functional group ($\text{C}=\text{O}$), except in the case of methanal (the first member of the group) where the hydrogen atom attaches to the functional group to form methanal ($\text{H}-\text{C}=\text{O}$). The functional group in alkanals is always at the end of the carbon chain.

Alkanones

Alkanones have a carbonyl group ($\text{C}=\text{O}$) between two alkyl groups (R and R') written as $\text{R}-\text{C}=\text{O}-\text{R}'$. The alkyl groups on either side of a carbonyl group, R and R', may not necessarily have equal number of carbon atoms.

7.4 Sources of alkanals and alkanones

Sources of alkanals

- Traces of alkanals are found in essential oils which often contribute to their favourable odours.
- Most sugars are derivatives of alkanals.
- Traces of methanal are present in the air. This is as a result of photochemical oxidation of hydrocarbons.
- Oxidation of primary alcohols under controlled conditions.

Sources of alkanones

- Alkanones are by-products obtained when body fat provides energy instead of glucose.
- Alkanones are also obtained from the oxidation of secondary alcohols under controlled conditions.

(a) Oxidation of primary alkanols to form alkanals

Experiment 7.1

Aim: To oxidise primary alkanols to form alkanal

Requirements

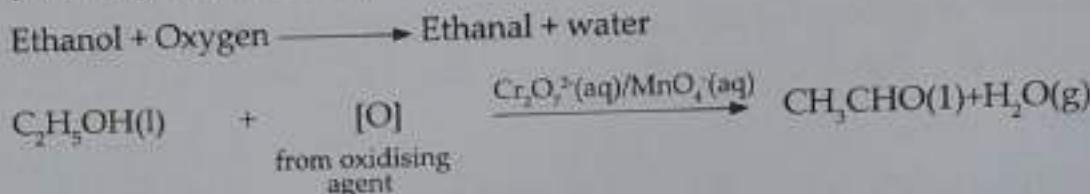
- | | |
|------------------|---------------------------------------|
| • Test tube | • Acidified potassium manganate (VII) |
| • Source of heat | • Ethanol |

Procedure

- Put about 2-3 cm³ of ethanol into a test tube.
- Add about 5 cm³ of acidified potassium manganate (VII) into the test tube.
- Warm gently.
- Note and record your observation.

Discussion

When acidified potassium manganate (VII) is added to ethanol, the purple colour changes to colourless. When the mixture was gently heated an "apple" smelling ethanal forms. Because it is difficult to control the amount of heat, the ethanal formed may easily get oxidized to produce ethanoic acid.



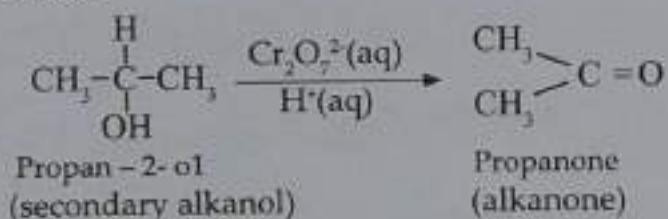
In this experiment potassium manganate(VII) is used as **oxidizing agent**. Potassium dichromate (VI) can also be in place of potassium manganate (VII).

(b) Oxidation of secondary alcohols (alkanol) to form alkanones

When secondary alcohols are oxidized using powerful oxidizing agents such as potassium manganate (VII) and potassium dichromate (VI) they form alkanones.

For example;

Oxidation of propan - 2 - ol by acidified potassium dichromate (VI) produces propanone.



Note: Alkanones are not easily oxidized, so even prolonged refluxing will not produce anything else. Heating under reflux means increasing the temperature of an organic reaction to boiling without losing volatile solvents, reactants or products. Any vapourised compounds are cooled, condense and drip back into the reaction mixture.

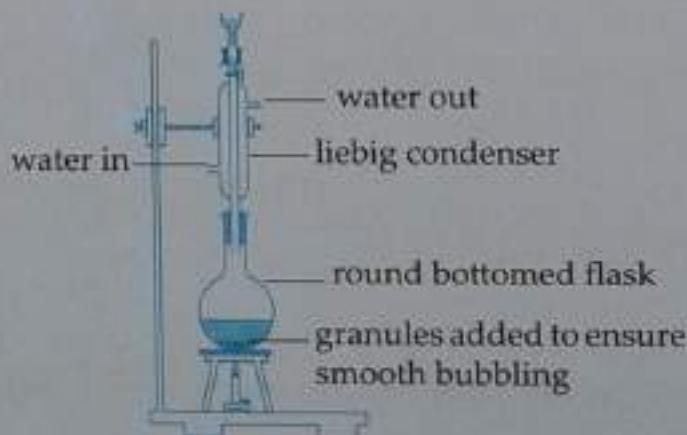


Fig 7.1: Reflux apparatus

Physical properties of alkanals

The general physical properties of alkanals are as shown in table 7.3.

Table 7.3: Trends in physical properties of alkanals

Name	R.M.M	Melting point, °C	Boiling point °C	Density g/cm³	Solubility in water	Physical state
Methanal	30	-92	-19	0.8153	Very soluble	Gas
Ethanal	44	-124	2	0.7840	Very soluble	Liquid
Propanal	58	-81	49	0.8050	Soluble	Liquid
Butanal	72	-99	76	0.8020	Soluble	Liquid
pentanal	86	-60	103	0.8095	Slightly soluble	Liquid

- (i) All alkanals are liquid except methanal which is a gas.
- (ii) Alkanals are colourless and have a characteristic smell.
- (iii) Alkanals solubility decreases down the homologous series.

The carbonyl group ($C = O$) is polar, thus the starting members of the homologous series (alkanals with less than 5 atoms) are appreciably soluble in water. They even dissolves both polar and non polar solutes. However, alkanals do not have ability to form hydrogen bonds like alcohols. Alkanals are also soluble in organic solvents. The carbonyl group has less effect on the intermolecular forces than the (OH) hydroxyl group because the hydroxyl group is able to participate in hydrogen bonding.

Note: that the bonds between carbonyl oxygen and water cause alkanals to have a higher level of water solubility than with hydrocarbons. But the degree of solubility in water decreases with increasing molecular weight.

- (iv) The melting and boiling points of alkanals generally increase with increase in relative molecular mass. As the molecular mass increase the intermolecular forces of attraction between molecules increase. As these forces increase, more energy is required to overcome them. The carbonyl group influences the physical properties, for example ethanal (CH_3CHO) with a boiling point of $20^\circ C$ is a liquid at room temperature while propane with a similar relative molecular mass is a gas at room temperature and with a boiling point of $-42^\circ C$. However, the boiling points of alkanals are generally lower than those of alkanols from which they are derived.

Physical properties of ethanal

- Ethanal is a colourless liquid.
- Has a pungent fruity apple odour.
- Soluble in water.
- Has a low boiling point of $20^\circ C$.

Chemical properties of Alkanals

Alkanals form a homologous series with similar chemical properties. The chemical properties of ethanal we shall study applies also to other alkanals.

Table 7.4: Investigating some of the chemical properties of ethanal

Procedure	Observation	Conclusion
1. Place a few drops of ethanal into a bottle top and ignite.		
2. Place about 2 - 3 cm ³ of ethanal in a test tube. Test with blue and red litmus papers.		
3. Place about 2-3 cm ³ of ethanal in a test tube. Add about 5 cm ³ of acidified potassium manganate (VII) into the test tube and warm gently.		
4. Repeat step 3 but add acidified potassium dichromate VI.		
5. Place 2-3 cm ³ of ethanol in a test tube. Add 3 cm ³ of 2, 4 – dinitrophenyl hydrazine reagent.		
6. Place 2 – 3 cm ³ of ethanol in a test tube. Add 2 – 3 cm ³ of Tollen's reagent and warm gently.		

1. Combustion of ethanal

When ethanal is ignited in plentiful supply of air or oxygen, it burns with a blue flame to produce carbon dioxide and water.

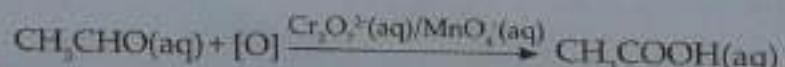
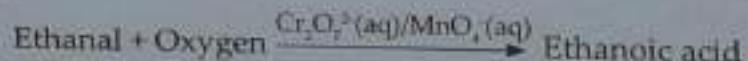


2. Effect on litmus

Ethanal is a neutral substance. It has no effect on both red and blue litmus papers.

3. Oxidation of ethanal

When acidified potassium manganate (VII) is added to ethanal, the colour changes from purple to colourless. When acidified potassium dichromate(VI) is added to ethanal the colour changes from orange to green. Potassium dichromate (VI) and potassium manganate (VII) are oxidizing agents. They oxidize ethanal to ethanoic acid.

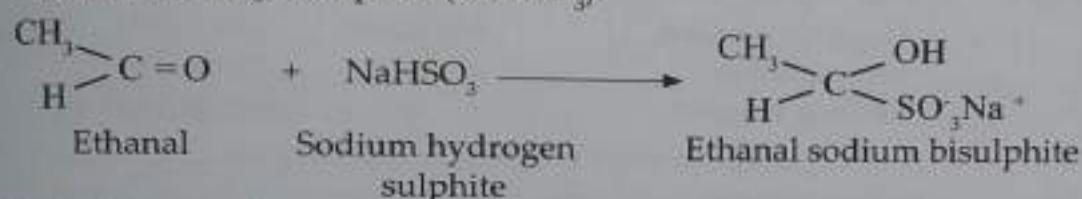


4. Addition reaction

- a) Ethanal can undergo addition reaction with hydrogen cyanide (HCN) to form 2 hydroxy propano nitrile. HCN adds across the carbonyl double bond ($C=O$) of the ethanal molecule.

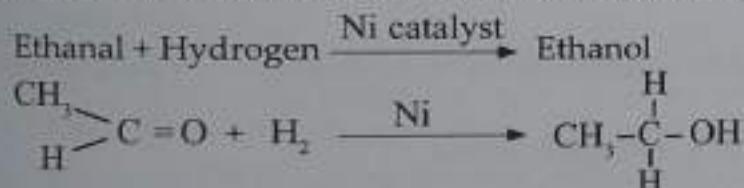


- b) Ethanal undergoes addition reaction when shaken with saturated solution of sodium hydrogensulphite (NaHSO_3).



5. Reduction reaction

Alkanal can also undergo addition reaction with hydrogen in presence of nickel metal catalyst or platinum metal catalyst to form primary alcohols.



Note: Addition of hydrogen to a substance is called reduction.

6. Polymerization

Alkanals can be readily converted to a variety of addition polymers just like alkenes.

7.5 Test for alkanals

a) Brady test

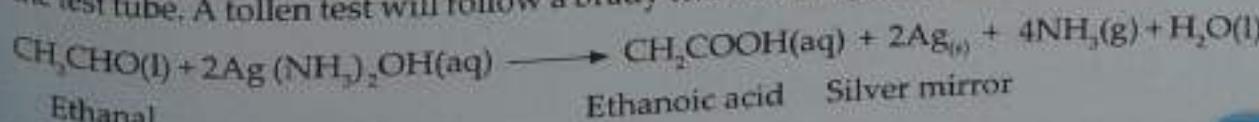
This is a test used to detect the presence a carbonyl functional group in a compound using 2, 4-DNPH reagent (2, 4-Dinitrophenyl hydrazine). The reagent is an orange powder. Formation of a yellow precipitate shows a positive identification of a carbonyl group.



b) Tollens test

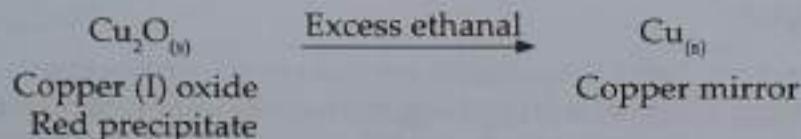
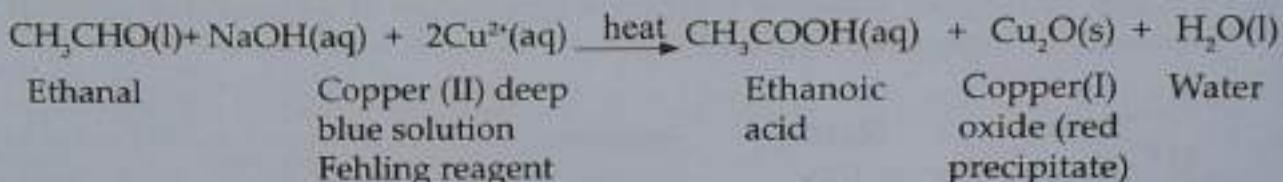
Tollens reagent is a mixture of excess ammonia solution and silver nitrate solution.

Tollens reagent oxidises ethanal to ethanoic acid while the silver ions present in the tollens reagent are reduced to silver element, forming a silver mirror on the inside of the test tube. A tollen test will follow a brady test to distinguish alkanal from alkanone.



c) Fehling's test or Benedict's solution

Fehlings solutions when mixed with ethanal change colour from blue to green to orange precipitate and then red precipitate (copper mirror). The ethanal forms ethanoic acid. A Fehling test would also be used to distinguish between alkanal and alkanone. Fehling's test give positive test with alkanals and sugars which are easily oxidized. Alkanone will not produce a red precipitate with fehlings test, the blue solution colour remains unchanged. Fehlings reagent contain copper ions under basic conditions. The copper ions are in the +2 oxidation state, and can be reduced to the +1 oxidation state, where they form red precipitate of Cu_2O in a basic solution.



Uses of ethanal

1. It is a raw material in production of cellulose acetates, ethylacetate and ethanoic acid.
2. It is used as a reducing agent in mirror production.
3. Used as a solvent in the rubber tanning and paper industries.
4. Used as a denaturant for alcohol.
5. Used in fuel composition.
6. Used in manufacture of perfumes.
7. Used in manufacture of plastics and synthetic rubber.
8. Formalin contains 40% methanal aqueous solution and thus used as a preservative.

Practice exercise 7A

1. State the physical properties of ethanol.
2. Give the functional group of an alkanal.
3. Write the molecular formula of the following alkanals.
 - (i) Butan-1-al
 - (ii) Pentan - 1-al
4. State tests that can be used to identify presence of a carbonyl group.
5. List three uses of ethanal.
6. The melting point of alkanals increases with increase in molecular mass. Explain.

Physical properties of Alkanones

Table 7.5: Trends in physical properties of alkanones

Name	RMM	Melting point/ °C	Boiling/ Point °C	Density g/cm ³	Physical state	Solubility in water
Propanone	58	-96°C	56	0.7840	Liquid	Miscible in all proportions
Butanone	72	-87°C	80	0.8050	Liquid	Very soluble
Pentan-2-one	86	-78°C	101	0.8080	Liquid	Very soluble
Hexan - 2-one	100	55°C	128	0.8113	Liquid	Soluble
Pentan-3-one	86	40°C	102	0.8150	Liquid	Soluble

- (i) All alkanones are liquids.
- (ii) Alkanones are polar because of the carbonyl group.
- (iii) Solubility of alkanes decreases down the homologous series.

Smaller alkanones are typically more soluble in water because of the ability to accept hydrogen bonds. Propanone is a good solvent and has a high miscibility with water due to the oxygen atom being able to form hydrogen bonds with water molecules.

Because alkanones are generally not hydrogen – bond donors or acceptors, they tend not to "self associate" and therefore are more volatile than alcohols and carboxylic acids (alkanoic acids) of similar molecular mass.

- (iv) Alkanones' boiling and melting points increase with increasing molecular mass.
- The boiling points of alkanones are higher than that of parent corresponding alkanes. For example butane (RMM 58) has a boiling point of 0°C while propanone (RMM 60) has a boiling point of 56°C. The difference in boiling points are due to differences in polarity and hydrogen-bonding ability. Most alkanones are polar but not extremely polar. They are good solvents for organic reactions.

Practice exercise 7B

1. Explain the trend in melting and boiling points of alkanones.
2. Compare the boiling point of alkanones to that of alkanols.

Physical properties of propanones

- (i) It is a colourless liquid.
- (ii) It is flammable.
- (iii) Miscible with water, alcohol and ether.
- (iv) It has low boiling point of 56°C.
- (v) Has a characteristic sweet odour.

Preparation of alkanones

Alkanones can be prepared by oxidation of alkanols.

Experiment 7.2

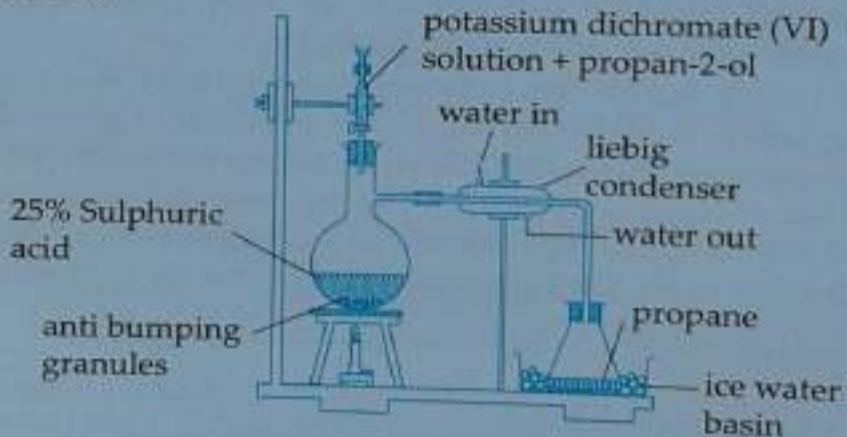
Aim: To prepare propanone by oxidation of propan-2-ol

Requirements

- Potassium dichromate (VI)
- Propan -2-ol
- Concentrated sulphuric acid
- Anti-bumping granules
- Distilled water
- Dropping funnel
- Round bottom flask
- Conical flask.

Procedure

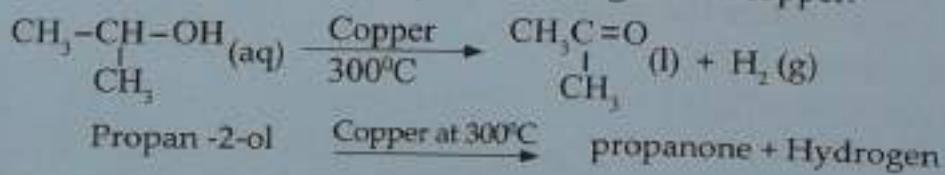
1. Place 25% sulphuric acid in a round bottomed flask.
2. Add some anti-bumping granules to the flasks and set the apparatus as shown below



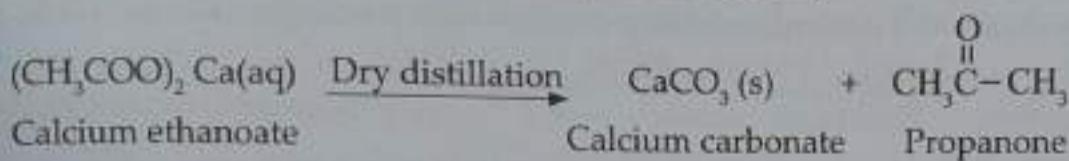
3. Heat the acid gently.
4. Drop a mixture of a propan-2-ol and aqueous potassium dichromate (VI) solution onto the hot acid.
5. Collect enough of the product.

Other methods of preparing propanone

- (i) By dehydrogenation of propan-2-ol using heated copper.

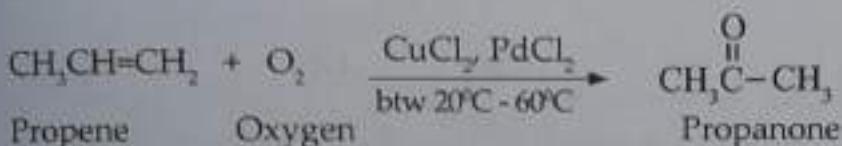


(ii) By dry distillation of calcium ethanoate (calcium acetate).



(iii) By Wacker process.

Propanone is prepared from propene by wacker process where propene and air mixture is passed through a solution of copper (II) chloride and palladium (II) chloride between 20°C and 60°C.



Chemical properties of alkanones

Alkanones all show similar chemical properties. The following reactions of propanone discussed also apply to other alkanones.

1. Combustion of propanone

When propanone is ignited in plentiful supply of air or oxygen it burns with a blue flame to produce carbon dioxide and water.



2. Effect on litmus

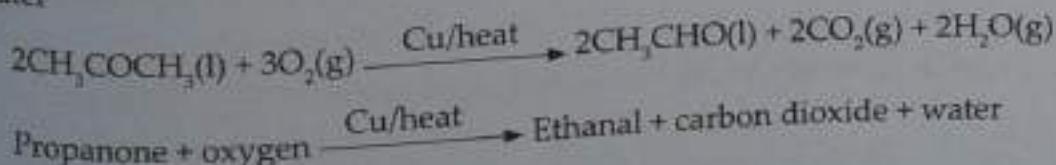
Propanone is a neutral substance. It has no effect on both red and blue litmus papers.

3. Oxidation of propanone

Alkanones are difficult to oxidize. They cannot be oxidised under conditions which alkanals get oxidized.

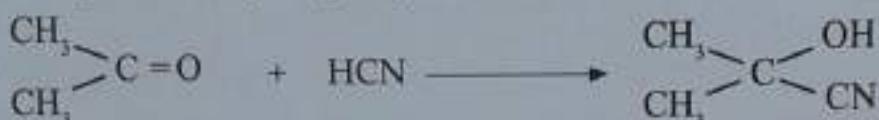
Any oxidation would break the carbon skeleton of alkanones. Strong oxidizing agent like hot concentrated nitric acid will oxidize alkanones with the effect of breaking the molecule to at least two molecules of alkanoic acid. Potassium manganate (VII) solution which is also a strong oxidizing agent will oxidise alkanones in a destructive way, breaking carbon-carbon bonds.

Hot copper metal catalyses oxidation of propanone to ethanal, carbon dioxide and water.

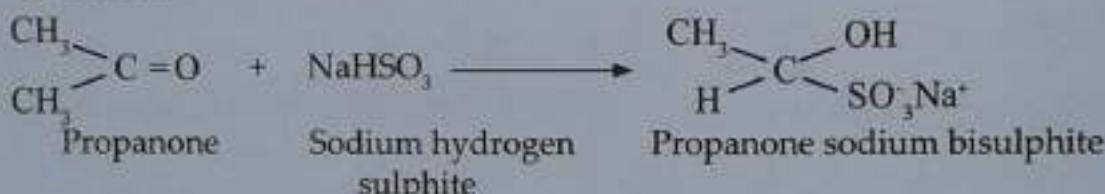


4. Addition reaction

- a) Propanone will undergo addition reaction with hydrogen cyanide, HCN, to give 2-hydroxy-2-methylpropanenitrile.

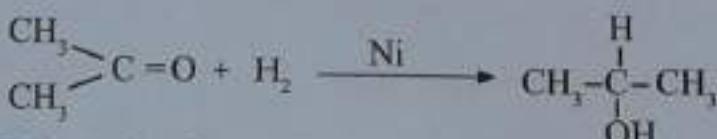
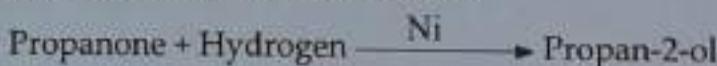


- b) Propanone will also undergo addition reaction when shaken with saturated aqueous sodium hydrogen sulphite (NaHSO_3). The reaction is not as fast as that of ethanal.



5. Reduction reaction

Alkanones are reduced by hydrogen in the presence of a platinum or nickel metal catalyst to form secondary alcohols.



6. Polymerization

Alkanones are not reactive enough to polymerize easily.

Test for alkanones

(a) Brady's test

Procedure

Place 2 cm³ of propanone in a test tube, add 2 cm³ of 2,4-DNPH reagent.

Observation

A yellow or orange precipitate is formed which gives a positive test for an alkanone (ketone). Both alkanals and alkanones give positive test with Brady's test.



Yellow - orange



b) Tollen's test

Procedure

Add 2-3 cm³ of propanone to 3 cm³ of Tollen's reagent. If no reaction occurs, warm the test tube in water bath for few minutes.

It is advisable not to use excessive heating because it will give a false appearance of positive test (a silver mirror) because of decomposition of the reagent.

Observation

A negative test result indicates the compound is alkanone i.e a silver mirror does not form.

c) Fehling's test or Benedict's solution

Procedure

Add 5 cm³ of propanone to 1cm³ of Fehling's solution and then heat in water bath for 5 minutes.

Observation

If the colour of the solution does not change alkanone is present. Alkanone will not change the colour of Fehling's solution. Fehling's solution and Benedict's solution are variants of the same thing. Both contain complexes copper (II) ions in an alkaline solution.

Uses of propanone

1. Propanone is used as a solvent for plastics and synthetic fibres.
2. Propanone is used as nail varnish remover.
3. Propanone is capable of dissolving plastic, glasses, jewelry, rayon's garments, pens and pencils.
4. Propanone is used as a solvent for both polar and non-polar compound.

Practice exercise 7C

1. State the physical properties of propanone.
2. Name the functional group of an alkanone.
3. Write the molecular formula and draw the structural formulae for:
 - (i) Butanone
 - (ii) Propanone
4. State a test that can be used to identify alkanone positively.
5. State two uses of propanone.
6. Explain the trend of melting points of alkanones in relation to their R.M.M.

Revision exercise 7



- 1 In what ways are alkanals and alkanones similar?
2. (a) Give the general formula of alkanals.
(b) Give the structural formula for the alkanes with 3, 4 and 5 carbons.
3. Give the structural difference between alkanols and alkanones.
4. (a) Why is it that alkanones are not easily oxidized?
(b) Explain the trend in melting and boiling points of alkanones.
5. State three physical properties of ethanal.
6. State the test that can be used to identify carbonyl group.
7. What is the effect of alkanones on litmus paper?
8. Write the molecular formula and draw the structural formula for
(i) Pentanone
(ii) Butanone

Topic 8:

Alkanoic acids

Success criteria

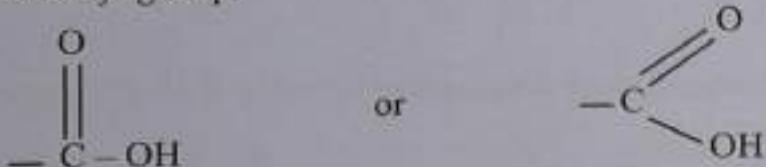
By the end of the topic, you should be able to:



- Identify the functional group of alkanoic acids.
- Name the first ten unbranched alkanoic acids.
- Draw the structure of first ten unbranched alkanoic acids.
- Write the molecular formula of alkanoic acid given the number of carbon atoms.
- Describe the sources of alkanoic acids.
- Explain the physical properties of alkanoic acids.
- Explain the chemical properties of alkanoic acids.
- Describe the uses of alkanoic acids.

Alkanoic acids are organic acids. They are also called **carboxylic acids**. They have a **carboxyl group** as their functional group. They may be regarded as being derived from alkanes by replacing one of the hydrogen atoms with a carboxyl group – COOH group.

Structure of the carboxyl group;



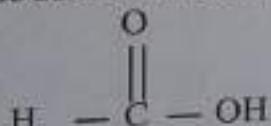
8.1 General formula and IUPAC nomenclature of alkanoic acids

Alkanoic acids form homologous series with a general formula R-COOH or $\text{C}_n\text{H}_{2n-1}\text{COOH}$ where R is an alkyl group or H in case of the first member of the series.

The systematic naming of a carboxylic acid corresponds with the number of carbon atoms in the molecule. The –e in the parent name of corresponding alkane is replaced with **-oic acid**. Let us name and draw the structures of the first three alkanoic acids.

- The first member of the series is **methanoic acid**. Its formula is HCOOH. In methanoic acid, R is represented by H while for the rest, R is represented by an alkyl group.

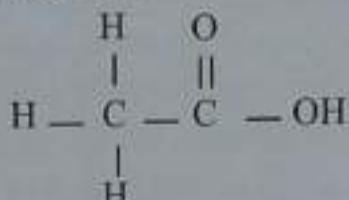
The structure of methanoic acid is therefore,



- The second member of the alkanoic acids series is **ethanoic acid**. It has two carbon atoms. Since one of the carbon atoms is already attached to the functional group, the value of n in the general formula $C_nH_{(2n+1)}COOH$ is 1. When we substitute, we get the molecular formula for ethanoic acid as follows.

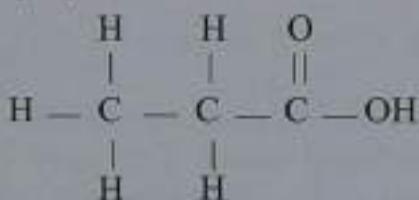


The structural formula is represented as:



Ethanoic acid

For the third member; n = 2 we substitute in $C_nH_{(2n+1)}COOH$ we get C_2H_5COOH as the molecular formula. It is called propanoic acid and its structural formula is as follows.



Propanoic acid

Structure of alkanoic acids

Table 8.1 shows the structural and molecular formula of alkanoic acids.

Table 8.1: Names, formulae and structure of some alkanoic acids

Name	Molecular formula	Structural formula
Methanoic acid	HCOOH	$\begin{array}{c} O \\ \\ H - C - OH \end{array}$
Ethanoic acid	CH ₃ COOH	$\begin{array}{c} H & O \\ & // \\ H - C - C - OH \\ \\ H \end{array}$
Propanoic acid	C ₂ H ₅ COOH	$\begin{array}{c} H & H & O \\ & & // \\ H - C - C - C - OH \\ & \\ H & H \end{array}$

Butanoic acid	C_3H_7COOH	$ \begin{array}{ccccccc} & H & H & H & O \\ & & & & \\ H & - C & - C & - C & - C & - OH \\ & & & & \\ & H & H & H & \end{array} $
Pentanoic acid	C_4H_9COOH	$ \begin{array}{ccccccc} & H & H & H & H & O \\ & & & & & \\ H & - C & - C & - C & - C & - C & - OH \\ & & & & & \\ & H & H & H & H & \end{array} $
Hexanoic acid	$C_5H_{11}COOH$	$ \begin{array}{ccccccc} & H & H & H & H & H & O \\ & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & \\ & H & H & H & H & H & \end{array} $
Heptanoic acid	$C_6H_{13}COOH$	$ \begin{array}{ccccccc} & H & H & H & H & H & H & O \\ & & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & & \\ & H & H & H & H & H & H & \end{array} $
Octanoic acid	$C_7H_{15}COOH$	$ \begin{array}{ccccccc} & H & H & H & H & H & H & H & O \\ & & & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & & & \\ & H & H & H & H & H & H & H & \end{array} $
Nonanoic acid	$C_8H_{17}COOH$	$ \begin{array}{ccccccc} & H & H & H & H & H & H & H & H & O \\ & & & & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & & & & \\ & H & H & H & H & H & H & H & H & \end{array} $
Decanoic acid	$C_9H_{19}COOH$	$ \begin{array}{ccccccc} & H & H & H & H & H & H & H & H & H & O \\ & & & & & & & & & & \\ H & - C & - C & - C & - C & - C & - C & - C & - C & - C & - C & - OH \\ & & & & & & & & & & \\ & H & H & H & H & H & H & H & H & H & \end{array} $

Table 8.2: Examples of alkanoic acid with their skeletal formula

Name	Condensed formula	Skeletal formula
Methanoic acid	HCOOH	HCOOH
Ethanoic acid	CH_3COOH	$\diagup COOH$
Propanoic acid	CH_3CH_2COOH	$\nearrow COOH$

Butanoic acid	$\text{CH}_3(\text{CH}_2)\text{COOH}$	
Pentanoic acid	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$	
Haxanoic acid	$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	
Heptanoic acid	$\text{CH}_3(\text{CH}_2)_5\text{COOH}$	
Octanoic acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	
Nonanoic acid	$\text{CH}_3(\text{CH}_2)_7\text{COOH}$	
Decanoic acid	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	

Alkanoic acids as homologous series

Alkanoic acids exhibit the following characteristic properties.

- (i) They have the functional group -COOH attached to the hydrocarbon chain.
- (ii) Their general formula is $\text{C}_n\text{H}_{2n+1}\text{COOH}$ or RCOOH , where $n = 0, 1, 2$
- (iii) Members of the series differ from the next by a $-\text{CH}_2-$ group.
- (iv) They have similar chemical properties.
- (v) They show a trend in their physical properties such as increase or decrease in melting points, boiling points and densities.



Practice exercise 8A

1. Name alkanoic acids with the following carbon atoms; 4, 6, 7, 9.
2. Draw the structures of the above alkanoic acids.
3. Write the molecular formulae of the alkanoic acids named in (1) above.

8.2 Natural sources of alkanoic acids

The taste of oranges, lemons and other citrus fruits is described as sour. The same applies to the taste of fermented milk and vinegar. All these substances contain acids which give them the sour taste. Some acids are found in both plant and animal materials. Such acids are referred to as **organic or natural acids**.

Table 8.3: Natural sources of alkanoic acid

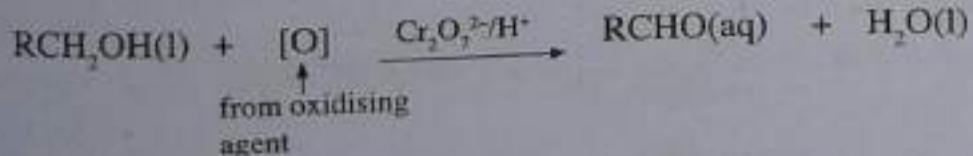
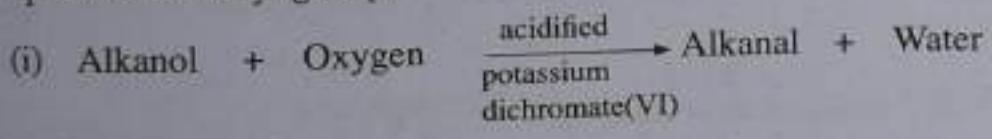
Name	Where found or used
1. Citric acid	Citrus fruits, such as oranges, lemons
2. Tartaric acid	Grapes, health salts, baking powder.
3. Lactic acid	Sour milk
4. Ethanoic acid	Vinegar
5. Methanoic acid	In ant, bee and nettle stings
6. Carbonic acid	Coke, lemonade and other fizzy drinks
7. Butanoic acid	Cheese
8. Tannic acid	Tea

Preparation of alkanoic acids

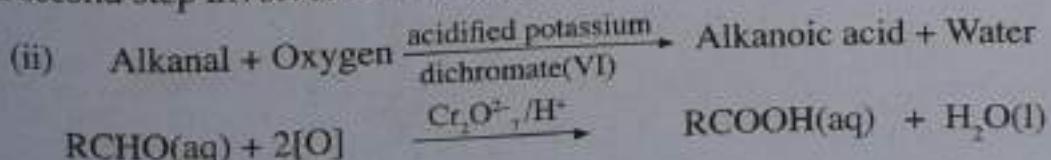
Alkanoic acids can be prepared by oxidation of the corresponding alcohol in two steps. The oxidising agents are:

- Acidified potassium dichromate(VI)
- Acidified potassium manganate(VII)

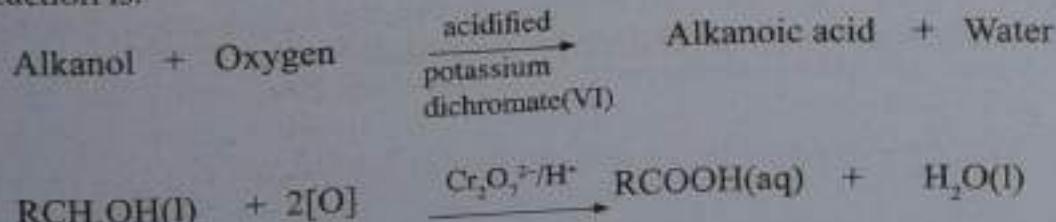
The alkanol is mixed with excess acidified potassium dichromate(VI) and warmed. In the first step an alkanal and water are formed as shown in the following general equation. R represents an alkyl group.



The second step involves further oxidation of alkanal to alkanoic acid.



Overall reaction is:

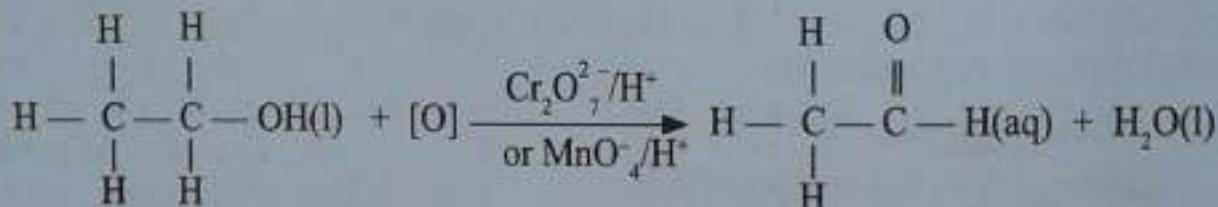
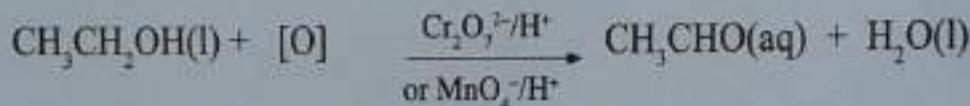
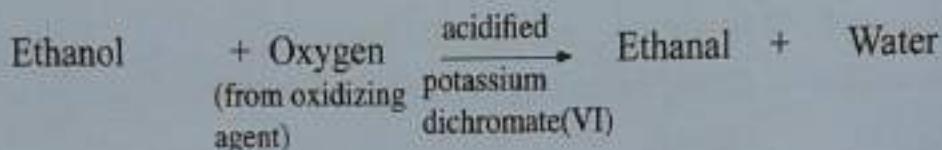


Preparation of ethanoic acid

Ethanoic acid can be prepared by warming a mixture of ethanol and excess acidified potassium dichromate(VI) or excess acidified potassium manganate(VII).

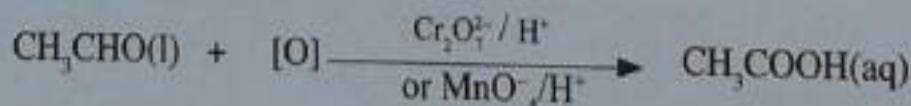
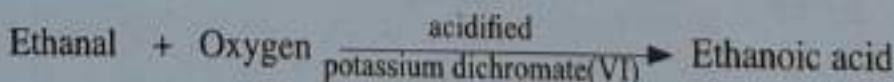
Step I

This involves the conversion of **ethanol** to **ethanal** as shown below. This is a slow process.

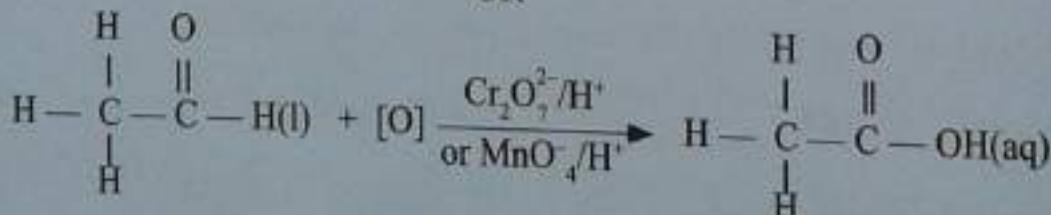


Step II

In this step, the ethanal is oxidised to ethanoic acid. This reaction takes place at a much faster rate.



OR



Eventually, the orange colour of potassium dichromate (VI) turns green as the oxidation progresses or if we use potassium manganate(VII), the purple colour turns colourless. The acid is obtained from the mixture by distillation.



Practice exercise 8B

1. Name the chemical reagents required in the preparation of butanoic acid.
2. Write down an outline of the procedure required in the preparation of butanoic acid.
3. Write step by step equations for the preparation of butanoic acid.
4. List the characteristics of homologous series of alkanoic acids.

8.3 Properties of alkanoic acids

Physical properties of alkanoic acids

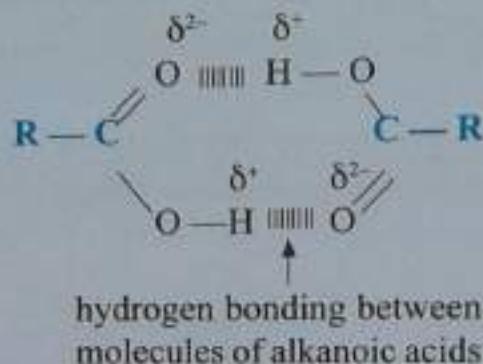
- (i) The first ten straight chain alkanoic acids are liquids at room temperature.
- (ii) The first five members with fewer than about five carbon atoms like methanoic and ethanoic acids are soluble in water. The rest are insoluble and actually float on water. The solubility of alkanoic acids generally decrease with increasing molecular mass. This is due to increasing larger hydrocarbon portion which is hydrophobic. Table 8.4 shows the physical properties of some alkanoic acids.

Table 8.4: Trends in physical properties of alkanoic acids

Name	Melting point (°C)	Boiling point (°C)	Density g/cm ³	Solubility in water
Methanoic acid	8.4	101	5.220	Soluble
Ethanoic acid	16.6	118	5.049	Soluble
Propanoic acid	-20.8	141	0.992	Soluble
Butanoic acid	-8	164	0.964	Soluble
Pentanoic acid	-19	187	0.939	Insoluble
Hexanoic acid	-3	205	0.927	Insoluble
Heptanoic acid	-10.5	223	0.920	Insoluble
Octanoic acid	16	239	0.910	Insoluble
Nonanoic acid	11	253	0.907	Insoluble
Decanoic acid	31	269	0.905	Insoluble

- (iii) The boiling points and melting points of alkanoic acids gradually increase as the length of the hydrocarbon chain increases. The increase in boiling points is due to the following reasons.
 - As the length of the hydrocarbon increases, the weak intermolecular forces (van der Waals forces) are increased.

- There is also formation of **hydrogen bonds** between the alkanoic acid molecules. This is brought about by the partial positive and negative charges on the H and O atoms of the carboxyl group (-COOH). These charges enable the molecules to attract each other and form strong hydrogen bonds.



- (iv) Density of methanoic acid and ethanoic acid is denser than that of water. Density of the other eight members is below that of water and decreases down the series.
- (v) Viscosity of alcanoic acids increases down the homologous series as the molecular mass increases. This is due to increasing stronger and more hydrogen bonds in the acid molecules.

Boiling and melting points of alkanols and alcanoic acids

The boiling point of ethanol is about 78°C while the boiling point of ethanoic acid is 118°C. What causes such a big difference? There are two reasons:

(a) The molecular mass

The molecular mass of ethanol is 46 and that of ethanoic acid is 60. The intermolecular forces of attraction in ethanoic acid are much stronger hence the high boiling point.

(b) Hydrogen bonds

Hydrogen bonds are found in both alkanols and alcanoic acids but there are more in alcanoic acids than in alkanols. This explains the higher boiling point of ethanoic acid than that of ethanol.

Alcanoic acids also form hydrogen bonded **dimers**. The capacity for hydrogen bonding makes the first few members of the homologous series soluble in water in all proportions. However the solubility decreases with increase in molecular mass.



Practice exercise 8C

- Describe the trend in melting and boiling points of the first ten alcanoic acids.
- Compare the melting and boiling points of alcanoic acids with the corresponding parent alkanes. Explain their differences.
- Compare the solubility of the first four alcanoic acids in water with those of alkanes. Explain the differences.

Chemical properties of alkanoic acids

Alkanoic acids are another homologous series of organic compounds which exhibit similar chemical properties. We shall learn about the chemical properties of ethanoic acid as a representative of alkanoic acids. Ethanoic acid is a colourless liquid with a sharp smell.

Experiment 8.1

Aim: To investigate the chemical properties of ethanoic acid.

Requirements

- Test tubes
- Beaker
- Spatula
- Source of heat
- Magnesium ribbon
- Ethanoic acid
- Sodium hydroxide solution
- Droppers
- Universal indicator or litmus papers
- Test tube holder
- Calcium carbonate
- Ethanol
- Concentrated sulphuric acid
- Phenolphthalein indicator

Procedure

Copy Table 8.5 in your notebook. Follow the procedures as outlined in the table and record your observations and conclusions in the spaces provided.

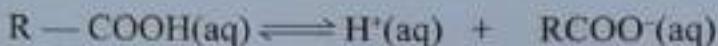
Table 8.5: Investigating chemical properties of alkanoic acids

Procedures	Observations	Conclusions
1. Place about 2 cm^3 of ethanoic acid in a test tube. Add a few drops of phenolphthalein and test with litmus papers and methyl orange indicator.		
2. Place about 2 cm^3 of ethanoic acid in a test tube. Add a small piece of clean magnesium ribbon and test for any gas produced. Repeat with sodium metal.		
3. Place about 2 cm^3 of ethanoic acid in a test tube. Add a spatula endful of calcium carbonate and test for any gas produced.		
4. Place about 2 cm^3 of ethanoic acid in a test tube. Add an equal amount of ethanol followed by two drops of concentrated sulphuric acid. Warm the mixture gently and pour the resulting mixture into a beaker with about 60 cm^3 of cold water. Smell the product formed.		

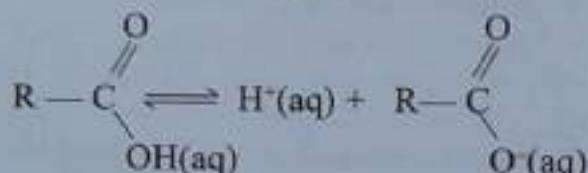
5. Place about 2cm³ of ethanoic acid in a test tube. Add two drops of either phenolphthalein or methyl orange indicator. Then add 2cm³ sodium hydroxide solution to the mixture drop by drop until there is colour change.

Discussion

Mineral acids dissolve in water and dissociate into their respective ions. For example, hydrochloric acid HCl produces hydrogen ions H⁺ and chloride ions Cl⁻ on dissolving in water. When an alkanoic acid is dissolved in water, it dissociates to form hydrogen ions, H⁺ and carboxylate anion, RCOO⁻ as illustrated in the following general equation.

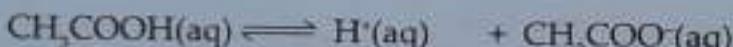
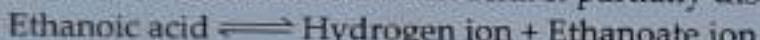


OR



Note: The functional group -COOH donates the H⁺ ion, **not** the alkyl group represented by R.

Ethanoic acid is said to be a weak acid. It partially dissociates in water.

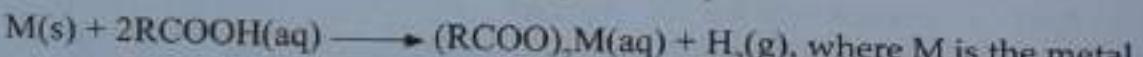


An aqueous solution of ethanoic acid has a pH of about 4.7 which indicates it is a weak acid. A solution of ethanoic acid will show characteristic reactions of a dilute acid as follows:

Ethanoic acid turned phenolphthalein indicator colourless. It also turns blue litmus paper red and changes methyl orange indicator red.

1. Reaction of ethanoic acid with metals

Alkanoic acids reacts with the metal displacing hydrogen from the carboxyl group (-COOH) as shown in the following general equation.



Ethanoic acid reacts with reactive metals such as magnesium to produce a salt and hydrogen gas. For example;



Note: That the metal displaces hydrogen in the -COOH functional group and not the other hydrogens.

Ethanoic acid reacts more vigorously with alkali metals e.g. sodium.



2. Reaction of ethanoic acid with carbonates

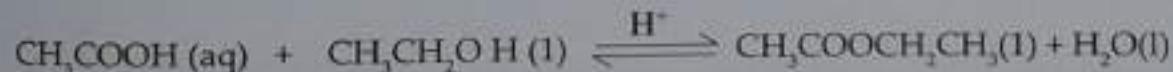
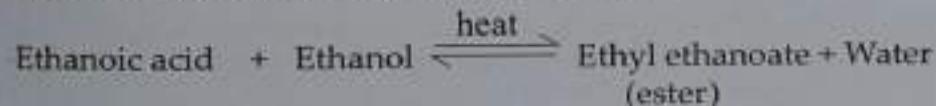
Ethanoic acid will react with carbonates to produce a salt, carbon dioxide and water. For example, it reacts with calcium carbonate to give calcium ethanoate, carbon dioxide and water.



Note: When writing the formula of an organic salt, the metal comes last. But when naming the salt, we start with the metal.

3. Reaction of ethanoic acid with ethanol

When organic acids are reacted with alkanols, they form esters and the reaction process is known as **esterification**. Ethanoic acid will react with ethanol in the presence of a few drops of concentrated sulphuric acid to form ethyl ethanoate. Concentrated sulphuric (VI) acid is a catalyst for the reaction.



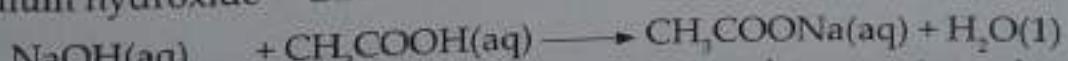
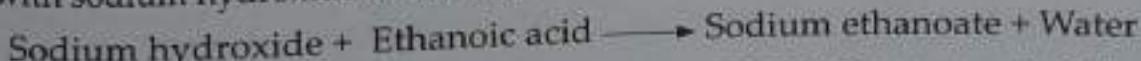
Ethyl ethanoate is one example of an ester.

Note: Always remember that the first part of the ester is derived from the acid while the second part is derived from the alcohol. In writing the name of the esters, we start with the alcohol part and end with the acid part.

Esters have strong pleasant smells. Esters are responsible for many odours in flowers and flavours in fruits such as bananas and pineapples.

4. Reaction of ethanoic acid with bases/alkalis

Ethanoic acid reacts with bases to form salt and water. For example, ethanoic acid reacts with sodium hydroxide as follows:



We have seen that an alkanol and alkanoic acid reacts to produce an ester and water in a process called esterification. Also we have seen that an alkali and a mineral acid react to form salt and water in a neutralisation process. Table 8.6 give the differences between esterification and neutralisation reactions.

Table 8.6: Differences between esterification and neutralisation

Esterification	Neutralisation
1. Reaction is between an alkanoic acid and alkanol.	Reaction is between an acid and an alkali (base).
2. The products are an ester and water.	The products are salt and water.
3. The process is catalysed by sulphuric acid.	The process is not catalysed.
4. The reaction is reversible.	The reaction is irreversible.

Electrical conductivity of weak alkanoic acids

Substances that conduct electricity in their aqueous solutions are called **electrolytes**. Most acids are electrolytes. They contain charged particles called **ions**. These ions conduct electricity of acids in aqueous solutions.

Electrical conductivity of acids depends on their strengths. Strong acids have higher conductivity compared to weak acids. This is because strong acids dissociate fully releasing all the ions which conduct electricity strongly. Weak acids partially dissociate providing only fewer ions which conduct electricity weakly.

Experiment 8.2

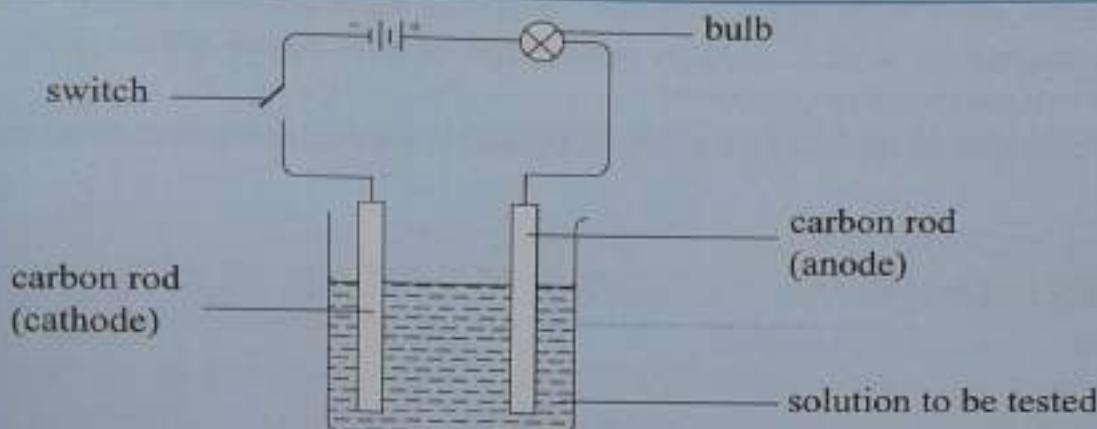
Aim: To determine the electrical conductivity of alkanols and alkanoic acids

Requirements

- 250 cm³ beaker
- Two 1.5 V dry cells
- 2.5 V bulb or torch bulb
- Carbon rods
- Connecting wires
- Switch
- 2M Ethanol
- 2M Ethanoic acid
- Distilled water

Procedure

1. Put 25 cm³ of ethanol and 25 cm³ of water into the beaker.
2. Make a complete circuit using carbon electrodes as shown below.



3. Switch on the current.
 - Does the bulb glow?
 - Note the brightness of the bulb.
 - What do you observe on the carbon rods? What does this indicate?
4. Repeat the experiment using 25 cm³ of 2M ethanoic acid mixed with 25 cm³ of water.
Note: Rinse the beaker and the rods thoroughly with distilled water before adding the next solution.
5. Note the changes occurring around the carbon rods, in the contents of the beaker and the brightness of the bulb if any.
6. Copy Table 8.7 in your notebook and record your observations and conclusions.

Table 8.7: Electrical conductivity in alkanols and alkanoic acids

Solution	Brightness of the bulb (bright or dim)	Conclusion
Ethanol		
2M ethanoic acid		

Discussion

When an alkanoic acid, for example ethanoic acid, dissolves in water it ionises as follows.



The ions produced enable the alkanoic acid to conduct electricity. However, alkanols do not ionise, hence they do not conduct electricity. For alkanoic acids, bulb does not glow brightly because ethanoic acid is weak acid. It ionises partially releasing only a few ions in solution.

Uses of alkanoic acids

1. Ethanoic acid in its fairly dilute form is used as vinegar. Vinegar is used in many food substances as preservative.
2. Production of ethyl ethanoate used in making a polymer extensively used in paints.

3. Alkanoic acids with long chains such as stearic acids are used in soap making.
4. Chloroethanoic acid is used in production of wall paper adhesive, herbicides, pharmaceuticals and cosmetics.
5. Manufacture of medicines e.g. ethanoic acid is used in manufacture of aspirin.

Revision Exercise 8



1. Methanoic acid is added to the same volume of ethanol in the presence of concentrated sulphuric acid and warmed.
 - (a) What is the name of the ester formed?
 - (b) Write an equation for the reaction in (a) above.
2. Write equations and name the formed products in the following reactions.
 - (a) Propanoic acid and potassium.
 - (b) Ethanoic acid and potassium hydroxide.
 - (c) Methanoic acid and lead carbonate.
 - (d) Butan-1-ol and ethanoic acid heated in the presence of concentrated sulphuric acid.
3. What is the functional group of an alkanoic acid?
4. Write the molecular formula and structural formula for butanoic acid and methanoic acid.
5. Ethanoic acid is a weak acid. Explain.
6. Explain why the boiling point of ethanoic acid (118°C) is higher than that of propan-1-ol (b.p. 97°C) and yet they have the same molecular mass.
7. Which ester forms between the reaction of methanol and ethanoic acid? Write a word equation for the reaction.
8. Describe with equations, the reaction between ethanoic acid and sodium metal.
9. The following ester, HCOOCH_3 , was hydrolysed. Write the formula and names of the organic acid and alcohol used to form the ester.

Topic 9:

Alkanoates

Success criteria

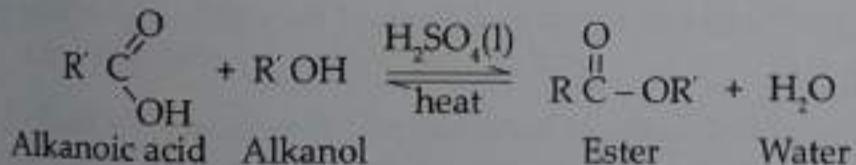
By the end of this unit, you should be able to:

- (a) Identify the functional group of alkanoates (esters).
- (b) Name and draw the structures of alkanoates.
- (c) Describe the sources of alkanoates.
- (d) Describe the properties of alkanoates.
- (e) State uses of alkanoates.
- (f) Describe the process of soap making (saponification).



9.0 Introduction

Alkanoates (esters) are compounds formed when alkanoic acids (organic acids) react with alkanols (alcohols) in the presence of an acid catalyst. The overall reaction involves elimination of water molecule. Therefore these reactions are condensation reaction.



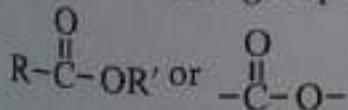
R and R' represent alkyl group that may represent the same or different.

Note: That R group of the acid can be hydrogen if methanoic acid is used in the reaction.

9.1 Functional group

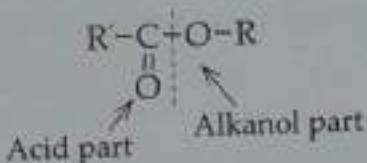
Functional group is a specific group of atoms or bonds within molecule of organic family that gives it characteristic chemical reactions.

The functional group of the alkanoates is RCOOR' . It can also be represented as



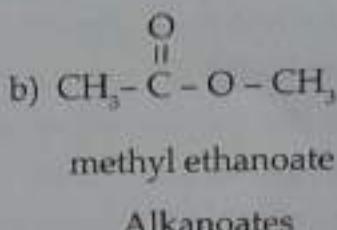
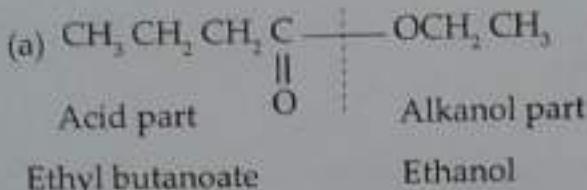
9.2 Nomenclature of alkanoates

Esters names are derived from their parent alcohol and the parent acid reacting.



In naming of esters the alkanol part comes first but modified to sound as the corresponding alkyl group. The acid name then is added but the -oic of the acid is replaced by -oate.

Example



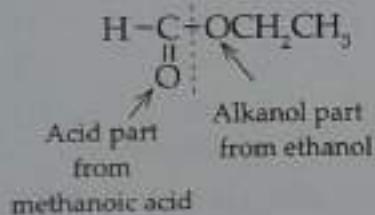
Note: The name is written with a space between the names of reacting acid and that of alkanol.

The written name appears is the reverse of its formulae.

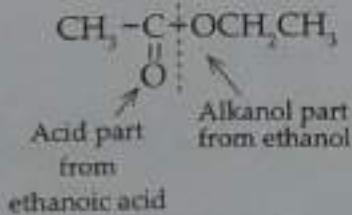
9.3 Structure of alkanoates

(i) Structures of alkanoates derived from reacting alkanoic acids with ethanol.

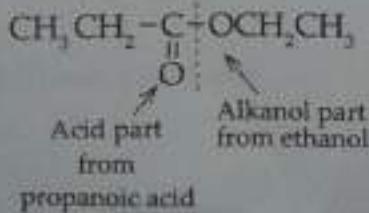
a) Ethyl methanoate



b) Ethyl ethanoate

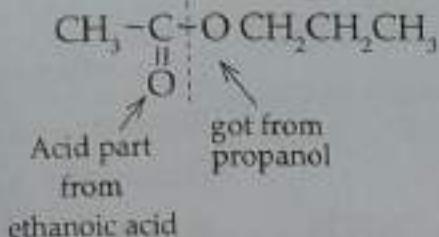


c) Ethyl propanoate

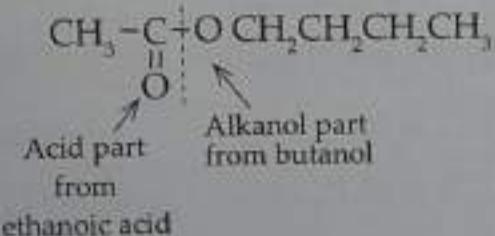


(ii) Structures of alkanoates obtained from reacting alkanols with ethanoic acid.

a. Propyl ethanoate



b. Butyl ethanoate



Deducing reactants of esterification

We now know that the first part of ester name comes from the alkanol part and that the second part of the name comes from the alkanoic acid ending with '**-oate**'. This knowledge helps us to work backward in identifying the alkanoic acid and alkanol used in making the ester. See Table 9.1.

Table 9.1: Examples of esters and their parent alkanol and alkanoic acid

Name of ester	Parent alkanol	Parent alkanoic acid
Ethyl propanoate	Ethanol	Propanoic acid
Propyl methanoate	Propanol	Methanoic acid
Pentyl butanoate	Pentanol	Butanoic acid
Butyl methanoate	Butanol	Methanoic acid



Practice exercise 9A

1. Name the acid and alcohol used in preparation of the ester, propyl ethanoate.
 2. Write equation for the formation of propyl ethanoate.

9.4 Sources of alkanoates

- Natural fruit flavours contain blends of some of the esters as shown in Table 9.2.

Table 9.2: Esters of some fruits

Name	Structural formula	Odour/flavour
Pentyl ethanoate	$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$	Banana
Methyl butanoate	$\text{CH}_3(\text{CH}_2)_2\text{COOCH}_3$	Pineapple
3-methylbutanoate	$\text{CH}_3(\text{CH}_2)_2\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	Apple
Octyl ethanoate	$\text{CH}_3\text{COO}(\text{CH}_2)_7\text{CH}(\text{CH}_3)$	Orange
Propyl ethanoate	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	Pear
Ethyl butanoate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$	Pineapple

- Alkanoates can be prepared synthetically by condensation reaction of alkanoic acids with alkanols.

Laboratory preparation of esters

Experiment 9.1

Aim: To prepare ethyl ethanoate ester.

Requirements

- Test tubes
- Measuring cylinder
- Dropper, beaker
- Ethanoic acid
- Ethanol
- Concentrated sulphuric acid
- Source of heat
- Water

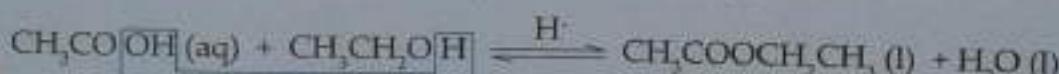
Procedure

- Place about 2 cm^3 of ethanoic acid in a test tube.
- Add an equal amount of ethanol followed by two drops of concentrated sulphuric acid.
- Warm the mixture gently.
- Pour the resulting mixture into a beaker with about 60 cm^3 of cold water.
- Smell the product.

Discussion

When ethanoic acid and ethanol are mixed and gently heated an ester is formed. However, the smell of the ester is not detected. This is because of the stronger smell of alkanoic acid. If the mixture is poured in cold water the insoluble esters form a thin layer on the water surface while the excess acid and alcohol dissolves in water hence making the odour of the ester now detectable. Concentrated sulphuric acid is the catalyst for this reaction. This process is called **esterification**.

Ethanoic acid reacts with ethanol in the presence of a few drops of concentrated sulphuric acid catalyst to form ethyl ethanoate.



9.5 Physical properties of esters

Odour

Esters are often volatile liquids with pleasant odour (smell).

Specific esters and mixtures of esters have characteristic scents of those of flowers, fruits, perfumes and flavourings. See Table 9.2 for the different scents of esters.

Solubility

Small chain esters are fairly soluble in water. However, solubility of esters decreases with increasing chain length as shown in Table 9.3.

Table 9.3: Solubility of some esters

Ester	Formula	Solubility (g per 100 g of water)
Ethyl methanoate	$\text{HCOOCH}_2\text{CH}_3$	10.5
Ethyl ethanoate	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	8.7
Ethyl propanoate	$\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$	1.7

Esters form hydrogen bonds with water, but this reduces in strength with increase in the length of the hydrocarbon chain which is hydrophobic. In general, esters are soluble in organic solvents.

Boiling points

Smaller chain esters have boiling points similar to those of alkanals and alkanones with the same number of carbon atoms. Since they do not form hydrogen bonds between their molecules, their boiling points are lower than those of corresponding alcanoic acids with same number of carbon atoms. For example;

- Ethyl ethanoate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$, has a boiling point of 77.1°C.
- Butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, has a boiling point of 174°C.

Melting points

Esters with more than 12 carbon atoms are solids and waxy in nature.

Animal and vegetable fats and oils are made of long chain complicated esters. The physical difference between a fat (like butter) and oil (like sunflower oil) is due to the differences in the melting points of the mixtures of esters contained in them. Oils are liquids because their melting points are below that of room temperature.

Fats contain saturated chains allowing more effective van der Waal's forces between the molecules. Therefore more energy is required to break the chains causing their higher melting points.

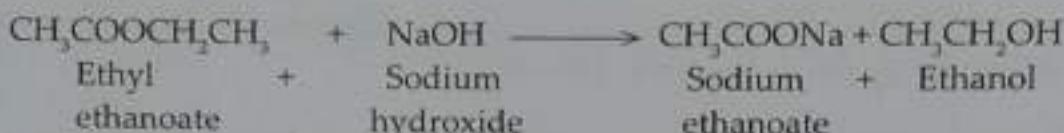
Unsaturation results in lower melting points because the van der Waals forces are less effective. This is because carbon-carbon double bonds make the molecules not to be closely packed together.

Chemical properties of esters

Hydrolysis of esters

When esters are heated under reflux with a dilute alkali such as sodium hydroxide solution it is hydrolysed. This reaction is one way. The products are easy to separate provided excess sodium hydroxide solution is used.

For example;



The products are a carboxylate salt and an alcohol which can be distilled off easily.

Uses of alkanoates

1. Many esters are used as flavours and perfumes.
2. Smaller esters are quite volatile and are used as solvents in adhesives, inks and paints.
3. Pentyl ethanoate is used in nail varnish.
4. Esters are used in making of soaps.

9.6 Saponification

The term **saponification** is derived from latin words "sapon" meaning soap and *facere* meaning "to make". When bases such as sodium hydroxide or potassium hydroxide are used to hydrolyse an ester, the products are a carboxylate and an alcohol. Soaps are prepared by alkaline hydrolysis of fats and oils. Therefore hydrolysis of esters using alkaline is referred to as **saponification**.

In saponification the alkali is a reactant, not a catalyst. The reaction goes fully to completion. Soaps are usually made by reacting esters with concentrated sodium hydroxide solution.

Experiment 9.2

Aim: To prepare soap in the laboratory.

Requirements

- 100 cm³ beaker
- Coconut oil, castor oil or animal fat
- Sodium hydroxide solution
- Sodium chloride
- Retort stand and clamp
- Wire gauze
- Filter paper
- Filter funnel
- Source of heat

Procedure

1. Pour about 4 cm^3 of castor oil or place about 40 g of animal fat into 100 cm^3 beaker.
 2. Add about 15 cm^3 of 4M sodium hydroxide solution.
 3. Boil the mixture for about 10-15 minutes stirring and adding small amounts of distilled water. The distilled water should make up for evaporation.
 4. Add about four spatulaful of sodium chloride and stir well.
 5. Allow the mixture to cool.
 6. Filter off the solid.
 7. Wash the solid residue with distilled cold water.
 8. Place the solid residue in a clean dry beaker.
 9. Place a small piece of the solid residue in two separate test tubes.
 - (i) In one test tube, add about 5 cm^3 of warm distilled water and shake well.
 - (ii) In the other test tube, add warm tap water and shake well.
 - What do you observe from each test tube? Explain your observations.
 - What do you conclude from the above observations?
 - Record your observations and conclusions in your notebook.
 - What would happen if you had added warm sea water? Explain your answer.

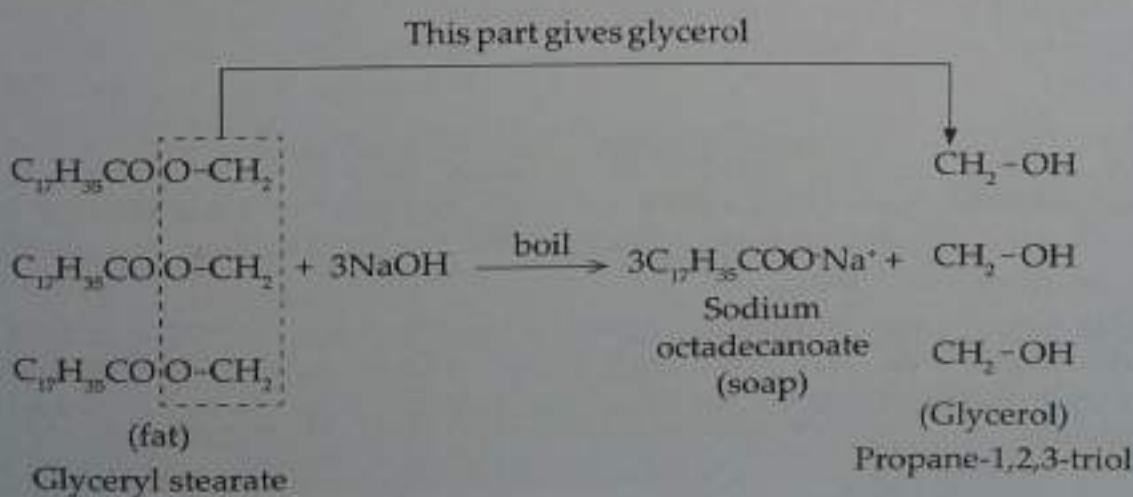
Discussion

When the castor oil reacts with concentrated sodium hydroxide solution, a saponification reaction takes place and soap is formed in the process.

Sodium chloride was added to help in precipitating the soap. It does this by reducing the solubility of the soap, a process called **salting out**.

Soap making process

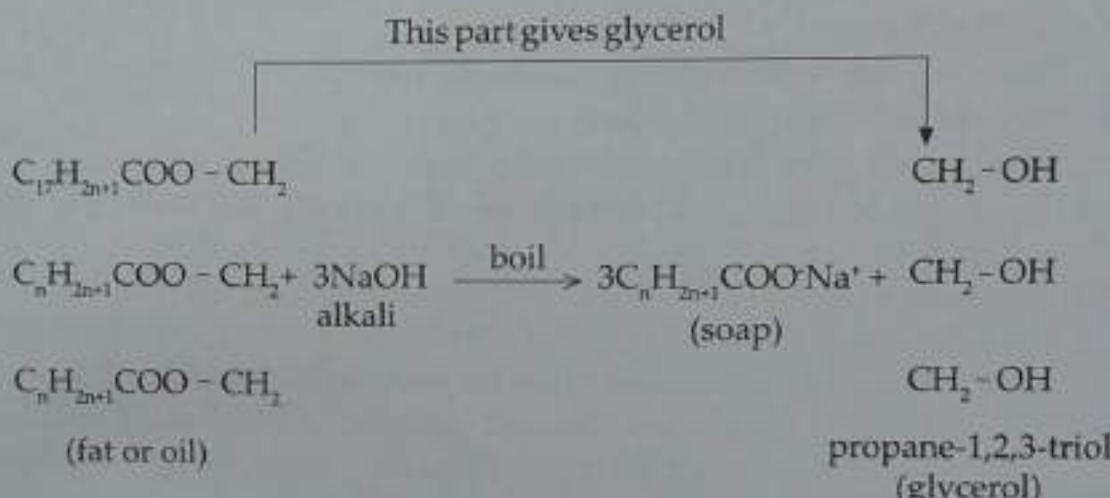
When a fat is boiled with strong alkaline solution e.g. concentrated sodium hydroxide solution, it is hydrolysed to give glycerol (propan- 1,2,3-triol) and soap (sodium octadecanoate).



Each part of the acid reacts with NaOH to form the salt i.e. sodium octadecanoate ($C_{18}H_{36}COO^- Na^+$) which is the soap. This is neutralization reaction.

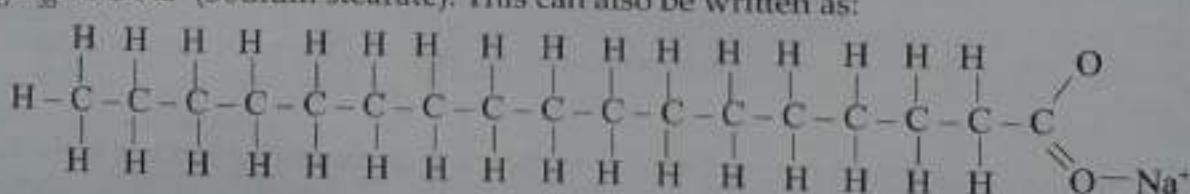


The following equation shows the general method of preparing soaps.

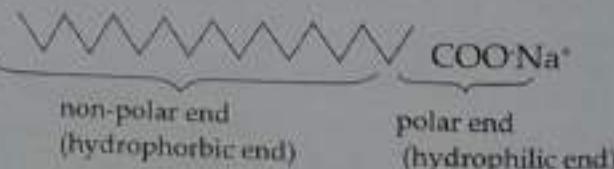


Note: That soap is the sodium salt of the fatty acid. The general formula for ordinary soap is $C_8H_{16}COO^-Na^+$ i.e.

$C_8H_{15}COO Na^+$ (Sodium stearate). This can also be used.



The above formula can be abbreviated as:



The non-polar part gets attracted to non-polar surfaces such as oil. It is called **hydrophobic** because of the dislike of the water. The polar part gets attracted to water which is polar. Hence it is said to be **hydrophilic**. The word hydrophilic means having a strong affinity for water.

The flow-chart below summarises how soap can be made through a process called **alkaline hydrolysis**. The word hydrophilic means having a strong affinity for water. It involves hydrolysis, neutralization, salting and finally addition of perfumes or colours.

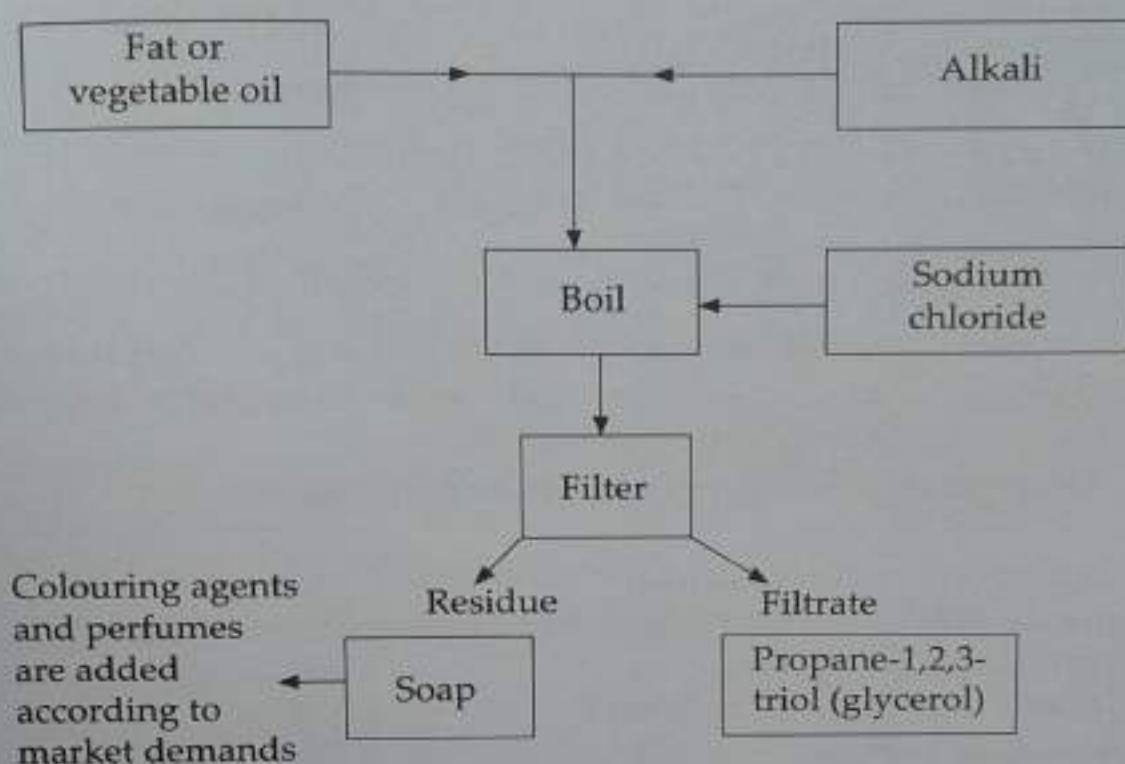


Fig. 9.1. Flowchart of soap preparation.

Revision Exercise 9



- What is saponification?
- List the reagents required for the preparation of a soapy detergent (soap).
- Draw the structure of the following alkanoates
 - Ethyl methanoate
 - Methyl methanoate
- What is the purpose of adding sodium chloride when preparing soap?
- Write a chemical equation for the formation of soap from animal fat.
- Draw skeletal structure for sodium stearate.
 - Label the hydrophobic end and hydrophilic end on the drawn structure of sodium stearate in 6 (a) above.
- Give two uses of esters.
- Draw the structure of the functional group of alkanoate.
- Write the formulae of the following alkanoates
 - Methyl propanoate
 - Ethyl methanoate
 - Propyl butanoate
- Name the parent alkanol and parent alkanoic acid used in producing the following esters.
 - Pentyl butanoate
 - Methyl methanoate

Topic 10:

Identification of unknown organic compounds

Success criteria

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

- (a) Deduce the family and structural formulae of an unknown organic compound given relevant information.
- (b) Distinguish organic compounds basing on their properties.



10.1 Deducing families and formulae of Organic compounds

Sometimes we may be required to identify unknown organic compounds or some of their aspects such as:

- (i) The family of an organic compound.
- (ii) Its structural formula.

We can easily predict or identify an organic compound when one is provided with relevant information such as: structural formulae, general formulae, products of chemical reactions and physical properties.

It is important to remember that families of organic compounds or homologous series have specific physical and chemical properties unique to each group. However, they do share some common properties. These properties can help us to guess to which family group an unknown organic compound belongs or simply identify a given unknown organic compound.

Empirical formula of organic compound

An empirical formula shows the simplest ratio of elements present in a compound. We can use empirical formula to identify the homologous series of an organic compound such as difference in alkanes from alkenes.

The composition of organic compounds is determined by combustion analysis. A known mass of the compound is subjected to combustion; the products, carbon dioxide and water formed are collected and weighed. The other elements present in a compound are estimated. The masses of carbon dioxide and water produced are then used to calculate the empirical formulae of the compound.

Example

An organic compound (y) containing carbon, hydrogen and oxygen was subjected to combustion analysis. 1 g of the compound on complete combustion gave 2.28 g of carbon dioxide and 0.931 g of water. Calculate the empirical formula of the compound.

Solution

Step 1: Determine percentage of carbon and hydrogen in the 1 g of the compound. Relative molecular masses of carbon dioxide and water are 44 and 18 respectively.

Reacting moles

$$\text{Carbon} = \left(\frac{12}{44}\right) \quad \text{Hydrogen} = \left(\frac{2}{18}\right)$$

Mass of carbon and hydrogen in the products

$$\text{Carbon} \quad \frac{12}{44} \times 2.28 \text{ g} = 0.621 \text{ g}$$

$$\text{Hydrogen} \quad \left(\frac{2}{18}\right) \times 0.931 = 0.103 \text{ g}$$

Total mass of carbon and hydrogen present in 1 g of the compound

$$0.621 + 0.103 = 0.724 \text{ g}$$

The mass of oxygen is thus

$$1 \text{ g} - 0.724 \text{ g} = 0.276 \text{ g}$$

Thus the ratio by mass becomes

	Carbon	Hydrogen	Oxygen
Mass ratio:	0.621	0.103	0.276
Mole ratio:	$\frac{0.621}{12}$	$\frac{0.103}{1}$	$\frac{0.276}{1}$
Divide by smallest	0.0173	0.0173	0.0173
	3	6	1

Empirical formula is $C_3H_6O_1$

From the empirical formula obtained, we can tell the unknown compound is an alkanal.

Relative molecular formula and structural formula

The relative molecular formula of a compound gives only the number of atoms of the different elements present in a molecule of the compound. It does not tell us how atoms are arranged. Structural formula shows both the elements present in organic compound as well as the arrangement of the atoms in the molecule.

The relative molecular formula of compound is calculated using the **relative molecular mass** of the compound provided. The relative molecular mass is measured using mass spectrometer. Relative molecular mass is a multiple of the empirical formula mass. For example;

Relative molecular mass = (Empirical formula) n where n is a whole number.

From the relative molecular formula and structural formula given, it is easy to identify the actual organic compound and the family they belong to.

For example;

- Alkanes have single bonds between the carbon atoms throughout the chain. Their general formulae is $C_n H_{2n+2}$.
 - Alkenes have double bonds in their structure. Their general formula is $C_n H_{2n}$.
 - Alkynes have the general formula, $C_n H_{2n-1}$.
- In brief, from the general or structural formulae of organic compounds, we can tell the identity of organic compounds.

Chemical reactions and the products in identification of organic compounds

Each homologous series has certain chemical characteristics dependent on its functional group or reactions particular to it. For example;

(i) Alkanes:

- They undergo substitution reactions with halogens in presence of U.V light.
- Alkanes burn with a blue flame due to the presence of a saturated bond.
- Alkanes are insoluble in water.

(ii) Alkenes.

- Undergo addition reactions with hydrogen, hydrogen halide and halogens.
- Burn with a sooty flame because they are unsaturated.
- Undergo polymerization reactions (self addition reactions).
- Oxidised by strong oxidizing agents.
- Hydrated to alkanols in the presence of concentrated sulphuric acid.
- Insoluble in water.

(iii) Alkanols

- They react with very electropositive metals to give a salt and hydrogen gas.
- React with alkanoic acids in the presence of concentrated sulphuric acid catalyst to form sweet smelling esters.
- Dehydrated by concentrated sulphuric acid to form alkenes.
- Oxidised by acidified potassium managanate VII and acidified potassium dichromate VI to form alkanals and then alkanoic acids.
- They are soluble in water.
- Burn with a pale blue flame.

(iv) Alkanoic acids

- They change the colour of indicators.
- Reacts with metal carbonates and hydrogencarbonates to form salt, water and carbon dioxide.
- They neutralize alkalis to form salt and water as the only products.
- They react with metals to form salt and hydrogen gas.

(v) Alkanals

- They have no effect on the colour of indicators.
- They are oxidized to alkanoic acids by oxidizing agents.
- They give positive test with fehling solution test, Brady's test and Tollens test.

(vi) Alkanones

- They give positive test with Brady's test only.

10.2 Tests for organic compounds

(i) Hydrocarbons

This is a class of compounds that consists of hydrogen and carbon only. They include alkanes, alkenes and alkynes.

Experiment 10.1

Aim: To test for unsaturated compounds.

Requirements

- Test tube
- Teat pipette
- Acidified potassium manganate (VII) solution
- Bromine water
- Source of ethene gas
- Source of methane gas

Procedure

1. Bubble ethene through potassium manganate (VII) solution. Record your observation.
2. Bubble ethene through bromine water. Record your observation.
3. Repeat the experiment using methane gas instead of ethene gas.

Discussion

Ethene decolourises acidified potassium manganate (VII) solution and bromine water. The decolourisation of these solutions is the test for unsaturation in organic compounds.

Methane does not decolourise acidified potassium manganate (VII) solution or bromine water because it is a saturated compound.

In general, tests that distinguish the hydrocarbons are:

- Unsaturation test.
- Combustion flame; alkenes burn with a sooty flame while alkanes burn with a blue flame.

(ii) Oxycarbons

Oxycarbon compounds consist of carbon atoms bonded with hydrogen and oxygen atoms. They include: alkanols, alkanals, alkanones and alkanoic acids.

Test for alkanoic acids

Alkanoic acids are easily distinguished from the rest of oxycarbon groups using the following tests;

- i. Indicators that give a definite colour change.
- ii. Carbonates or hydrogencarbonates to test for effervescence. Carbon dioxide gas is produced which turn lime water milky.

Experiment 10.2

Aim: To test for the presence of alkanoic acids

Requirements

- Test tubes
- Droppers
- Beaker
- Litmus paper
- Spatula
- Ethanoic acid
- Sodium carbonate

Procedure

1. Place about 2 cm^3 of ethanoic acid in a test tube. Test with litmus papers.
2. Place about 2 cm^3 of ethanoic acid in a test tube. Add a spatula endful of sodium carbonate and test for any gas produced.

Discussion

Blue litmus paper turns red in ethanoic acid. This is a positive test for acids. When sodium carbonate was added to the acid, effervescence occurred. A colourless gas evolved that extinguishes a burning splint. The gas is carbon dioxide. This is a characteristic reaction of acids with carbonates and hydrogencarbonates.

Test to distinguish between alkanals and alkanones

Alkanals and alkanones are both characterized by the presence of a carbonyl group as their functional group.

Tollens reagent is used to distinguish between the alkanals and alkanones which gives a silver mirror with alkanals and a negative test with alkanones.

Test for alkanols

Alkanols are tested by mixing them with equal volumes of alkanoic acids. A few drops of concentrated sulphuric acid are added to the mixture and warmed gently producing a sweet-smelling ester. The fruity smell of the ester is detected by pouring the reaction mixture into a beaker of cold water.

10.3 Flow diagrams

Flow diagrams can be used to identify unknown organic substances. The flow diagram indicates the different stages, reagents or reactions involved. They also examine the nature or structure of the organic compound by separating it into its different parts. The process of doing all this is called **analysis**. In order to analyze a substance, we need to know how it reacts with some reagents (chemicals). The following are aspects of substances for analysis.

1. Solubility of the substance in water.
2. How the substance affects the colour change of:
 - Potassium manganate (VII) solution
 - Bromine solution (bromine water),
 - Potassium dichromate (VI) solution.

Revision Exercise 10

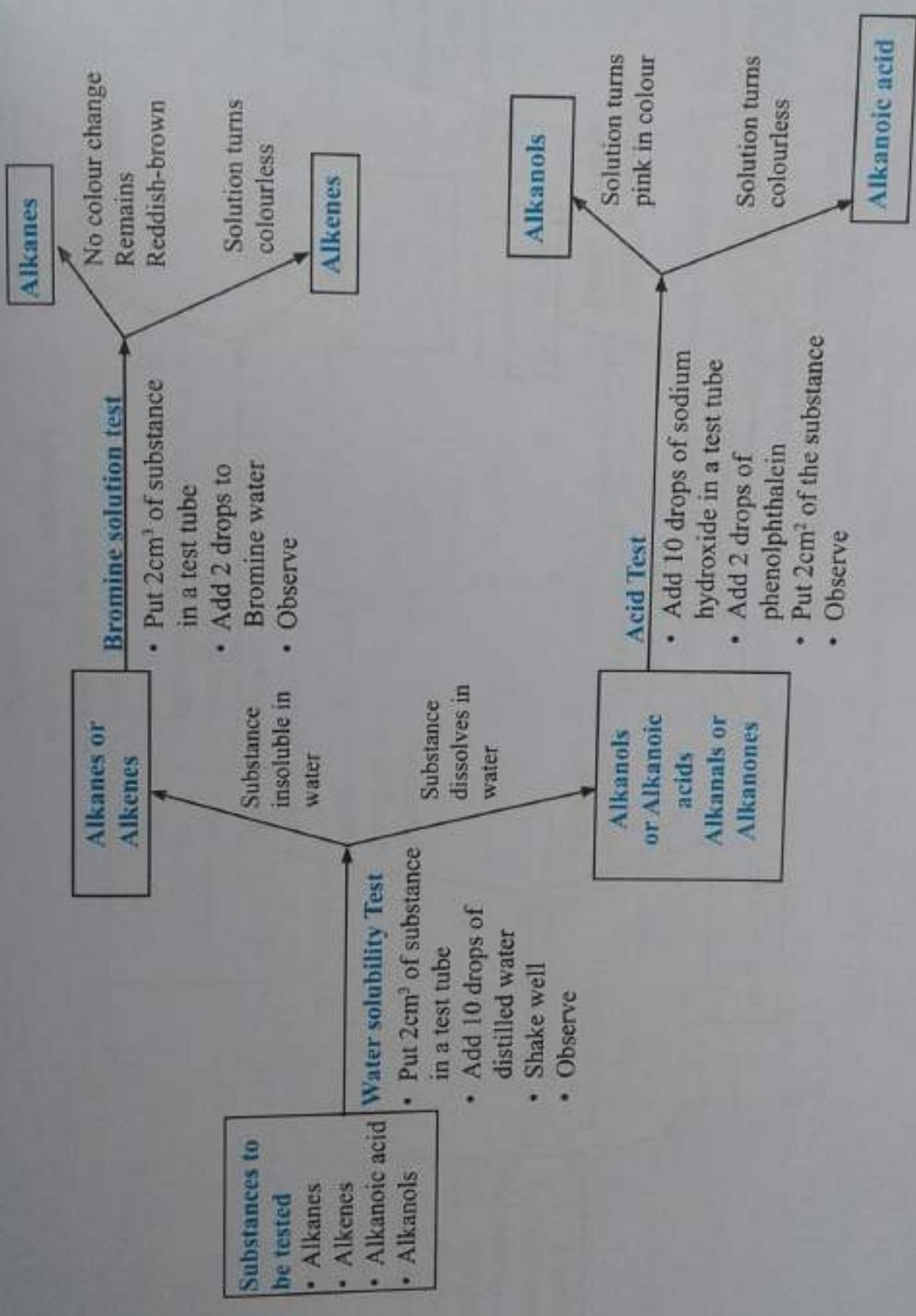


Give the tests that can be used to distinguish between.

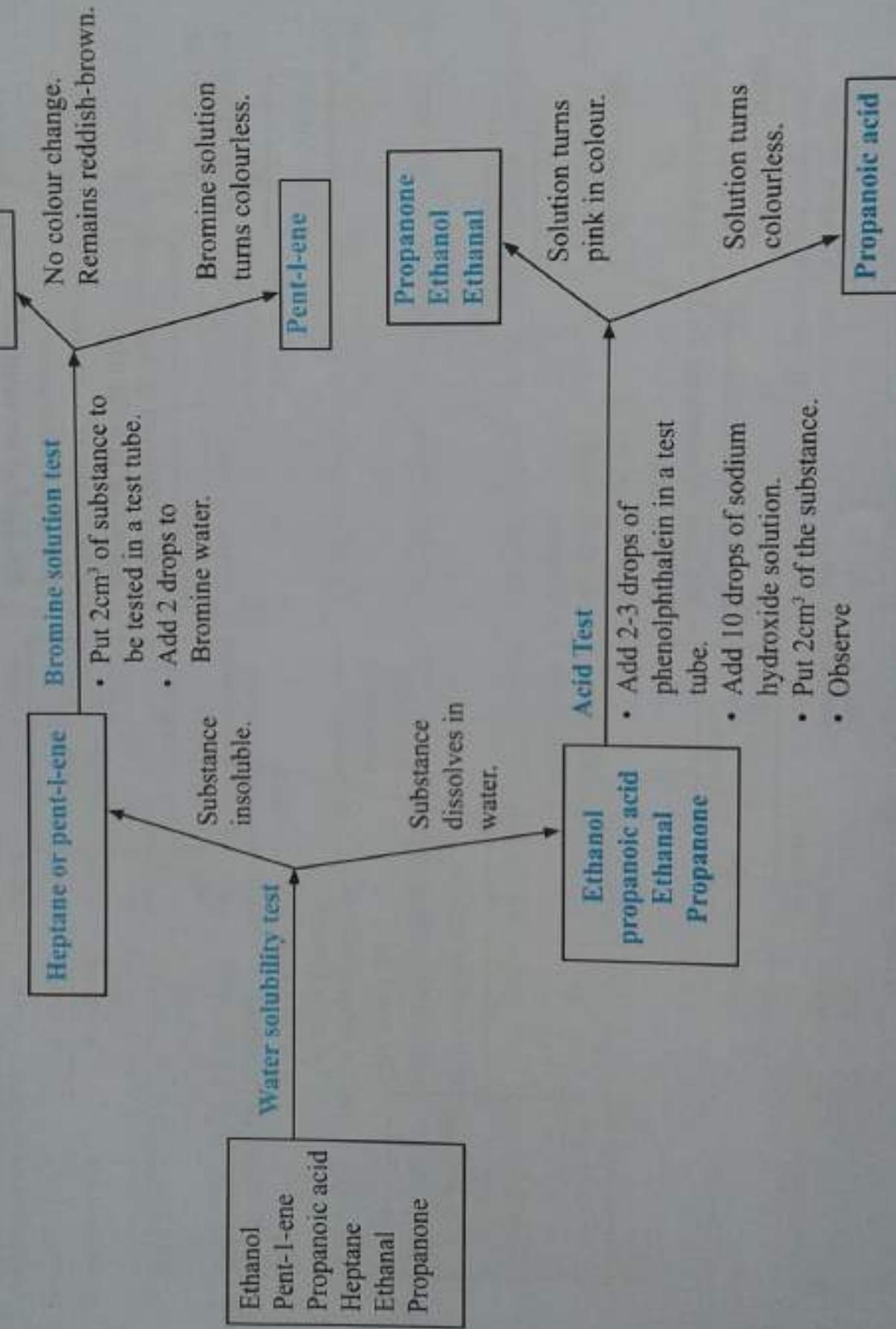
- i. Alkanones and alkanols.
 - ii. Alcanoic acids and alkanols.

Table 10.1: Identification test table

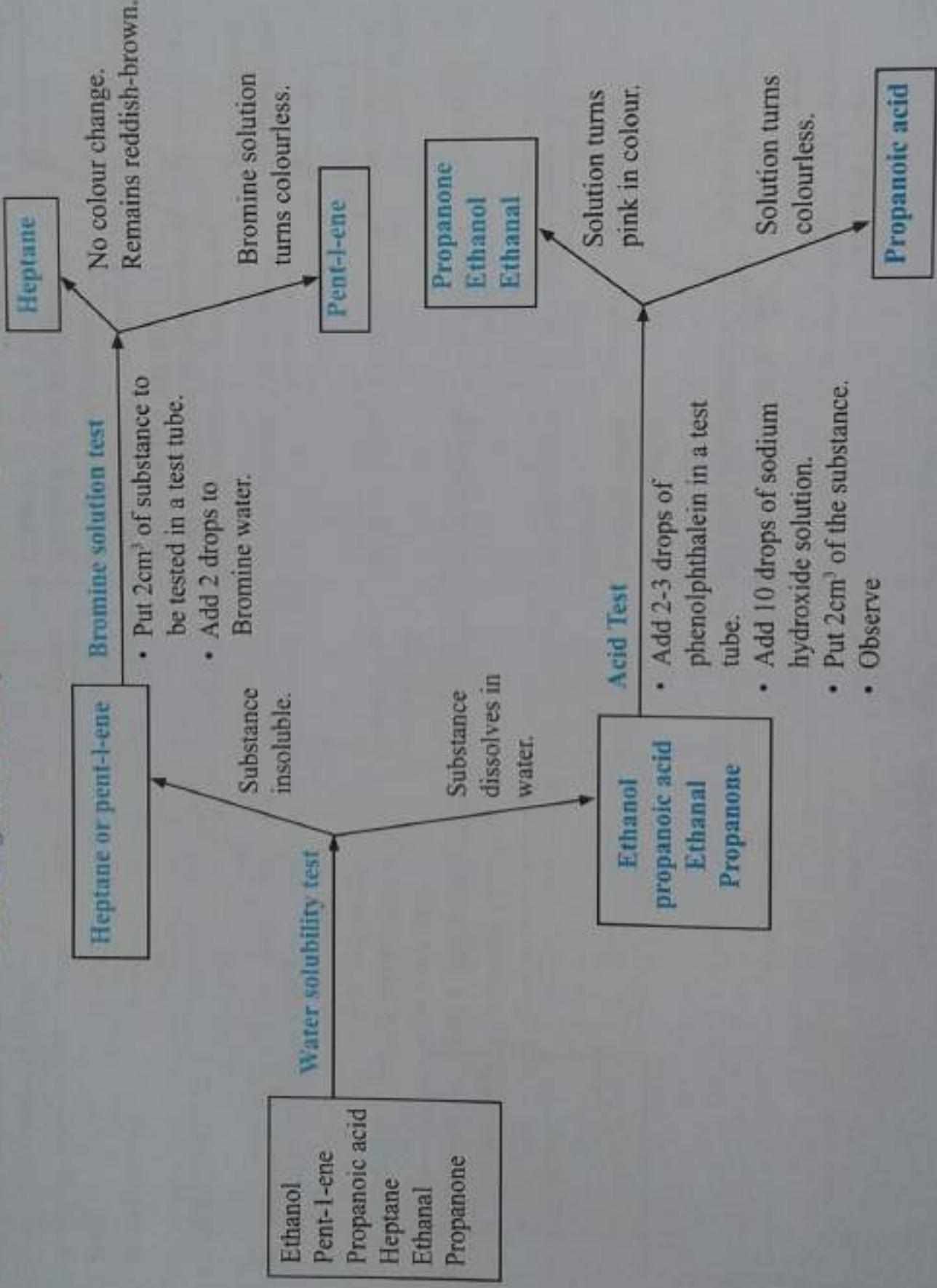
A flow diagram to identify unknown organic compounds



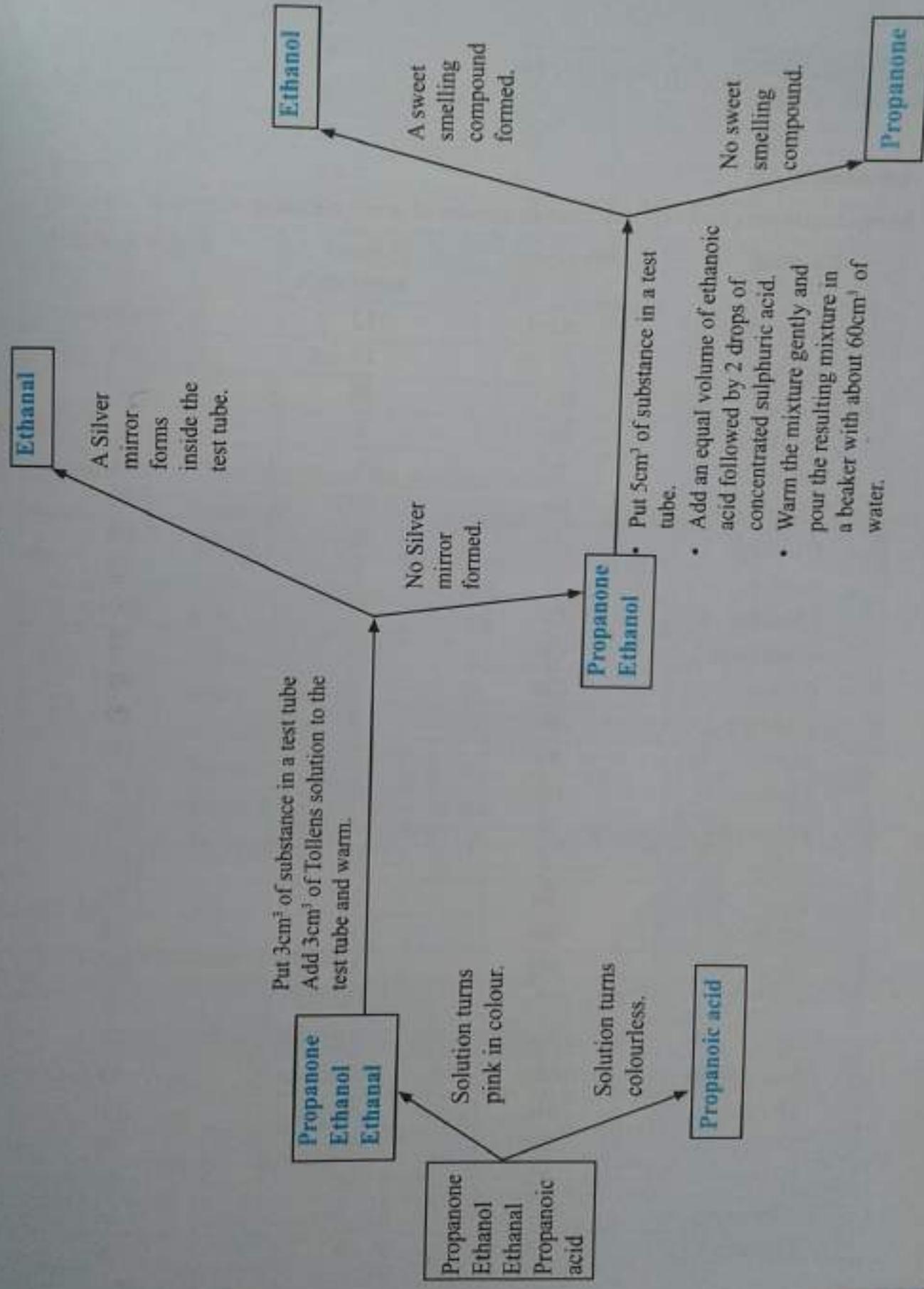
A flow diagram to identify some selected organic compounds



A flow diagram to identify some selected organic compounds



A flow diagram to identify some selected organic compounds



Appendices

Appendix I

Atomic numbers and relative atomic masses of some common elements.

Element	Symbol	Atomic number	Relative atomic mass
Aluminium	Al	13	27
Argon	Ar	18	40
Barium	Ba	56	137
Beryllium	Be	4	9
Boron	B	5	11
Bromine	Br	35	80
Calcium	Ca	20	40
Carbon	C	6	12
Chlorine	Cl	17	35.5
Chromium	Cr	24	52
Copper	Cu	29	64
Flourine	F	9	19
Gold	Au	79	197
Helium	He	2	4
Hydrogen	H	1	1
Iodine	I	53	127
Iron	Fe	26	56
Krypton	Kr	36	84
Lead	Pb	82	207
Lithium	Li	3	7
Magnesium	Mg	12	24
Manganese	Mn	25	55
Mercury	Hg	80	201
Neon	Ne	10	20
Nickel	Ni	28	59
Nitrogen	N	7	14
Oxygen	O	8	16

Phosphorous	P	15	31
Potassium	K	19	39
Silicon	Si	14	28
Silver	Ag	47	108
Sodium	Na	11	23
Sulphur	S	16	32
Tin	Sn	50	119
Vanadium	V	23	51
Zinc	Zn	30	65

Appendix II

Valencies of some of the elements in the periodic table.

Name of metal	Symbol	Valency
Zinc	Zn	2
Iron	Fe	2 or 3
Tin	Sn	4
Lead	Pb	2
Copper	Cu	1 or 2
Silver	Ag	1
Barium	Ba	2
Phosphorous	P	3 or 5

Appendix III

Valencies of some common radicals.

Valency 1		Valency 2		Valency 3	
Radical	Formula	Radical	Formula	Radical	Formula
Ammonium	NH_4^+	Carbonate	CO_3^{2-}	Phosphate	PO_4^{3-}
Hydroxide	OH^-	Sulphate	SO_4^{2-}		
Nitrate	NO_3^-	Sulphite	SO_3^{2-}		
Chloride	Cl^-				

Hydrogen carbonate	HCO_3^-	I
Hydrogen sulphate	HSO_4^-	I

Appendix IV

Valencies of some elements in some compounds.

Compound	Element	Valency
Copper(I) oxide	Copper	1
Copper(II) oxide	Copper	2
Iron(II) sulphate	Iron	2
Iron(III) chloride	Iron	3
Sulphur(IV) oxide	Sulphur	4
Sulphur(VI) oxide	Sulphur	6
Carbon(IV) oxide	Carbon	4
Carbon(II) oxide	Carbon	2

Glossary

- **Activation energy** – the minimum quantity of energy that the reacting species must possess in order to undergo a specified reaction.
- **Addition reaction** – organic reaction where two or more molecules combine to form a larger one.
- **Addition polymerization** – Polymerization that occurs through the coupling of monomers using their multiple bonds.
- **Alkene** – hydrocarbons which contain one or more double bonds between carbon atoms.
- **Alcohol** – organic compounds which contain OH attached to saturated carbon atom as functional group.
- **Allotropes** – Are different forms of the same element under the same physical state.
- **Allotropy** – Is the existence of an element in more than one form under the same physical state.
- **Amorphous** – a substance without a clearly defined shape or form.
- **Aqua regia** - is a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3.
- **Antacids** – substances that neutralise the acid present in the stomach.
- **Acid-base titration** - the determination of the concentration of an acid or base by exactly neutralising the acid or base of known concentration.
- **Anion** – Negative ion.
- **Anode** – Positive electrode connected to positive terminal of d.c. source.
- **Alkene** – hydrocarbons which contain one or more double bonds between carbon atoms.
- **Alcohol** – organic compounds which contain OH attached to saturated carbon atom as functional group.
- **Cations** – are positively charged ions.
- **Catalyst** – substance which increase the rate of a chemical reaction but remain unchanged at the end of reaction.
- **Collision** – an instance of one moving particle striking violently against another.
- **Carbonate** – a salt of the anion CO_3^{2-} . typically formed by reaction of carbon dioxide with bases.
- **Cracking** – The process of breaking down complex chemical compounds by heating them.
- **Claus process** – a gas desulfurising process for recovering elemental sulfur from gaseous hydrogen sulfide.

- **Concentration** – in industry and consumer world, the most common method of expressing concentration is based on quantity of solute in a fixed quantity of solution.
- **Cathode** – Negative electrode connected to negative terminal of d.c. source.
- **Cation** – positive ion.
- **Condensation polymerization** - Monomers are connected by a reaction in which two molecules are covalently bonded to each other through loss of a water molecule.
- **Carboxyl groups** – weak acids, dissociating partially to release hydrogen ions.
- **Dehydrating agent** – a substance that dries or removes water from a material.
- **Dichlorodiphenyltrichloroethane (DDT)** – was a commonly-used pesticide for insect control. It was banned in many countries due to its side effects.
- **Dioxins** – are a group of chemically-related compounds that are persistent environmental pollutants.
- **Environment** – The immediate surroundings of an organism.
- **Esterification** – reaction between an alcohol and carboxylic acid to form an ester as the only organic compound.
- **Energy** – the strength and power required to sustain chemical reaction.
- **Equivalence point** - the point in a titration where the amount of titrant added is enough to completely neutralize the analyte solution.
- **End point** – the point in a titration at which a reaction is complete, often marked by a colour change.
- **Dilution** – the action of making a liquid more dilute.
- **Standard solution** – a solution whose concentration is known.
- **Percent composition (by mass or by weight)** – parts of solute per 100 parts of solution or the fraction of solute in a solution multiplied by 100.
- **Molarity** – the number of moles of solute in exactly one liter of solution.
- **Mole fraction** – the mole fraction of a component in a solution is the ratio of the number of moles of that component to the total number of moles of all components in the solution.
- **Volume percent** – the ratio of solute in a solution multiplied by 100. Often used when preparing solutions of liquids.
- **Discharge** – the removal of electrons from negative ions to form atoms or the gain of electrons of positive ions to become atoms.
- **Electrolysis** – decomposition of a compound using electricity.
- **Electrolyte** – an ionic compound which conducts electric current in molten or aqueous solution, being decomposed in the process.

- **Electrode** – a rod or plate where electricity enters or leaves electrolyte during electrolysis. Reactions occur at electrodes.
- **Electroplating** – the process of plating one metal onto another by hydrolysis.
- **Esterification** – the reaction between an alcohol and carboxylic acid to form an ester as the only organic compound.
- **Fractional distillation** – separation of a liquid mixture into fractions differing in boiling point (and hence chemical composition) by means of distillation, typically using a fractionating column.
- **Frasch process** – a method to extract sulfur from underground deposits.
- **Fractional distillation** – the process of separation of mixtures which are miscible to each other basing on their differences on their boiling points.
- **Fossil fuel** – a natural fuel such as coal or gas, formed in the geological past from the remains of living organism.
- **Hard water** – water that has high mineral content.
- **Haber process** – is a specific step by step procedure used in the manufacture of ammonia.
- **Halogens** – a group of five non-metallic elements found in group 7 of the periodic table. The term “halogen” means “salt-former” and compounds containing halogens are called “salts.”
- **Hygroscopic** – the property of a substance tending to absorb moisture from the air.
- **Indicator** – any substance that gives a visible sign, usually by a colour change.
- **Metahemoglobin** – a stable oxidized form of hemoglobin that is unable to release oxygen to the tissues due to poisoning.
- **Monomer** – The repeating units that serve as the building blocks of a polymer.
- **Nomenclature** – a system of naming substances.
- **Natural resources** – materials or substances such as minerals, forests, water, and fertile land that occur in nature and can be used for economic gain.
- **Neutralisation** – a chemical reaction in which an acid and a base interact with the formation of a salt.
- **Ostwald process** – a chemical process for making nitric acid (HNO_3).
- **Oleum** - a dense, corrosive liquid consisting of concentrated sulfuric acid containing excess sulfur trioxide in solution.
- **Pollution** – the presence in or introduction into the environment of a substance or thing that has harmful or poisonous effects
- **Polymer** – A long molecule consisting of many identical or similar building blocks linked by covalent bonds.

- **Polymerisation** – the process by which small molecules called monomers combine to form large molecules called polymers.
- **Product** – a substance that is manufactured during a chemical reaction.
- **Oxidation** – the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.
- **Rate of reaction** – the rate of change of an amount or concentration of a particular reactant or product per unit of time.
- **Reactant** – a substance that takes part in and undergoes change during a reaction.
- **Reduction** – the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.
- **Refrigerant** – a substance used for cooling (refrigeration).
- **Soft water** – water which has relatively low concentration of calcium carbonate and other ions.
- **Solvay process** – industrial process for the production of sodium carbonate.
- **Saturation** – the state of a substance in which the atoms are linked by single bonds. A fully saturated compound contains no double or triple bonds.

Appendix IV: The Periodic Table

\bar{x} is the Relative Atomic Mass (RAM)
 Z is the symbol of the element
 y is the Atomic Number of the element

Groups	I	II	III	IV	V	VI	VII	VIII
Periods	1	2	3	4	5	6	7	8
1	H Hydrogen	Li	Be	Sc	Cr	Mn	Ni	Cu
2	Li	Be	B	Sc	Tc	Co	Cr	O
3	Na	Mg	Al	V	Cr	Fe	F	Ne
4	K	Ca	Sc	Cr	Co	Ni	Cl	Ar
5	Rb	Sr	Y	Tc	Pd	Pt	S	He
6	Cs	Ba	Zr	Mo	Ru	Au	Se	
7	Fr	Ra	Hf	Ta	Os	U	Te	
Lanthanide elements	La	Ce	Pr	Nd	Eu	Tb	Dy	
Actinide elements	Th	Pa	U	Am	Cm	Bk	Cf	

Transition metals

Lanthanide elements	257 La	140 Ce	141 Pr	144 Nd	147 Pm	150 Sm	152 Eu	157 Gd	159 Tb	163 Dy	165 Ho	167 Er	169 Tm	173 Yb
Actinide elements	227 Ac	232 Th	231 Pa	238 U	237 Np	242 Pu	243 Am	247 Cm	249 Bk	251 Cf	254 Es	253 Fm	256 Md	254 No
	89 Fr	91 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

KEY

Metals

Non-metals

Excel & Succeed Senior Secondary Chemistry Student's Book Form 3 is a new, concise and comprehensive coursebook that has been developed in line with the revised curriculum.

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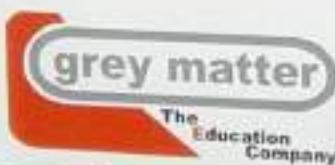
The book:

- is beautifully designed to easily capture the student's attention;
- enhances the learning of Chemistry through investigative approach and use of participatory learning techniques;
- provides clearly stated objectives at the start of each chapter;
- provides numerous examples and activities based on everyday life experiences;
- has chapter summaries that focus on key features of the topics;
- provides review questions to test achievement of learning objectives;
- uses simple language hence making it easier for the learners to understand the various concepts.

The authors have served in the education sector in various capacities and have vast experiences in the field of Chemistry.



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